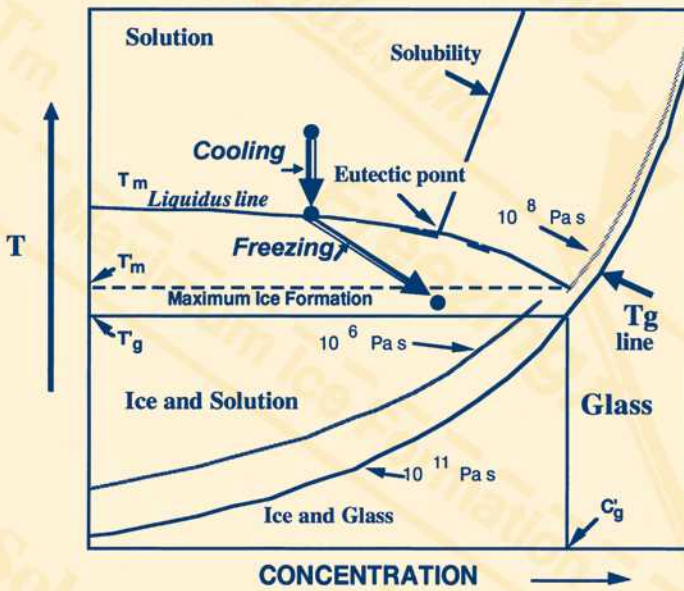


PHYSICAL PRINCIPLES OF FOOD PRESERVATION

SECOND EDITION, REVISED AND EXPANDED



MARCUS KAREL
DARYL B. LUND

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SECOND EDITION, REVISED AND EXPANDED

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To the many undergraduate, graduate, and postdoctoral students who studied and worked with us over the past four decades. Most of the ideas and concepts underlying this book were forged in our interactions with these talented and productive young women and men.

Foreword

Physical Principles of Food Preservation, by Marcus Karel, Owen Fennema, and Daryl Lund, was first published in 1975 and served as a popular textbook far longer than is typical, apparently because a suitable replacement was not available. Preparation of a new edition has been contemplated since about 1985, but impediments of various kinds precluded its completion. Marcus Karel and Daryl Lund have finally overcome these obstacles and have given birth to the second edition. This was not easily accomplished, but the product is one of considerable significance because the topic is important and the approach taken is highly suitable for the intended audience—majors in food science and practicing food scientists and technologists. The topic of this book was important in 1975 but has become much more so today because of increasing population and the pressing need for sustainable processing procedures, of little concern in 1975. Sustainable processing procedures are absolutely necessary if we are to leave our descendants with access to an adequate supply of safe and nutritious food, clean air, potable water, fertile soil, and adequate natural resources. The authors have recognized these needs and addressed them well—a very formidable task.

Appropriateness of the approach is also of great importance. Students majoring in food science as well as practicing food scientists and technologists are typically well founded in chemistry, physics, mathematics, biology, and microbiology but are less skilled in engineering. This fact must be fully

recognized if a book for these readers is to be effective. The authors, in my view, have successfully met this challenge.

After more than a quarter of a century, one expects many changes in a book of this kind, and they have been incorporated. The book is structured differently, all of the information has been updated, a vast amount of new information has been added (e.g., a new chapter on nonthermal processes), and the approach is appropriately more quantitative, often with a different emphasis than before. Thus, the book is quite different from the first edition, except for constancy in purpose and in most of the topics covered.

It is an honor and genuine pleasure to introduce the reader to this fine second edition of *Physical Principles of Food Preservation*. I believe you will find it of great value.

Owen Fennema
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Preface to the Second Edition

In the 28 years since the first edition of this textbook, significant advances have been made in our understanding of physical chemistry of foods, and in particular of the effects of environmental factors on rates of changes in foods. These advances in knowledge have led to refinements in formulation of principles of food preservation and in the development and application of new processes for preservation of foods. As predicted in the preface of the first edition, processes today seek optimization of nutritional and quality factors (such as nutrients, biologically active ingredients, taste, flavor, color, and texture), energy utilization, waste generation, and cost.

Advances in knowledge also resulted in descriptions of physical methods of food preservation, which are based on theoretical principles and are increasingly quantitative. The contents of this textbook reflect the emphasis on qualitatively and quantitatively formulating the principles of food preservation and of storage stability.

Quantitative description is aided by providing the reader with fundamental physical chemistry and engineering chapters (Chapters 1–5) on thermodynamics, kinetics, heat transfer, mass transfer, and water activity. These chapters are intended to introduce fundamental concepts and rely on the reader's background in mathematics, chemistry, and physics. Subsequent chapters (Chapters 6–11) are devoted to specific processes for food preservation. They include processes

currently in use, as well as those in advanced stages of development, including heat processes, chilling, freezing, concentration processes, dehydration, and nonthermal processes including irradiation. To achieve their objective of food stabilization, preservation processes must include protective packaging, a subject that is covered in the last chapter.

This textbook is intended for students in a food science undergraduate program in which they are introduced to food processing principles after having taken courses in calculus, physics, chemistry, and microbiology. Students in a graduate program in food science who do not have an undergraduate degree in food science will also find this textbook of benefit in understanding the principles of food preservation processes. This applies also to students in related fields (e.g., chemical and biochemical engineering, chemistry, material science) who wish to learn about application of their disciplines to food preservation. Finally, it is our hope that the book finds good use as a general reference text by those in professions using food science, such as government and industry professionals.

Marcus Karel
Daryl B. Lund

Preface to the First Edition

The subject of food processing occupies a position of major importance in the food science curriculum, and this emphasis is likely to continue. Thus it is both puzzling and reprehensible that a university-level textbook tailored to the needs of typical students in food science does not exist. In the United States, the two largest categories of students represented in food processing courses are (1) upper-level undergraduates in food science and (2) graduate students that are entering food science from other disciplines. These students generally have solid backgrounds in chemistry, bacteriology, biology, mathematics, and physics and minimal backgrounds in engineering. This book on *Physical Principles of Food Preservation* is intended primarily for these students, and secondarily for persons in the food industry and for scientists in food-related groups of the government.

In the past, knowledge of food preservation has been used to develop new or improved products or more economical (labor-saving) processes. In the future, knowledge of food preservation techniques will no doubt be applied increasingly to matters of a more critical nature, i.e., to reducing wastage of the World's food supply and to devising processes that optimize the factors of cost, nutritional quality, environmental impact, and consumption of resources and energy.

In this book, a qualitative and semiquantitative approach is used, and stress is given to long-enduring principles rather than to detail. This approach is

necessary if one is to adapt successfully to the changing objectives of food preservation, as discussed above.

In the introductory chapter, attention is drawn to the fact that food wastage is a major problem on a world-wide basis, that much of this wastage can be prevented by proper application of food-preservation techniques, and that processing advances must be accomplished with due consideration given to the amounts of energy and resources consumed and to the environmental effects. The remainder of the book is divided into four sections: the first deals with preservation by means of temporary increases in the product's energy content (heat processing, irradiation); the second deals with preservation by controlled reduction of the product's temperature (chilling, freezing); the third deals with preservation by controlled reduction of the product's water content (concentration, air—dehydration, freeze—drying); and the last deals with packaging—an important means of protecting foods during storage. Chapters are also included at appropriate places to familiarize the reader with the principles of phase equilibria, heat transfer, mass transfer, and water activity.

It is hoped that this book shall enlighten readers with respect to the principles of physical methods of food preservation and thereby encourage use of methods that are most suitable to the needs of society.

Marcus Karel
Owen Fennema
Daryl B. Lund

Acknowledgments

We have been encouraged to produce the second edition of this popular textbook for at least the past 15 years. To the professors, instructors, colleagues, friends, and students who provided this encouragement, we express our deep appreciation for their confidence in our ability to contribute to the teaching of food science principles. Our production editor, Theresa Dominick Stockton, and acquisitions editor, Maria Allegra, were sources of constant encouragement. We would be remiss, however, if we did not acknowledge the special encouragement and support we received from our respective wives, Cal and Dawn, and from the original series editor, Owen Fennema. Thank you one and all.

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1

Thermodynamics

I. INTRODUCTION

The development of chemical engineering occurred in part because the fundamental laws of cause and effect associated with chemical transformations and phenomena were expressed quantitatively and codified. For food engineering, significant progress occurred in engineering design of food processes when these same fundamental principles were applied to complex mixtures of chemicals and biochemicals called *food*. Unfortunately, with food the mixtures are very complex and the chemical and thermodynamic parameters are not easily estimated from first principles or easily determined experimentally. Although this situation has led to empiricism, nonetheless, knowledge of physical-chemical principles is essential to enhance our understanding of unit operations and behavior of foods.

II. THERMODYNAMIC FUNDAMENTALS

Food engineering requires an appreciation for the fundamental laws of thermodynamics even though some principles apply in only highly select conditions. Here we will briefly introduce the laws of thermodynamics recognizing that the reader may wish to refer to more extensive treatments elsewhere [e.g., Chang (1977), Tinoco et al. (2002), Baianu (1992)].

A. Definition of Systems

When an operation is described, frequently it is helpful to envision a physical boundary around the operation. The elements contained within the boundary is called a *system*.

If no mass or energy crosses the boundary of the system, the system is said to be *isolated*; if mass and energy crosses the boundary, the system is *open*; and if no mass crosses the boundary, the systems is said to be *closed*. A system with no heat flow across the boundary is *adiabatic*, whereas one with no work transfer is *anergic*. If the pressure does not change, the system is *isopiestic* or *isobaric* and if the temperature of the system does not change, the system is *isothermal*.

B. First Law of Thermodynamics

In many closed systems, energy of one form will come into a system and subsequently be transformed into another form. For example, mechanical energy can be used to transport material within a system and ultimately be converted to heat energy. This concept of interconvertability of energy led to the formulation of the first law of thermodynamics.

The first law is the conservation of energy and states that energy can be neither created nor destroyed but can be converted from one form to another. In a closed system, the system can interact with its surroundings only in the form of transfer of heat (Q) to the system, or the performance of work (W) on the system. The total change in internal energy (ΔU) for the system in going from state 1 to state 2 is, therefore,

$$\Delta U = Q + W \quad (1)$$

Where ΔU is the change in internal energy, Q is heat energy, and W is work. Thus, when a substance undergoes a change in state, it is necessary to specify the path in order to determine the efficiency of the process. From a thermodynamic standpoint, we define a reversible path as one in which all connecting intermediate states are *equilibrium states*. The process carried out along such an equilibrium path is called a *reversible process*.

For example, if a gas is compressed reversibly, the pressure must increase sufficiently slowly so that at every instant the pressure is constant and equal throughout the gas and is just equal to the pressure on the piston. Reversible processes are never actually accomplished because they must be carried out infinitely slowly. However, the reversible path is the limiting path, which can be approached if a real process is carried out under conditions that more and more closely approach equilibrium. Since we can define a reversible path exactly and calculate the work in moving along it, we can ultimately compare our real

processes to the ideal reversible process to assess the efficiency of alternative real processes.

If the work done is of the pressure-volume type (as distinguished from kinetic energy, potential energy, or frictional energy), the system is *closed*, the process is *reversible*, and the pressure is constant, then Eq. (1) can be written

$$dU = dQ + dW \quad (1a)$$

and

$$dW = -pdV \quad (2)$$

Note that for compression, $dV < 0$ and dW is positive (i.e., work is done on the system). For expansion, $dV > 0$ and dW is negative (i.e., the system does work). Combining Eqs. (1a) and (2) results in

$$dU = dQ - P dV \quad (3)$$

or

$$dQ = dU + P dV \quad (4)$$

Equation (4) is a special case of a more generalized thermodynamic quantity called *enthalpy*. Enthalpy (H) is defined as

$$H = U + PV \quad (5)$$

or

$$dH = dU + d PV = dU + P dV + V dP$$

Like internal energy (U), enthalpy is also a function of state and is independent of the path of the process. For a closed system with constant pressure,

$$dH = dU + P dV = dQ \quad (6)$$

For a closed system with constant volume and pressure

$$dQ = dU \quad (7)$$

The temperature dependence of the energy of systems is very important since temperature is one of the state variables which can be easily measured and controlled. Equation (3) can be used to define temperature dependence for constant volume and constant pressure reversible processes applied to closed systems.

Then for $dV = 0$ (constant volume)

$$\frac{(\partial U)}{(\partial T)_V} = \frac{(\partial Q)}{(\partial T)_V} C_V \quad (8)$$

where C_V is the change in internal energy with temperature at constant volume and is equal to the change in heat content with temperature at constant volume. From Eq. (3)

$$\frac{(\partial Q)}{(\partial T)_P} = \frac{(\partial U)}{(\partial T)_P} + P \frac{(\partial V)}{(\partial T)_P} \quad (9)$$

$$\frac{(\partial Q)}{(\partial T)_P} = \frac{(\partial H)}{(\partial T)_P} = C_P \quad (10)$$

where C_P is the heat capacity at constant pressure and is equal to the change in enthalpy with temperature at constant pressure for a closed reversible system. Solving Eq. (10) for an ideal gas in which enthalpy is the only function of temperature and assuming C_P is independent of temperature,

$$\Delta H = \int_{T_1}^{T_2} C_P dT = C_P(T_2 - T_1) = C_P \Delta T \quad (11)$$

Equation (11) will also be used extensively in heat balances to determine sensible heat changes (thermal energy changes resulting in temperature change rather than phase change) in real systems. The heat capacity at constant pressure is usually larger than that at constant volume because at constant pressure some of the added heat may be used to expand the material, whereas at constant volume all the added heat produces a rise in temperature. From Eqs. (9) and (10), it follows that

$$C_P - C_V = \frac{(\partial H)}{(\partial T)_P} - \frac{(\partial U)}{(\partial T)_V} = \frac{(\partial U)}{(\partial T)_P} + \frac{P(\partial U)}{(\partial T)_P} - \frac{(\partial U)}{(\partial T)_V} \quad (12)$$

Since

$$dU = \frac{(\partial U)}{(\partial V)_T} dV + \frac{(\partial U)}{(\partial T)_V} dT \text{ and } dV = \frac{(\partial V)}{(\partial VT)_P} dT + \frac{(\partial V)}{(\partial P)_T} dP$$

then

$$\frac{(\partial U)}{(\partial T)_P} = \frac{(\partial U)}{(\partial V)_T} \frac{(\partial V)}{(\partial T)_P} + \frac{(\partial U)}{(\partial T)_V} \quad (13)$$

Substituting Eq. (13) into Eq. (12) yields

$$C_P - C_V = \left[P + \frac{(\partial U)}{(\partial V)_T} \right] \frac{(\partial V)}{(\partial T)_P} \quad (14)$$

The term $P(\partial V)/(\partial T)_P$ represents the contribution to the heat capacity caused by the change in volume of the system against the external pressure P . The term $[(\partial U)/(\partial V)_T][(\partial V)/(\partial T)_P]$ is the contribution from the energy required for the change in volume against the internal cohesive or repulsive forces of the substance. The term $(\partial U/\partial V)_T$ is called the *internal pressure*, which is large for liquids and solids and very small for gases. For an ideal gas $(\partial U/\partial T)_T = 0$. Since the equation of state is $PV = nRT$, then

$$C_P - C_V = P \frac{(\partial V)}{(\partial T)_P} nR \quad (15)$$

The concept of enthalpy is very important in thermochemistry, the study of heat effects that accompany chemical reaction, the formation of solutions, and change in state of aggregation like melting and vaporization. Physicochemical changes are called *endothermic* if they are accompanied by the adsorption of heat and *exothermic* if there is evolution of heat. From the definition of enthalpy, $\Delta H > 0$ for endothermic changes and $\Delta H < 0$ for exothermic changes. Using enthalpy and a definition of standard state, it is possible to calculate the enthalpy of formation for chemical compounds. A discussion of this is beyond the scope of this text, and the reader is referred to physical chemistry textbooks [cf. Tinoco et al. (2002) and Baianu (1992)].

C. Second Law of Thermodynamics

The second law of thermodynamics requires the introduction of the concept of *entropy*. Entropy can be regarded as a measure of the order or disorder of a system and is ultimately defined on the basis of statistical mechanics. There are many texts which have devised clever examples to illustrate the concept of entropy, but only a brief one will be introduced here. Consider the three states of water: ice, liquid, and vapor. In ice, the position of each water molecule can be described at any point in time because it is highly restricted in motion due to molecular forces holding the crystal together. When the crystal melts producing liquid water, the probability of knowing the exact location of a particular water molecule at any point in time is greatly diminished because the molecule has much greater flexibility of motion. Finally, if the liquid water evaporates creating water vapor, the disorder increases even further. Thus, the water has become increasingly disordered as it changed from ice to liquid to vapor. As disorder increased, the entropy of the system is said to have increased.

The second law of thermodynamics states that any spontaneous process in an isolated system must lead to an increase in entropy. Stated even more macroscopically, the total entropy of the universe tends to a maximum. As $\Delta S > 0$ defines a spontaneous process, $\Delta S = 0$ defines a reversible cyclic process

in which the system may change states, but upon completion of the cycle the final state is the same as the initial state.

It can be shown from thermodynamic principles that for a closed system with a reversible, constant pressure process,

$$dS = \frac{dQ_{rev}}{T} = \frac{dH_{rev}}{T} \text{ or } dH_{rev} = dQ_{rev} = T dS \quad (16)$$

where Q_{rev} is the change in heat in a reversible process and T is the absolute temperature at which the process is carried out. The advantage of entropy defined by Eq. (16) rather than by statistical mechanics is that entropy can now be measured conveniently from other thermodynamic quantities such as ΔH for constant pressure processes. It can also be seen that a reversible adiabatic ($dQ_{rev} = 0$) process is the same as an isentropic process ($dS = 0$).

D. Thermodynamic Potential: Gibbs Free Energy

Thermodynamic changes in a closed system can also be separated diagrammatically on pressure-volume (P - V) diagrams or on temperature-entropy (T - S) diagrams. These will both be used to characterize important processes applied to real food products or their components.

From the first law of thermodynamics, we can calculate the energy balance, and from the second law we can determine which processes can occur spontaneously. Although this is all that is needed to thoroughly define real processes, what we have so far is not the most convenient to apply in practice. To get to a more practical form, consider the following. From the second law, the entropy of the universe is positive and increasing. For any system the gain in entropy of the universe is the sum of the gain in entropy of the system plus the gain in entropy from the surroundings:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0 \quad (17)$$

The change in entropy from the surroundings for a reversible constant pressure process is Eq. (16):

$$\Delta S_{surr} = \left(\frac{Q_{rev}}{T} \right)_{surr} = \frac{\Delta H_{surr}}{T} \quad (18)$$

If the temperature is the same in the system and the surroundings, then substituting Eq. (18) into (17) yields

$$\Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T} \geq 0 \quad (19)$$

or

$$-T \Delta S_{univ} = \Delta H_{sys} - T \Delta S_{sys} \leq 0 \quad (20)$$

Equation (20) expresses the total entropy of the universe only in terms of properties of the system. Now a new thermodynamic function G is defined, called the *Gibbs free energy*, free enthalpy, or simply free energy as

$$G = H - TS \quad (21)$$

or

$$dG = dH - TdS$$

At constant T ,

$$dG = dH - T dS \quad (22)$$

At constant T and P ,

$$dG = dH - T dS \leq 0 \quad (23)$$

Equation (23) is a more useful equation because it allows us to consider both enthalpy and entropy changes in the system, and ΔG_{sys} is frequently referred to as the thermodynamic potential. For example, the criteria for equilibrium and spontaneity can now be given by the changes in free energy of the system:

$$\Delta G = 0 \quad \text{system at equilibrium} \quad \Delta G < 0 \quad \text{spontaneous process}$$

For processes at constant T and V , a similar quantity, the Helmholtz free energy A , can also be defined:

$$A = U - TS \quad (24)$$

This is less useful because most processes are at constant pressure rather than constant volume.

If a system contains more than one component in a given phase, then the specification of the state also requires specification of composition in addition to P , T , and V . For thermodynamic variables, the chemical measure is the number of moles of component 1, 2, ..., n in the particular phases being considered. Thus, thermodynamic functions will depend on the number of moles, n_1, n_2, \dots, n_i , as well as T , P and V . For example, the Gibbs function becomes

$$dG = \frac{(\partial G)}{(\partial T)_{P,n_i}} dT + \frac{(\partial G)}{(\partial P)_{T,n_i}} dP + \sum_{\lambda} \frac{(\partial G)}{(\partial n_i)_{T,P,n_j}} dn_i \quad (25)$$

where Gibbs called the coefficient $(\partial G)/(\partial n_i)_{T,P,n_j}$ the chemical potential of component i when the number of moles of all other constituents n_1, n_2, \dots, n_i are held constant and gave it the symbol μ_i . The significance of chemical potential will be seen later when we discuss water relations in foods and phase equilibria. Suffice it to say that it can be shown that for equilibrium, the chemical potential

of a species for each phase must be equal. If α and β are two phases, then at equilibrium:

$$\mu_i^\alpha = \mu_i^\beta \quad (26)$$

From Eq. (23), for a spontaneous process,

$$\begin{aligned} \Delta H - T \Delta S &< 0 \\ \text{or } \Delta H &< T \Delta S. \end{aligned} \quad (27)$$

We can now consider if a process is enthalpy-driven or entropy-driven. If ΔH and ΔS are both positive, the process may occur spontaneously at sufficiently high temperature, and the process is said to be entropy-driven. If ΔH and ΔS are negative, the process may occur spontaneously at sufficiently low temperature, and the process is enthalpy-driven. If $\Delta H > 0$ and $\Delta S < 0$, no process can occur at any temperature, and if $\Delta H < 0$ and $\Delta S > 0$, the process is spontaneous at all temperatures.

So far, thermodynamics can prove useful to determine *if* a process will occur spontaneously. Unfortunately, it cannot tell us a priori the rate at which the process occurs. For many processes, especially those involving chemical reactions or phase changes, it is necessary to overcome an energy barrier, frequently referred to as the activation energy barrier (see Chapter 2 on reaction kinetics).

For most practical applications, temperature and pressure are two of the most important process variables. Consequently, it is necessary to consider the dependence of free energy on T and P . By definition,

$$G = H - TS = U + PV - TS \quad (28)$$

$$dG = dU + P dV + V dP - T dS - S dT$$

For reversible processes involving only P - V work,

$$dU = dQ - P dV = T dS - P dV \quad (29)$$

Substitution of Eq. (29) into Eq. (28) yields the temperature and pressure dependence of free energy:

$$dG = V dP - S dT \quad (30)$$

and

$$\frac{dG_T}{dP_T} = V \quad \text{and} \quad \frac{dG_P}{dT_P} = -S$$

For example, for an ideal gas at constant temperature ($dT = 0$), $PV = nRT$ and $dG = V dP$.

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} V dP = \int_{P_1}^{P_2} \frac{nRT}{P} dP$$

$$\Delta G = G_2 - G_1 = nRT \ln \frac{P_2}{P_1} \quad (31)$$

If $P_1 = 1$ atm, then

$$G = G^\circ + RT \ln P \quad (32)$$

and G° is called the standard free energy.

III. SOLUTION PROPERTIES

An appreciation for thermodynamics of multicomponent mixtures is extremely important in food systems since we are often interested in separating components, optimizing fragrance of products, or controlling gases or water in foods. In this section, we will consider the behavior of ideal multicomponent systems with ultimate application to real food systems.

A. Partial Molar Quantities

For pure substances, it is acceptable to use the ordinary thermodynamic functions just described. However, for solutions the thermodynamic theory is expressed in terms of partial molar functions. This can best be explained by considering a solution containing n_A mol of A and n_B mol of B. If we have a very large volume of solution so that adding 1 mol of A or B does not change the concentration appreciably, then we can measure the increase in volume when 1 mol is added at constant T and P . The increase in volume is called the partial molar volume of the component in the solution at the specified temperature, pressure, and composition. It is denoted by the symbol V_A and is written

$$V_A = \left(\frac{\partial V}{\partial n_A} \right)_{T, P, n_B} \quad (33)$$

These partial molar functions are necessary because adding pure components together to form solutions does not result in properties of the solution equal to the sum of the properties in pure state. For example, if 100 cm³ of ethanol are mixed at 25°C with 100 cm³ of water, the volume is 190 cm³. It can be shown that a property of partial molar functions is that the total value of the function is the sum of the product of moles of the component and its partial

molar function. For example, the total volume of a mixture of n_A mol of A and n_B mol of B is

$$V = n_A V_A + n_B V_B \quad (34)$$

Partial molar functions can be defined for all state functions. For example,

$$S_A = \frac{(\partial S)}{(\partial n_A)_{T,P,n_B}} \quad H_A = \frac{(\partial H)}{(\partial n_A)_{T,P,n_B}} \quad G_A = \frac{(\partial G)}{(\partial n_A)_{T,P,n_B}} = \mu_A \quad (35)$$

In addition, all thermodynamic relations that applied to state functions for pure components also apply to partial molar functions. For example,

$$\frac{(\partial G_A)}{(\partial P)_T} = \frac{(\partial \mu_A)}{(\partial P)_T} = V_A \quad \frac{(\partial \mu_A)}{(\partial P)_P} = -S_A \quad \frac{(\partial H_A)}{(\partial T)_P} = C_{PA} \quad (36)$$

To illustrate its application, consider the formation of a binary solution from n_A mol of A and n_B mol of B:

$$n_A + n_B \quad \text{solution} \quad (37)$$

At a given T and P , the ΔG , for the solution process is

$$\Delta G = G_{\text{soln}} - n_A G_A^\circ + n_B G_B^\circ \quad (38)$$

Where G_A° and G_B° denote the molar free energies of the pure components. By analogy to Eq. (34),

$$G_{\text{soln}} - n_A G_A + n_B G_B \quad (39)$$

Therefore,

$$\Delta G = n_A G_A + n_B G_B - n_A G_A^\circ - n_B G_B^\circ \quad (40)$$

or

$$\Delta G = n_A(G_A - G_A^\circ) + n_B(G_B - G_B^\circ)$$

Exactly analogous equations can be written for any extensive thermodynamic state variable (U , H , S , V , A , C_v , C_p , etc.) ultimately defining quantities such as enthalpy of solution, entropy of solution, etc.

B. Chemical Potential

As we have seen, the partial molar Gibbs free energy G_A is equivalent to the chemical potential μ_A . Instead of chemical potential, it is often convenient to use a related function, the absolute activity λ_A , defined by

$$\mu_A = RT \ln \lambda_A \quad (41)$$

Relations expressed for μ_A also apply to λ_A . For example, the condition for equilibrium of component A between gas and liquid phases is

$$\lambda_A^g = \lambda_A^l \quad (42)$$

For solutions, it is convenient also to express the difference between the value of μ_A in the solution and its value in some reference state. That is,

$$\mu_A - \mu_A^+ = RT \ln \frac{\lambda_A}{\lambda_A^+} = RT \ln a_A \quad (43)$$

where the ratio of absolute activity to the activity in some reference state defines a relative activity a_A .

For nonelectrolyte solutions of liquids, a convenient reference state is the pure liquid at $P = 1$ atm and the temperature specified for the solution. If the reference state is identified at μ_A° and λ_A° , Eq. (43) becomes

$$\mu_A - \mu_A^\circ = RT \ln \frac{\lambda_A}{\lambda_A^\circ} = RT \ln a_A \quad (44)$$

and

$$a_A = \frac{\lambda_A}{\lambda_A^\circ}$$

Defined in this way, the relative activity is called simply activity. Furthermore, the ratio of the activity to the mole fraction x_A is called the activity coefficient:

$$\gamma_A = \frac{a_A}{x_A} \quad (45)$$

where γ_A is the activity coefficient. For an ideal solution $\gamma_A = 1.0$. The activity coefficient for a homologous series of aromatic compounds given in Table 1.1.

C. Ideal Mixtures

An ideal gas is one in which there are no cohesive forces acting on the molecules and hence the internal pressure is zero $[(\partial U/\partial V)_T = 0]$. For an ideal solution the cohesive forces are equal and uniform between all species. For example, if there are two components A and B, the intermolecular forces between A and A, B and B, and A and B are all the same. Just as the ideal gas law has served a useful purpose in treating practical cases even when large deviations from ideality occurs, the concept of an ideal solution serves the same purpose.

An important property of solutions is the vapor pressure of a component above the solution. Since this partial vapor pressure is a measure of the given species to escape from the solution into the vapor phase, its study provides information on the physical state within the solution.

TABLE 1.1 Relative Vapor Pressure of a Homologous Series of Aromatic Compounds at 25°C

| Compound | Normal boiling point (°C) | Vapor pressure (mmHg) | Activity coefficient γ_i^∞ | Berehend β_{iw}^∞ | Experimental β_{iw}^∞ |
|-------------------|------------------------------|--------------------------|---|---------------------------------|-------------------------------------|
| Butanol | 117.4 | 8.5 | 43 | 15 | 16 |
| Hexanol | 155.5 | 1.2 | 680 | 34 | 30 |
| Octanol | 194.5 | 0.18 | 11000 | 85 | 43 |
| Acetone | 56.2 | 230 | 7.8 | 75 | 70 |
| Butan-2-one | 79.6 | 91 | 27 | 100 | 82 |
| Pentan-2-one | 102 | 37 | 100 | 160 | 110 |
| Heptan-2-one | 151.5 | 4.8 | 1600 | 330 | 260 |
| Octan-2-one | 172.9 | 1.9 | 6600 | 530 | 330 |
| Nonan-2-one | 195 | 0.76 | 27000 | 870 | 650 |
| Undecan-2-one | 228 | 0.19 | 460000 | 3700 | 1100 |
| Acetaldehyde | 21 | 910 | 4.2 | 160 | 120 |
| Propanal | 48 | 290 | 16 | 190 | 130 |
| Butanol | 75 | 91 | 61 | 240 | 200 |
| Pentanal | 103 | 38 | 250 | 400 | 260 |
| Hexanal | 131 | 12 | 1000 | 500 | 310 |
| Heptanal | 153 | 4.7 | 4200 | 820 | 610 |
| Octanal | 177 | 1.7 | 17000 | 1200 | 910 |
| Nonanal | 191 | 0.89 | 71000 | 2700 | 1300 |
| Methyl acetate | 57.5 | 170 | 24 | 240 | 200 |
| Methyl propionate | 79.7 | 70 | 95 | 380 | 310 |
| Methyl butyrate | 102.3 | 25 | 390 | 560 | 370 |
| Methyl pentanoate | 130 | 7.3 | 1300 | 560 | 560 |
| Methyl hexanoate | 150 | 2.9 | 7100 | 1200 | 650 |
| Methyl octanoate | 193 | 0.37 | 13000 | 2800 | 1000 |

For a mixture of two ideal components in an ideal mixture (one in which the two components do not interact), the vapor pressures of components 1 and 2 are given by Raoult's law as

$$P_1 = x_1 P_1^\circ \quad (46)$$

$$P_2 = x_2 P_2^\circ \quad (47)$$

where x_1 and x_2 are the mole fractions and P_1° and P_2° are the vapor pressures of pure liquids, respectively. From Dalton's law of additive pressure, the total pressure is

$$P = P_1 + P_2 \quad (48)$$

Since most solutions behave nonideally, positive and negative deviations from Raoult's law occur.

If the solute is volatile, and the solution is dilute and ideal, then Henry's law applies:

$$P_2 = kx_2 \quad (49)$$

where k is Henry's law constant and depends on the nature of both the solute and solvent. Henry's law can also be written in terms of molality of the solution, and the constant k^1 has units $\text{atm mol}^{-1} \text{kg}^{-1}$ of the solvent.

$$P_2 = k^1 m \quad (50)$$

Values for k^1 for several gases are given in Table 1.2.

We defined the chemical potential in terms of thermodynamic potential as

$$\frac{(\partial G)}{(\partial n_i)_{T,P,n_j}} = \mu_i$$

TABLE 1.2 Henry's Law Constants for Gases in Water at 298K

| Gas | k^1 ($\text{atm mol}^{-1} \text{kg}^{-1} \text{H}_2\text{O}$) |
|------------------|---|
| H ₂ | 1311 |
| He | 2649 |
| Ar | 662 |
| N ₂ | 1610 |
| O ₂ | 773 |
| CO ₂ | 29.3 |
| H ₂ S | 10.1 |

[see Eq. (25)]. In a manner analogous to that for free energy, the chemical potential of the i th component in a mixture of ideal gases is

$$\mu_i = \mu_i^+(T) + RT \ln P_i \quad (51)$$

where $\mu_i^+(T)$ is the standard chemical potential of component i and P_i is the partial pressure. Substituting $P_i = x_i P$, where P is total pressure, into Eq. (51) yields

$$\mu_i = \mu_i^+(T) + RT \ln P + RT \ln x_i \quad (52)$$

The first two terms on the right correspond to the chemical potential of the i th component in the pure state at pressure P . Consequently, Eq. (52) can be written

$$\mu_i = \mu_{i,T,P=1\text{ atm}}^\circ + RT \ln x_i \quad (53)$$

Equation (53) can be generalized to include condensed phases in which case a two-component system can be represented as

$$\mu_1 = \mu_{1,T,P}^\circ + RT \ln x_1 \quad \text{solvent} \quad (54)$$

$$\mu_2 = \mu_{2,T,P}^\circ + RT \ln x_2 \quad \text{solute} \quad (55)$$

Usually Eqs. (54) and (55) are written in terms of activity, a_1 and a_2 , since for an ideal solution $a_i = x_i$ [see Eq. (45)]:

$$\mu_1 = \mu_{1,T,P}^\circ + RT \ln a_1 \quad (56)$$

D. Nonideal Mixtures

We have just seen for an ideal gas at constant temperature

$$G = G^\circ + RT \ln P \quad (32)$$

and for an ideal mixture or solution, we have

$$\mu_A = \mu_{A,T}^+ + RT \ln P_A \quad (51)$$

or for an ideal gas ($PV = nRT$),

$$d\mu_A = d(RT \ln P_A) = V dP \quad (57)$$

Since real systems deviate from ideality, Eqs. (32) and (51) required modification. However, the utility of maintaining the form of these equations

for convenience in thermodynamic analysis was recognized, and a new function called *fugacity* (f) was defined analogously to Eq. (57).

$$d\mu_a = RT \ln f_A \quad (58)$$

Integrating Eq. (58) between the given state and some arbitrary reference state yields

$$\mu_A = \mu_A^+ + RT \ln \frac{f_A}{f_A^+} \quad (59)$$

In solutions, fugacity can be thought of as the true measure of the escaping tendency of a component from the solution or an idealized partial pressure which becomes equal to the partial pressure only when the vapor behaves as an ideal gas. Fugacity and fugacity coefficients for water vapor in equilibrium with liquid water at saturation and 1 atm pressure are given in Table 1.3.

It can be seen from comparison to Eq. (43) that

$$\frac{f_A}{f_A^+} = \frac{\lambda_A}{\lambda_A^+} = a_A \quad (60)$$

indicating that fugacity is related to absolute activity λ and to the activity a_A . Furthermore, the ratio of fugacity to pressure is an indication of the deviation from nonideality. The fugacity coefficient expresses this ratio:

$$\gamma = \frac{f}{p} \quad (61)$$

where $\gamma = 1.0$ for an ideal gas.

IV. PHASE EQUILIBRIA

One of the most important applications of the concept of thermodynamics is phase equilibria. A phase is a homogeneous region of a system and we most frequently think of phases as solid, liquid, and vapor. Figure 1 is a phase diagram for water. A phase diagram represents the relationship between pressure and temperature for the phases of a system. For pure water, region S represents solid ice, L represents liquid water, and V represents water vapor. The solid lines represent the conditions under which two phases coexist in equilibrium. The point where all three phases coexist is called the triple point and is at $T = 273.16\text{K}$ and $P = 0.00603 \text{ atm}$. Finally, there exists a pressure and temperature, called the critical point, above which the liquid and vapor phases are indistinguishable (for water at 547.6K and 219.5 atm). Properties of fluids above the critical point take on characteristics distinct from either the liquid or vapor and consequently may be used uniquely in processing. An example is the use of supercritical carbon dioxide for separation of food components.

TABLE 1.3 Fugacity and Fugacity Coefficients of Water Vapor in Equilibrium with Liquid at Saturation and at 1 Atmosphere Pressure

| Temperature (°C) 0.01 ^a | At saturation | | | |
|---------------------------------------|---|----------------------------|-------------------------------------|---|
| | Pressure (bars) ^b (± 0.1%) | Fugacity (bars)(± 0.1%) | Fugacity coefficient (± 0.1%) | Fugacity (bars) at 1 atm (0.01325 bars) (± 0.1%) |
| | 0.00611 | 0.00611 | 0.995 | |
| 10.00 | 0.01227 | 0.01226 | 0.9992 | |
| 20.00 | 0.0337 | 0.0334 | 0.9988 | |
| 30.00 | 0.04242 | 0.04235 | 0.9982 | |
| 40.00 | 0.7376 | 0.07357 | 0.9974 | |
| 50.00 | 0.12336 | 0.12291 | 0.9954 | |
| 60.00 | 0.19920 | 0.19821 | 0.9950 | |
| 70.00 | 0.31163 | 0.30955 | 0.9933 | |
| 80.00 | 0.47362 | 0.46945 | 0.9912 | |
| 90.00 | 0.70114 | 0.69315 | 0.9886 | |
| 100.00 | 1.0132 | 0.99856 | 0.9855 | 0.9986 |
| 110.00 | 1.4326 | 1.4065 | 0.9818 | 1.0004 |
| 120.00 | 1.9853 | 1.9407 | 0.9775 | 1.0019 |
| 130.00 | 2.7011 | 2.6271 | 0.9726 | 1.0031 |
| 140.00 | 3.6135 | 3.4943 | 0.9670 | 1.0042 |
| 150.00 | 4.7596 | 4.5726 | 0.9607 | 1.0051 |
| 160.00 | 6.1804 | 5.8940 | 0.9537 | 1.0059 |
| 170.00 | 7.9202 | 7.4917 | 0.9459 | 1.0066 |
| 180.00 | 10.027 | 9.3993 | 0.9374 | 1.0072 |
| 190.00 | 12.552 | 11.650 | 0.9282 | 1.0077 |
| 200.00 | 15.550 | 14.278 | 0.9182 | 1.0081 |
| 210.00 | 19.079 | 17.316 | 0.9076 | 1.0085 |
| 220.00 | 23.201 | 20.793 | 0.8962 | 1.0089 |
| 230.00 | 27.978 | 24.793 | 0.8842 | 1.0092 |
| 240.00 | 33.480 | 29.181 | 0.8716 | 1.0095 |
| 250.00 | 33.775 | 34.141 | 0.8584 | 1.0098 |
| 260.00 | 46.940 | 39.063 | 0.8445 | 1.0100 |
| 270.00 | 55.051 | 45.702 | 0.8302 | 1.0103 |
| 280.00 | 64.191 | 52.335 | 0.8153 | 1.0105 |
| 290.00 | 74.448 | 59.554 | 0.7999 | 1.0106 |
| 300.00 | 85.916 | 67.367 | 0.7841 | 1.0108 |

^a Ice-liquid-vapor triple point.^b bar = 0.9869 atm.

Source: Hass (1970).

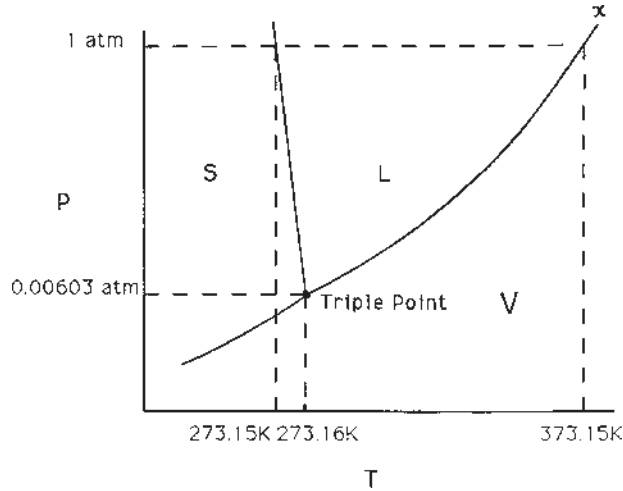


FIGURE 1.1 Phase diagram of water. The liquid-vapor curve stops at x , the critical point (547.6K and 219.5 atm).

A. Liquid-Vapor Equilibria

For phase equilibria between liquid and vapor, the free energy per mole must be the same in both phases. If this were not the case, then the system would spontaneously adjust to achieve equal free energy in both phases. Thus at some P and T ,

$$\bar{G}_A^l = \bar{G}_A^g \quad (62)$$

If T and P are both shifted some infinitesimal amount so that the molar free energies become $\bar{G}_L + d\bar{G}_L$ and $\bar{G}_V + d\bar{G}_V$, then the equilibrium condition will still hold and

$$\bar{G}_L + d\bar{G}_L = \bar{G}_V + d\bar{G}_V \quad (63)$$

From Eq. (62), $d\bar{G}_L = d\bar{G}_V$, and from Eq. (30)

$$d\bar{G}_L = \bar{V}_L dP - \bar{S}_L dT = d\bar{G}_V = \bar{V}_V dP - \bar{S}_V dT \quad (64)$$

or

$$\frac{dP}{dT} = \frac{\bar{S}_V - \bar{S}_L}{\bar{V}_V - \bar{V}_L} = \frac{\Delta \bar{S}_{vap}}{\Delta \bar{V}_{vap}} \quad (65)$$

where $\Delta\bar{S}_{vap}$ and $\Delta\bar{V}_{vap}$ are the molar entropy and molar volume change of vaporization, respectively. Since $\Delta\bar{G}_{vap} = \Delta\bar{H}_{vap} - T\Delta\bar{S}_{vap} = 0$ for a reversible process, then

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{vap}}{T\Delta\bar{V}_{vap}} \quad (66)$$

where $\Delta\bar{H}_{vap}$ is the molar enthalpy of vaporization. Equation (66) is extremely important and is a form of the Clausius-Clapeyron equation. Its usefulness can be seen by considering phase equilibria for water. At moderate temperature and over a limited range, $\Delta\bar{H}_{vap}$ may be assumed constant, and since $V_v \gg V_L$, $\Delta\bar{V}_{vap} \sim \bar{V}_v$. For atmospheric conditions and applying the ideal gas law, $\bar{V}_v = RT/P$, then

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{vap}P}{RT^2} \quad (67)$$

or

$$\ln \frac{P_2}{P_1} = \frac{\Delta\bar{H}_{vap}(T_2 - T_1)}{RT_1T_2} \quad (68)$$

Thus, a plot of $\ln P$ versus $1/T$ gives a straight line with slope $\Delta\bar{H}_{vap}/R$. Equation (68) is the most popular form of the Clausius-Clapeyron equation.

B. Solid-Liquid Equilibria

Similarly, analysis of phase equilibria between ice and liquid water leads to

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{fus}}{\Delta\bar{V}_{fus}} \quad (69)$$

Water is unique in that the molar volume of liquid is less than that of ice $\Delta\bar{V}_{fus} = \Delta\bar{V}_L - \Delta\bar{V}_S < 0$ which results in a negative slope on the P - T diagram for the ice-liquid equilibrium line. Furthermore, since $\Delta\bar{V}_L$ and $\Delta\bar{V}_S$ are similar in magnitude (at 273.15K, $\bar{V}_L = 0.01802$ L and $\Delta\bar{V}_V = 0.01963$ L), the slope is very large.

C. Solid-Vapor Equilibria

For solid-vapor equilibria, the Clausius-Clapeyron equation is

$$\frac{dP}{dT} = \frac{\Delta\bar{H}_{sub}}{T\Delta\bar{V}_{sub}} \quad (70)$$

where the subscript denotes sublimation. According to Hess's law, $\Delta\bar{H}_{sub}$ may be calculated as the sum of $\Delta\bar{H}_{vap} + \Delta\bar{H}_{fus}$. Consequently, the slope

of the equilibrium line between solid and vapor is greater than that between liquid and vapor because of the additional heat of fusion.

An example of the application of the Clausius-Clapeyron equation is calculation of the heat of vaporization of food products as proposed by Othmer (1940). The water vapor pressure of the product (or equilibrium relative humidity) is measured as a function of temperature. From Eq. (31) and knowing the vapor pressure of water at corresponding temperatures, the following applies:

$$\frac{\Delta\bar{H}_{vap,w}}{T\Delta\bar{V}_{vap,p}} = \frac{(\log P_2 - \log P_1)_w}{(\log P_2 - \log P_1)_p} \quad (71)$$

where w refers to water and p refers to product.

Example: The equilibrium relative humidity for precooked freeze-dried beef containing 10% moisture was 0.065, 0.1, 0.38, and 0.44 at 3, 9, 21, and 36°C, respectively. Compute the heat of vaporization for the product at 30°C.

Solution:

- Using Eq. (35), plot logarithm of product vapor pressure versus logarithm of water vapor pressure to obtain the ratio of heat of vaporization (Othmer plot).

| Temperature (°C) | P_p/P_w | P_w | P_p |
|------------------|-----------|--------|-------|
| 3 | 0.065 | 0.7577 | 0.049 |
| 9 | 0.10 | 1.1477 | 0.115 |
| 21 | 0.38 | 2.487 | 0.945 |
| 39 | 0.44 | 5.947 | 2.617 |

- From the plot of $\log P_p$ versus $\log P_w$,

$$\text{Slope} = 2.169 = \frac{\Delta\bar{H}_{vap,w}}{\Delta\bar{H}_{vap,p}}$$

- $\Delta\bar{H}_{vap,p} = 2.169\Delta\bar{H}_{vap,w}$,

$$\Delta\bar{H}_{vap,p} = 2.169(2430.5) \frac{kJ}{kg} = 5272 \frac{kJ}{kg}$$

D. Phase Rule

A useful rule regarding phase equilibria was derived by Gibbs and is called the *phase rule*:

$$f = c - p + 2 \quad (72)$$

where c is the number of components, p is the number of phases present, and f gives the degree of freedom on number of variables (pressure, temperature, composition), which must be fixed to completely describe the system. For example, for pure water vapor (v), $c = 1$ and $p = 1$ so that $f = 2$. Thus knowing two out of the three P , V , and T , the system is completely described. The third variable (P , V , or T) can be calculated from the equation of state (gas law). In any pure-phase region of the phase diagram, $f = 2$. Along any boundary, however, $p = 2$ and $f = 1$. Thus, for any value of P there is only one unique value of T at which both phases exist in equilibrium. At the triple point, $p = 3$ and $f = 0$, indicating that there is only one unique pressure-temperature combination where all three phases exist simultaneously. Some caution should be used when applying the phase rule because of additional constraints which may be applied to the relationships between components. Extra relationships include, for example, balanced chemical relationships and electrical neutrality in ionic solutions.

E. Pressure-Composition Diagram

One of the most important processes in the food industry is the removal of water in either evaporation or in drying with minimum removal of flavor or aroma compounds. In addition, the food flavor and fragrance industry uses fractional distillation to separate components creating desired food additives that enhance flavor and taste. These processes are all based on the difference of vapor pressure of components at a given temperature. In order to design processes, it is useful to construct diagrams that show the vapor pressure of a solution as a function of mole fractions as well as composition of the vapor in equilibrium with the solution.

From Eqs. (46) and (47) and Dalton's law, we can derive the following:

$$P_1 = x_1 P_1^\circ, \quad P_2 = x_2 P_2^\circ$$

$$x_1^v = \frac{P_1}{P_1 + P_2} \quad x_2^v = \frac{P_2}{P_1 + P_2} \quad (73)$$

where x_1^v and x_2^v are the mole fractions of components 1 and 2 in the vapor phase, then

$$x_1^v = \frac{x_1 P_1^\circ}{P_1 + P_2} \quad (74)$$

and

$$\frac{x_1^v}{x_2^v} = \frac{x_1 P_1^\circ}{x_2 P_2^\circ} \quad (75)$$

Equation (75) allows us to calculate the composition of liquid and vapor when the pressure is known. The pressure-composition diagram for benzene-toluene is given in Fig. 1.2. At point a on the liquid curve, the mole fractions are $x_{\text{benzene}} = 0.2$ and $x_{\text{toluene}} = 0.8$. The composition of the vapor in equilibrium with the solution (point b) is $x_{\text{benzene}}^v = 0.5$ and $x_{\text{toluene}}^v = 0.5$. Thus the vapor is richer in benzene than the liquid. If we condense the vapor (b-c) and re-evaporate the liquid (c-d), the mole fraction of benzene will be even higher in the vapor phase. By repeating this process of condensing–re-evaporating in several stages, eventually the two components will be separated to the desired level.

The previous example is for a constant temperature process. In practice, distillations are usually carried out at constant temperature. Since the relation between temperature and composition is complex, the temperature-composition or boiling point diagram is determined experimentally. Figure 1.3 is the temperature-composition diagram for benzene-toluene. From Fig. 1.3, it can be seen that benzene, the component with the higher vapor pressure, has the lower boiling point. The process can be tracked as it was on the P - C diagram through a series of evaporation-condensation stages at constant pressure to produce a liquid

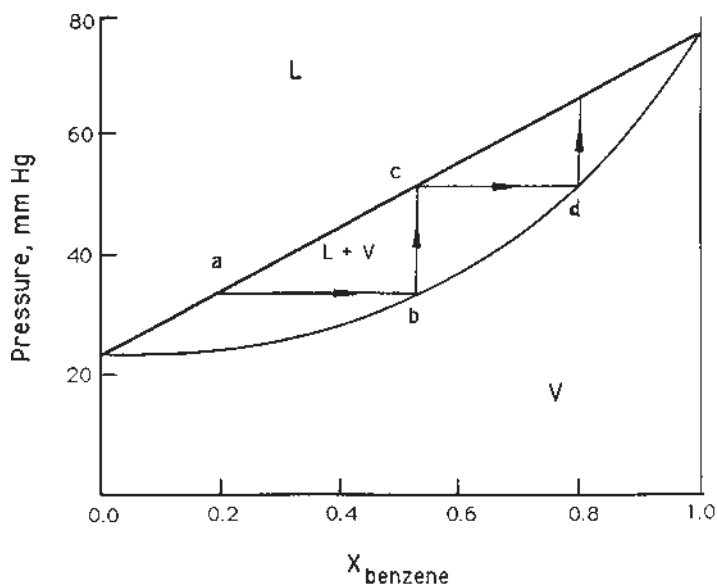


FIGURE 1.2 Pressure-composition diagram of the benzene-toluene system. (From Chang, 1977, p. 264.)

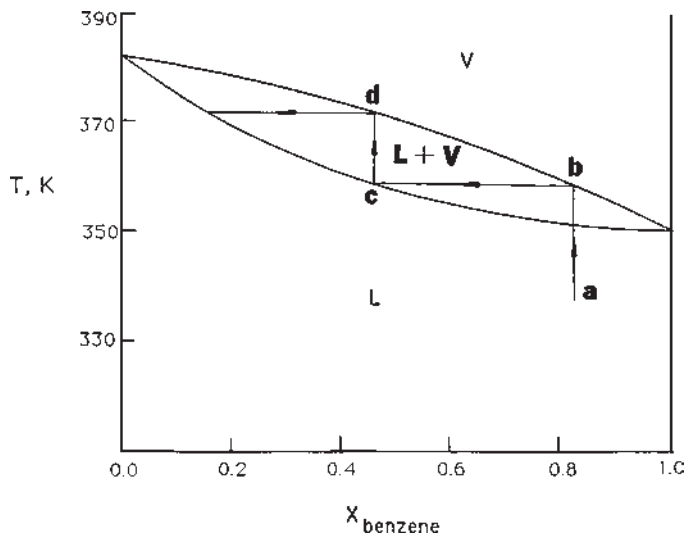


FIGURE 1.3 Temperature-composition diagram of the benzene-toluene system. (From Chang, 1977, p. 264.)

phase rich in toluene and poor in benzene. Eventually the two components will be completely separated.

Since most solutions are nonideal, the experimentally determined T - C diagrams will be more complex. If the system deviates in a positive direction from Raoult's law, the curve will show a minimum boiling point, whereas a negative deviation will produce a maximum boiling point. Under these circumstances, eventually the vapor and liquid will have the same composition, and further separation by distillation is not possible. The resulting equilibrium mixture is called an *azeotrope*. In most mixtures of importance to food processing, deviation is positive and minimum boiling mixtures are produced. Examples include ethanol-water and *n*-propanal-water.

V. COLLIGATIVE PROPERTIES

The colligative properties of dilute ideal solutions are those properties which depend only on the number of solute molecules present (number of moles or mole fraction) and not on the size or molecular weight of the molecules. As we shall see presently, these properties include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. As pointed out above, these properties of aqueous solutions are very important for proper design of food processing operations.

A. Vapor Pressure Lowering

Assume we have a dilute aqueous solution containing a nonvolatile solute, for example, sucrose in water. Since the vapor pressure of sucrose is small (1×10^{-23} atm), we can neglect it and apply Raoult's law to the solvent.

$$P_w = x_w P_w^\circ \quad (76)$$

where w refers to water. Since $x_w = 1 - x_s$, where x_s is the mole fraction of sucrose, then

$$P_w = (1 - x_s) P_w^\circ \quad (77)$$

Rearrangement gives

$$P_w^\circ - P_w = \Delta P_w = x_s P_w^\circ \quad (78)$$

where ΔP_w is the vapor pressure lowering of the presence of x_s mole fraction of sucrose.

B. Boiling Point Elevation

The boiling point of a solution is the temperature at which its vapor pressure is equal to the external pressure. From the previous analysis, adding a nonvolatile solute to water lowers the vapor pressure resulting in an elevated boiling point.

The boiling point elevation can be estimated by writing the Clausius-Clapeyron equation [Eq. (68)] for the solution

$$\ln \frac{P_o}{P} = \frac{\Delta \bar{H}_{vap}(T - T_o)}{RTT_o} \quad (79)$$

where P_o and T_o are the vapor pressure and temperature of water at its boiling point and P and T are the corresponding solution properties. ΔH is the molar heat of vaporization of water from the solution and, for dilute solutions, may be taken as the molar heat of vaporization of the pure water. In addition, since the boiling point elevation is generally small for a dilute solution $TT_o \cong T_o^2$. From Raoult's law,

$$P = x_w P_o \quad \text{and} \quad \ln \frac{P}{P_o} = \ln x_w \quad (80)$$

Since $\ln x_w = \ln(1 - x_s)$, and for $x_s \leq 0.2$,

$$\ln(1 - x_s) = \frac{x_s^2}{2} - \frac{x_s^3}{3} - \dots \cong -x_s$$

Then

$$\ln \frac{P_o}{P} = x_s \quad (81)$$

for $x_s \leq 0.2$. Substituting Eq. (81) into Eq. (79) gives

$$\begin{aligned} x_s &= \frac{\Delta \bar{H}_{vap}(T - T_o)}{RT_o^2} \\ &= \frac{\Delta \bar{H}_{vap} \Delta T_{bp}}{RT_o^2} \end{aligned} \quad (82)$$

where ΔT_{bp} is boiling point elevation. Solving Eq. (82) for boiling point elevation gives

$$\Delta T_{bp} = \frac{RT_o^2 x_s}{\Delta \bar{H}_{vap}} \quad (83)$$

Generally, this equation is written in terms of molality by noting that

$$x_s = \frac{n_s}{n_w + n_s} \sim \frac{n_s}{n_w} = \frac{W_s M_s}{W_w M_w} \quad (84)$$

for $n_w \gg n_s$, where W_s and W_w are the mass of solute and water, respectively, and M_s and M_w are the respective molecular weights. Then

$$\Delta T_{bp} = \frac{18RT_o^2}{1000 \Delta \bar{H}_{vap}} \left(\frac{1000W_s}{W_s M_s} \right) \quad (85)$$

All the quantities in the first term are constants for a given solute-water system and can be expressed as K_b . The second term is the molality (M_w) of the solution. Thus,

$$\Delta T_{bp} = K_b M_w \quad (86)$$

For dilute aqueous solutions, $K_b = 0.52^\circ\text{C}$.

C. Freezing Point Depression

In an analogous thermodynamic analysis, freezing point depression for dilute aqueous solution leads to

$$\Delta T_{bp} = \frac{-18RT_o^2 M_w}{1000 \Delta \bar{H}_{fus}} \quad (87)$$

or

$$\Delta T_{fp} = -K_f M_w \quad (88)$$

For aqueous solutions $K_f = 1.86^\circ\text{C}$.

Example for Freezing Point Depression: Calculate the temperature at which ice formation is initiated in an ice cream mix with the following composition: 10% butterfat, 12% solids-not-fat (54.5% lactose), 15% sucrose, and 0.22% stabilizer.

Solution: We will assume that the only constituent influencing the freezing point is the dissolved sucrose and lactose and that the solution is sufficiently dilute so that Eq. (88) applies.

$$\Delta T_{fp} = -1.8m \quad (\text{where } m = \text{molality})$$

$$\text{Molality} = \frac{\text{moles solute}}{1000 \text{ g water}} = \frac{\text{g solute}}{M_s 1000 \text{ g water}}$$

$$\text{Mass fraction sucrose + lactose} = 0.15 + 0.12(0.545) = 0.2154 \frac{\text{g}}{\text{g}_{\text{product}}}$$

$$0.2154 \frac{\text{g}}{\text{g}_p} \frac{(1 \text{ g product})}{(0.6728 \text{ g water})} = 0.3431 \frac{\text{g solute}}{\text{g water}} = 343.1 \frac{\text{g solute}}{1000 \text{ water}}$$

$$\frac{343.1 \text{ solute}}{342 \text{ water}} \text{mol} = 1.003 \text{ molality}$$

$$\Delta T_{fp} = -1.86(1.003) = -1.86^\circ\text{C}$$

Therefore, initial freezing begins at -1.86°C or 271.14K

D. Osmotic Pressure

The concept of osmotic pressure can be illustrated by considering two compartments, one containing solvent, e.g., water, and the other containing a solution separated by a semipermeable membrane (allows water to pass through but not solute). Practically speaking this system has two different phases, and at equilibrium, sufficient water will have migrated through the semipermeable membrane so that the hydrostatic head of the solution exactly counterbalances the difference in chemical potential between the pure water and the solution.

From thermodynamic principles, it can be shown that

$$\pi = \frac{c}{M_2} RT \quad (89)$$

where π is the osmotic pressure, c is concentration of solute in gl^{-1} of solution and M_2 is molecular weight of the solute.

One of the many uses of Eq. (89) was determination of molecular weight. In that connection, osmotic pressure was measured at several different concentrations and extrapolated to zero concentration to reduce deviation from the assumption of ideal behavior.

SYMBOLS

| | |
|-----------|---|
| U | internal energy (kJ) |
| W | work (kJ) |
| Q | heat energy (kJ) |
| V | volume (m^3) |
| P | pressure (bars or atm) |
| H | enthalpy (kJ/kg) |
| T | temperature (K) |
| C_V | heat capacity at constant volume (kJ/kg K) |
| C_P | heat capacity at constant pressure (kJ/kg K) |
| R | universal gas law constant (8.314 J/mol K) |
| n | moles (mol) |
| S | entropy (kJ/K or entropy unit) |
| G | Gibbs free energy (kJ) |
| A | Helmholtz free energy (kJ) |
| M | chemical potential (kJ/kmol) |
| G° | standard free energy (kJ) |
| λ | absolute activity (dimensionless) |
| a | relative activity (dimensionless) |
| γ | activity coefficient (dimensionless) |
| x | mole fraction (dimensionless) |
| k | Henry's law constant ($\text{atm mol}^{-1} \text{kg}^{-1}$) |
| f | fugacity (bars) or degrees of freedom (dimensionless) |
| c | number of components (dimensionless) |
| p | number of phases (dimensionless) |
| K_b | boiling point elevation constant (K or $^\circ\text{C}$) |
| K_f | freezing point depression constant (K or $^\circ\text{C}$) |
| π | osmotic pressure (bars or atm) |
| M | molecular weight (kg/kmol) |

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2

Reaction Kinetics

I. INTRODUCTION

Processes are designed to cause an action. In the case of food processing, the processor is interested in changing the flavor, color, or texture; inactivating undesirable microorganisms, enzymes, or toxicants; or extending the shelf life of the product. To design a process with a specific outcome in mind requires that the rate at which the desired attribute changes with time must be quantified. This general topic is called *kinetics*, and if chemical modification is involved, it is referred to as *chemical kinetics*. Furthermore, the rate at which change occurs is generally dependent on numerous environmental factors such as moisture content (even when water is not a reactant or product of the reaction), pH, temperature, catalysts, oxygen tension, and presence of other chemicals in the milieu. The purpose of this chapter is to provide the reader with a fundamental understanding of chemical kinetics, describe processes for determining kinetic parameters, quantify the effect of the most important environmental parameters on kinetics, and provide examples of kinetic parameters important in food processing.

II. GENERAL CONSIDERATIONS

A. Concept of Rate-Limiting Step

Later in this chapter, we will discuss important aspects to consider when determining chemical kinetics. However, one of the most important aspects is to determine what is actually controlling the rate of the process. Although a chemical species may be used up in a reaction (e.g., destruction of a nutrient) or produced by a reaction (e.g., generation of browning reaction products), the rate at which this occurs may be controlled by a variable other than that described by chemical kinetics of the reaction. Thus, the overall rate may depend not only on the reaction itself but also on other environmental factors.

Consider, for example, a heterogeneous food which contains an oxygen-sensitive nutrient such as vitamin A or C. Oxidation of the vitamin to products that do not exhibit biological activity is obviously undesirable, and packaging systems are designed to prevent oxygen from entering the food. In measuring the rate at which vitamin concentration is decreasing, it is probable that the kinetic parameters will describe the rate of diffusion of oxygen through the packaging material and into the product rather than the actual rate of vitamin oxidation. Thus, the rate-controlling step is mass transfer, not chemical reaction.

Knowing the rate-controlling step is critically important in the design of food processing systems so that appropriate factors are considered in the design. Taking the vitamin example a step further, suppose it is desired to maintain a minimum concentration of the vitamin at the end of a specified storage period. As a product or process designer one has several options for achieving the objective. One option is to increase the concentration of the vitamin initially present in the product, an option that could work well for a formulated food product but may not be applicable to a natural food product. If you know that the loss of vitamin potency is limited by diffusion of oxygen into the product, then another option is to improve the packaging system to further restrict diffusion of oxygen into the product. Options that are available to you are apparent only if there is a clear understanding of the rate-controlling step of the overall process.

Although the above example illustrates potential mass transfer limitations, another environmental factor that can significantly control a process is temperature. The influence of temperature on chemical reaction kinetics will be discussed elsewhere in this chapter, and the rate of heat transfer in food will be covered in Chapter 3. Suffice it to say, at this point, that temperature is one of the most important factors influencing rates of processes and a good process designer must know the temperature history of the product throughout the process.

B. Basic Chemical Kinetics

Chemical reactions are controlled by the law of mass action; that is, the rate is proportional to the product of the concentration of reactants. Consider, for example, the unimolecular reaction $A \xrightleftharpoons[k_{-1}]{k_1} P$ and the bimolecular reactions $A + B \xrightleftharpoons[k_{-2}]{k_2} P$. The rate of formation of product P for each reaction is, respectively,

$$\frac{d[P]}{dt} = k_1[A] - k_{-1}[P] \quad (1)$$

and

$$\frac{d[P]}{dt} = k_2[A][B] - k_{-2}[P] \quad (2)$$

where k_1 and k_2 are rate constants for the forward reactions and k_{-1} and k_{-2} are rate constants for the reverse (or backward) reactions; $[A]$, $[B]$, and $[P]$ are the molar concentrations of chemical species A , B , and P , respectively. The rate constant k is a function of environmental conditions including temperature.

Most chemical reactions are reversible at least to some extent, and the ratio of the rate of the forward reaction to the rate of the backward reaction is the equilibrium constant.

$$K = \frac{k_1}{k_{-1}} \text{ or } \frac{k_2}{k_{-2}} \quad (3)$$

For many reactions in which we have primary interest, the rate of the reverse (backward) reaction is very small compared to the forward reaction and, at least initially, the concentration of product $[P]$ is zero. Consequently, Eqs. (1) and (2) are written, respectively, as

$$\frac{d[P]}{dt} = k_1[A] \quad (4)$$

$$\frac{d[P]}{dt} = k_2[A][B] \quad (5)$$

Frequently we are interested in the rate of disappearance of a particular chemical species rather than the rate of appearance of a product. For example, in the case of the vitamin discussed earlier, the concentration of the vitamin as a function of time is more interesting than the formation of the breakdown products. In fact, there may be several parallel reactions in which the vitamin is the reactant and the overall rate of disappearance is the sum of all the pathways. Under these circumstances, it is much more desirable to express the overall rate of disappearance.

The rate expressions comparable to Eqs. (1) and (2) for chemical species A are, respectively,

$$\frac{d[A]}{dt} = -k_1[A] \quad (6)$$

and

$$\frac{d[A]}{dt} = -k_2[A][B] \quad (7)$$

The negative sign arises from the fact that the concentration of A is decreasing with time, and, therefore, $d[A]/dt$ (the slope of the curve describing $[A]$ versus time) is negative.

C. Order of Reaction

Strictly speaking, the number of molecules participating in a reaction as reactants is referred to as the *order of the reaction*. In our example $A \rightarrow P$ and $A + B \rightarrow P$, the order of reaction is 1 and 2, respectively. Thus, in $A \rightarrow P$, the reaction is first-order in A and first-order overall. In $A + B \rightarrow P$, the reaction is first-order in A or B and second order overall. In the reaction $A + A \rightarrow P$, the reaction is second order in A and second order overall. Thus, the overall order is the sum of the orders for each reacting species.

An easy way to quickly determine the order of the reaction from kinetic expressions such as Eqs. (4) and (6) or (5) and (7) is to sum the exponents on the reactant species. In Eqs. (4) and (6), the exponent on $[A]$ is 1 and, therefore, the reaction is first-order in $[A]$ and first-order overall. In Eqs. (5) and (7) the exponent on $[A]$ is 1 and on $[B]$ is 1. Therefore, the reaction is first-order in A or B and second order overall.

In many reactions occurring in foods, the reactions can be described mathematically as first-order even though the reaction is not mechanistically first-order. The reaction is then referred to as pseudo first-order. For example, in the bimolecular reaction $A + B \rightarrow P$, the concentration of reactant B may be much larger than A , and for all practical purposes, its concentration will not change significantly during the course of the reaction (at least, it will not change much compared with the dramatic changes that occur in the concentration of A). Then Eq. (7) can be transformed as follows:

$$\frac{d[A]}{dt} = -k_2[A][B] = -k_3[A] \quad (8)$$

where $k_3 = k_2 [B]$.

There are many examples of this in food systems, and these result in many important reactions in foods appearing to be first-order. Describing these reactions as pseudo-first-order leads to simple ways of quantifying the reaction. Specific examples include hydrolysis reactions where water is a reactant and is present in high concentration compared to the other reactant and oxidative reactions where oxygen or an oxidant or reductant is a reactant and present in high concentration.

III. FIRST-ORDER RATE PROCESSES

Equations (6) and (8) express first-order rate processes. The reaction that results in Eq. (6) is referred to as a homogeneous, simple reaction since the rate expression represents the true molecular event that occurred in the reaction. Equation (8), on the other hand, represents a model for the chemical reaction that it depicts since it is not possible to describe the true molecular events that occurred based on the quantitative description. This is perfectly acceptable provided we appreciate the difference between a rate expression that accurately depicts the molecular phenomena and a rate expression that is only modeling a process. For most of the literature values of rate constants for changes in food, the rate constant is for a model and does not accurately depict the molecular phenomena.

Equations (6) and (8) represent ordinary differential equations and can be solved easily.

$$\frac{d[A]}{dt} = -k_1[A] \quad \frac{d[A]}{[A]} = -k_1 dt \quad (9)$$

$$\frac{d[A]}{[A]} = \int_t^0 -k_1 dt \quad (10)$$

$$\ln \frac{d[A]}{[A]} = -k_1 t \text{ or } \ln[A] = \ln[A]_0 - k_1 t \quad (11)$$

where $[A]_0$ is the initial concentration of A (at time zero) and \ln is the natural (Eperian based) logarithm.

A graph of $\ln [A]$ versus time is linear with a negative slope equal to k_1 (Fig. 2.1). In fact, a simple test to determine if a reaction can be describe by first order kinetics is to consider the linearity of \ln (concentration) versus time. If this relationship can be adequately described by a straight line, then the reaction is first-order or pseudo-first order.

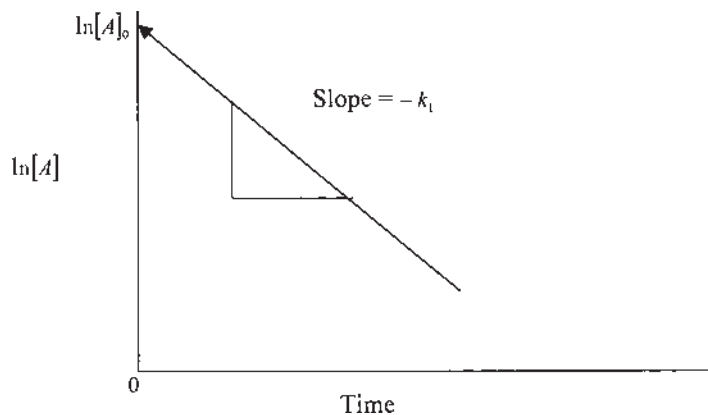


FIGURE 2.1 $\ln [A]$ versus time for a first-order chemical reaction.

From this result, two important parameters can be defined for chemical reactions, the half-life and the decimal reduction time. The half-life of a reaction or chemical species is the time it takes to decrease the concentration by 50%. From Eq. (11),

$$\ln \frac{[A]}{[A]_0} = \ln \frac{[A]_0}{2[A]_0} = \ln \frac{1}{2} = -\ln 2 = k_1 t_{1/2} \quad (12)$$

where $[A] = [A]_0/2$ and $t = t_{1/2}$. Solving Eq. (12) for $t_{1/2}$ yields

$$t_{1/2} = \frac{\ln 2}{k_1} = \frac{0.693}{k_1} \quad (13)$$

Thus, knowing the rate constant for a first-order process (not just limited to chemical reactions) allows one to easily estimate the time to accomplish 50% of the process. It is important to note that having achieved one half-life of the process reduces the original value to 50% and the second half-life reduces the 50% value by 50%; i.e., there are diminishing returns, and one never gets to zero or the true end of a process, only infinitesimally close to the end.

Another important parameter which can be easily calculated for a first-order process for which the rate constant is known is the decimal reduction time (D -value). The D -value is the time to reduce the concentration to 10% of its initial value (90% reduction).

From Eq. (11), $\ln[A]/[A]_0 = -k_1t$ with $[A] = 0.1[A]_0$, then

$$\ln \frac{0.1[A]_0}{[A]_0} = \ln(0.1) = \ln \frac{1}{10} = -k_1t_{1/10} = -k_1D - \ln 10 = -k_1D \quad (14)$$

$$\ln 10 = k_1D \Rightarrow D = \frac{\ln 10}{k_1} = \frac{2.303}{k_1} \quad (15)$$

Equation (15) can be used to rewrite Eq. (11) in terms of D -value.

$$\ln \frac{[A]}{[A]_0} = -k_1t = \frac{-2.303t}{D}$$

$$\frac{1}{2.303} \ln \frac{[A]}{[A]_0} = \log \frac{[A]}{[A]_0} = -\frac{t}{D}$$

$$\log[A] = \log[A]_0 - \frac{t}{D} \quad (16)$$

Figure 2.2 represents Eq. (16) and demonstrates that the D -value represents the time for the concentration of the reactant to decrease by 90%, in other words, for the dependent variable to change by one log cycle.

The concept of decimal reduction time is very useful as we shall see when we discuss design of thermal processes. However, it is also useful in thinking quantitatively about the rate at which first-order processes proceed. For example, if the D -value is 10 min, then the process value (dependent variable) will decrease by 90% in 10 min (for example, decrease from an initial value of 100 units

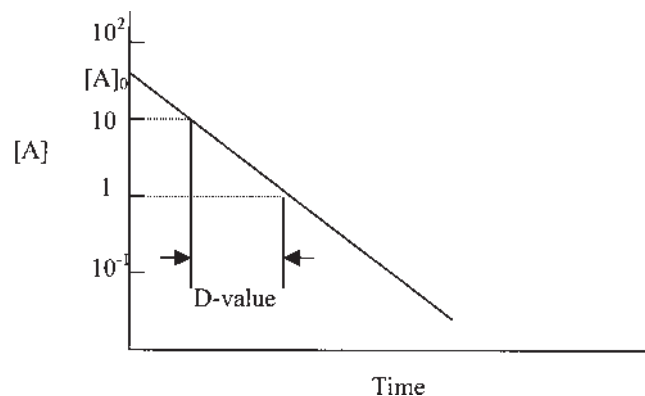


FIGURE 2.2 $[A]$ versus time for a first-order process on semilogarithmic paper illustrates the D -value (decimal reduction time).

to a value of 10 units). In the second 10-min period the process value will decrease from 10 units to 1 unit. Using this concept, one can easily determine the change in the process value by calculating the number of D -values. In the example just cited, if the process time is 50 min and the D -value is 10 min, then the process is $5D$ and the process value is reduced from 100 units to 10^{-3} units (5 log cycles). This concept will be very useful when we discuss and describe thermal process calculation and design.

A similar concept is widely used in engineering to describe processes in which decay or growth of the process value follows a first-order model and is referred to as the time constant. If the initial value of a variable is e^2 and the final value is e , then the value of the variable has decreased one natural logarithm cycle. The time for this to occur (time constant) can be calculated from Eq. (11) as

$$\ln \frac{e^2}{e} = -k_1 t_e = \ln \frac{1}{e} = -\ln(e) = -1$$

$$t_e = \frac{1}{k_1} \quad (17)$$

The fractional change in the process variable which occurs in one time constant is

$$\frac{e^2 - e}{e^2} = 1 - \frac{1}{e} = \frac{e - 1}{e} = 0.632$$

Thus, for each time-constant period, the process value changes by 63.2%. Although this concept is not widely used in chemical reaction kinetics, it is widely used in electrical engineering and in industrial engineering to describe process control.

From the preceding discussion, two important characteristics of first-order processes emerge. The first is that the relative change per unit time is constant. For example, if the D -value is 9 min, then the relative rate of change is 10%/min (90% change in 9 min) and is constant. Every minute the concentration at the end of the minute will be 10% less than the concentration at the start of the minute. The second characteristic of first-(or pseudo-first-) order processes is that the absolute rate is dependent on initial concentration. That is, changing the process value from 10 to 1 and from 1 to 0.1 takes the same time, but the absolute change in the process value is 9 and 0.9, respectively.

IV. DETERMINING KINETIC PARAMETERS

A. General Considerations

Compared to characterizing chemical reactions in chemical laboratory settings, characterizing reactions and changes in foods is often not easy. As pointed out

earlier, environmental factors such as pH, temperature, moisture content (and its closely related variable, water activity), oxidation-reduction potential, presence of constituents (such as microorganisms, enzymes, metal ions, and chelating or requesting substances), and state of the tissue (e.g., whole or mascerated, age, cultivar) all influence the rate of chemical reaction. Furthermore, the food itself is not homogeneous; i.e., there can be concentration gradients in whole tissue and temperature and pH profiles in the cross section. Due to this heterogeneity, it is essential to ultimately carry out reaction rate studies in the food itself. Furthermore, it is important to keep in mind that we are going to model the rate process, and the model will not necessarily reflect the actual mechanism of the reaction.

As we noted earlier, many reactions which are of interest in food process design and food stability are hydrolysis or oxidation-reduction reactions. The influence of water on reactions in foods will be covered more extensively in Chapter 5 on water activity. Here we will briefly introduce the subject. Hydrolysis and oxidation-reduction reactions are usually complex and composed of several reactions in series. Furthermore, hydrolysis reactions depend on H^+ and OH^- , not on molecular water, H_2O . Oxidation-reduction reactions may involve free radicals and may involve molecular oxygen O_2 . For simplicity, the rate of change for hydrolysis or oxidation and reduction can be written, respectively, as

$$\frac{d[C]}{dt} = -k[C]^n[H_2O]^m \quad (18)$$

and

$$\frac{d[C]}{dt} = -k[C]^n[O]^m \quad (19)$$

where n represents the order of the reaction for reactant C and $[H_2O]^m$ and $[O]^m$ represent the effective concentrations of water and oxidant (or reductant) of order m , respectively. This simplification should not be interpreted as the mechanism of the reaction.

Although reactions involving water are covered more extensively in Chapter 5 on water activity, a few observations will be made here. Water can influence the reaction rate in several ways. Since it is a reactant, it may become rate limiting as in the case of foods that have low water activity. It also serves as a solvent for distribution of reactants, catalysts, and products. In some cases, lack of water can limit redistribution of reaction products resulting in a reduced reaction rate or even reversing the reaction through the law of mass action. Oxidation-reduction reactions can be limited by low concentration of oxidant or reductant or increased by diffusion of molecular oxygen through the packaging material and into the food. Regardless of the simplicity of describing the kinetics

of oxidation-reduction reactions, they generally are very complex reactions mechanistically.

As a consequence of the potential influence of water and/or oxygen on reactions in food, it is commonplace to make simplifying assumptions. In foods with water activity greater than 0.9, it is generally assumed that water is neither a limiting reactant nor a limiting solvent, and therefore, hydrolysis reactions may be assumed to be zero order with respect to water. For oxidative reactions, such simplifying assumptions are not generally made and the reactions are modeled as zero, first, or second order in oxygen. The general rule of thumb is to first assume a reaction is first-order only in the reactant of interest (colorant, flavor compound, vitamin, etc.) and zero order in all other constituents. If that model does not adequately represent the concentration of the desired reactant over time, then more complex models are assumed and statistically tested to determine one which best describes the disappearance of the reactant.

In the design of experiments to determine kinetic parameters, Hill (1977) suggested that several questions be addressed:

1. Is the reaction under study properly identified?
2. Are side reactions important? What is the stoichiometry of the reaction?
3. Are the conditions of the reaction properly specified?
4. Does the analytical method properly measure the extent of reaction?
5. Is the experiment properly planned to provide significant data, and is the time period adequate to allow models to be distinguished?
6. Are the data reproducible?
7. Is there a good mechanism for quenching the reaction (i.e., stopping the reaction at precise times)?

Once the system is thoroughly understood, it is necessary to generate data on concentration over time. Table 2.1 provides a description of several reactor types, the type of data obtained, and the usual methods of treating the raw data to generate the kinetic parameters. For liquids or semisolids, all of these methods are applicable provided the material can be pumped or stirred. For solids, only the batch reactor is available.

Analysis of the data can be accomplished either by treating the data differentially,

$$\frac{d[C]}{dt} = -k[C]^n \quad (20)$$

or integrally,

$$\int \frac{d[C]}{[C]^n} = \int -k dt \quad (21)$$

TABLE 2.1 Reactor Types for Determining Kinetic Parameters

| Reactor type | Data procured | Treatment of data | Comments |
|---------------------------------|--------------------|--|---|
| Batch | c vs t | Differential Integral | Limited to slow reactions |
| Plug flow | c vs \emptyset | Differential Integral | Control of flow rate and plug flow is essential |
| Continuous stirred tank reactor | Rate vs c | Material balance gives rate: log-log plot of rate vs c gives order (n) and k | Requires large conversions for good precision |

c = concentration; t = time; \emptyset = holding time.

B. Differential Methods

In the differential methods, the data generally are treated in the following manner:

1. Model approach
 - a. Choose a form of concentration dependence on time (i.e., zero, first, second order)

$$\frac{d[C]}{dt} = \text{rate} = -kF(C) \quad (22)$$

- b. Determine reaction rate at various times (i.e., $\frac{dc}{dt}$ versus t). This can be done either graphically from plots of C versus t or numerically using a polynomial to estimate the slope at various times.
 - c. Calculate $F(C)$ at various times corresponding to the calculated $d[C]/dt$ (i.e., C^0 , C^1 , C^2 , etc.).
 - d. Plot or regress reaction rate versus $F(C)$. If the plot (or regression equation) is linear and goes through the origin [i.e., rate is zero when $F(C)$ is zero], the assumed model is consistent with the data. If nonlinear or does not go through the origin (0, 0), then guess a new $F(C)$ and try again.
 - e. Repeat items a through d until you are successful.
2. Unknown form of $F(C)$. Then

$$\frac{d[C]}{dt} = \text{rate}(r) = -kF(C) = -k[C]^\beta \quad (23)$$

$\log r = -\log k + \beta \log[C]$. Plot or regress $\log r$ versus $\log C$. The intercept at $C = 1$ is $-\log k$ ($= \log 1/k$) and the slope is β (the order of the reaction).

3. Initial rate measurement.

This method is generally restricted to very small conversions (i.e., $[C]/[C]_i \geq 0.9$; less than 10% conversion) and requires that the experiment be repeated at various initial concentrations. It is most useful for complex rate functions which would be difficult to integrate.

C. Integral Methods

Integral methods are obviously closely related to differential methods.

1. Graphical Procedure

This is a trial-and-error procedure in which one hypothesizes a reaction functional form.

$$\frac{d[C]}{dt} = -kF(C) \quad (24)$$

Separating variables and integrating yields

$$\int_{[C]_i}^{[C]_f} \frac{d[C]}{F[C]} = \int_0^t -k dt = -kt \quad (25)$$

One then calculates $\int_{[C]_i}^{[C]_f} (d[C]/F[C])$ from the data.

If plotting or regressing $\int_{[C]_i}^{[C]_f} (d[C]/F[C])$ versus time produces a linear function going through the origin (0, 0) with slope $-k$, then the hypothesis on the reaction functional form was correct. If not, then try again.

Since many mathematical functions are linear over short ranges of variables, it is imperative that the experiment be carried out until at least 80–90% of the reactant has disappeared (i.e., 3–5 half-lives).

If the guessed functional form is incorrect, guessing for the next try can be improved by observing the curvature of the $\int_{[C]_i}^{[C]_f} (d[C]/F[C])$ versus time plot. If it deviates in a concave manner, the assumed order is greater than the true order. If the deviation is convex, the assumed order is less than the true order.

2. Numerical Procedure

In this procedure, the rate constant is calculated between successive pairs of data points (concentration versus time). Thus, from $n + 1$ measurements of c versus t , one can calculate n k 's. Regressing k on time using unweighted

linear least squares then produces k . For first-order,

$$\bar{k} = \frac{\sum(t_i \ln[C]_i) - [(\sum t_i)(\sum \ln[C]_i)/n]}{[(\sum t_i)^2/n] - \sum t_i^2} \quad (26)$$

This method has limitations because all points are assigned equal weight and functions of the measured concentration must be used in equations defining residuals. These drawbacks can be somewhat overcome by using weighted linear least squares programs when the precision of measurement of concentration is a function of concentration.

D. Accuracy of Rate Constants

To be most useful, it is important to have accurate estimates of rate constants for use in design of processing and packaging systems for foods. There are two main variables affecting the accuracy of estimated rate constants: (1) analytical precision for measuring the reactant and (2) the percent change in the reactant species monitored. Benson (1960) produced Table 2.2 to show the influence of analytical errors and extent of reaction on percent error in the rate constant k .

Since food systems are chemically complex, it is not unusual to have 1–2% variability in the determination of concentration of chemical species. This variability results from lack of precision in the analytical method and, frequently, from sampling problems. Consequently, if you want to determine a rate constant with an error on the order of 5–10%, it is imperative to carry out the reaction at least through 30% reduction in reactant species and generally through at least one half-life. Unfortunately, there are many examples in the literature where rate constants and order of reaction are reported based on studies carried out under conditions where the results are not statistically valid.

TABLE 2.2 Errors in Calculated Rate Constant Caused by Analytical Errors

| Analytical precision (%) | Percent change in reactant species monitored | | | | | | |
|--------------------------|--|-----|-----|-----|-----|-----|-----|
| | 1 | 5 | 10 | 20 | 30 | 40 | 50 |
| | Error in k (%) | | | | | | |
| ±0.1 | 14 | 2.8 | 1.4 | 0.7 | 0.5 | 0.4 | 0.3 |
| ±0.5 | 70 | 14 | 7 | 3.5 | 2.5 | 2 | 1.5 |
| ±1.0 | >100 | 28 | 14 | 7 | 5 | 4 | 3 |
| ±2.0 | >100 | 56 | 38 | 15 | 10 | 8 | 6 |

Source: Benson (1960).

V. TEMPERATURE DEPENDENCE OF REACTION KINETICS

As noted earlier, there are several environmental parameters which have a marked effect on the magnitude of a reaction rate. One of the most important parameters is temperature. Heat (or lack of it — coldness) is used extensively in processing and preservation of food. In these processes, temperature is a function of time, and therefore, chemical, physical, and biological changes are a complex function of time since the rate constants are temperature dependent.

For applications in food science, three models have been used to describe the temperature dependence of rate processes. One is theoretically and thermodynamically based (Arrhenius model) and two are empirical [thermal death time (TDT) model and Q_{10} model]. In this chapter, we shall examine all three models without going into derivation detail.

A. Arrhenius Model

Around the turn of the nineteenth century, there was a flurry of activity in the physical sciences to explain observations on physical and chemical phenomena according to the laws of thermodynamics. Temperature dependence of chemical reaction rate constants were no exception, and in 1898 Arrhenius postulated that rate constants were quantitatively related to absolute temperature (K) through the Arrhenius equation:

$$k = s e^{-E_a/RT} = s \exp \frac{-E_a}{RT} \quad (27)$$

where s is the frequency factor (same units as k), E_a is the activation energy (kJ/mol), R is the gas law constant (8.3144 kJ/mol K), T is absolute temperature, and k is the reaction rate constant.

Equation (27) is transformed into the base 10 logarithm form as

$$\log k = \log s - \frac{E_a}{2.303RT} \quad (28)$$

Thus, if one measures the rate constant at various temperatures, then the plot or regression of $\log k$ versus $1/T$ (absolute) will result in a straight line of intercept at $k = 1$ of $\log s$ and slope $-E_a/2.303R$.

Conversely, if one knows the rate constant at one temperature and the activation energy, then the rate constant at any other temperature can be calculated. For example, if the rate constant is k_1 at T_1 , then applying Eq. (28) results in the following:

$$\log \frac{k}{k_1} = \frac{-E_a}{2.303R} \left(\frac{1}{T} - \frac{1}{T_1} \right) \quad (29)$$

Before we discuss relative values of E_a for various rate processes important in foods, the TDT model and Q_{10} model will be discussed. That way we can also make some comparisons between the various models.

B. Thermal Death Time Model

As noted earlier, around the turn of the nineteenth century scientists were committed to describing all phenomena mechanistically. Since Pasteur's discovery in the 1850s that microorganisms were responsible for spoilage of food, mathematically describing the inactivation of microorganisms by application of heat was thoroughly investigated. Although Arrhenius had presented a thermodynamic argument for the dependence of rate constants on temperature, the early modelers of thermal processing proceeded to develop empirical models for temperature dependence. Furthermore, rather than using the rate constant for time dependence of destruction of microorganisms, they chose to use the decimal reduction time (D -value) [Eqs. (15) and (16)] — the time at a constant temperature to reduce the population of microorganisms by 90% (or one log cycle).

To mathematically express the temperature dependence of D -value, it was observed that over a relatively narrow temperature range (20–30°C or 50–80°F), $\log D$ is linearly related to temperature (°C or °F). Using a reference D -value (D_R) at a reference temperature (T_R) results in

$$\log \frac{D}{D_R} = \frac{-(T - T_R)}{z} = \frac{(T_R - T)}{z} \quad (30)$$

where $-1/z$ is the slope of the line for $\log D$ versus T . Generally, the reference temperature for thermal processing is 121.1°C (250°F).

Graphically this relationship is shown in Fig. 2.3. Physically z represents the temperature change necessary to increase or decrease the decimal reduction time by 90% or one log cycle. Consequently, a large z value indicates that the rate process is not very temperature sensitive (i.e., it requires a large change in temperature to change the rate by a factor of 10), and a small z value means the rate process is highly temperature sensitive.

C. Q_{10} Model

In biological systems (plants, animals, and microorganisms), most reactions are catalyzed by enzymes. Since enzyme activity is highly temperature sensitive, the Q_{10} model was developed to indicate the relative change in the rate constant for a 10°C temperature change. Mathematically this is expressed as

$$Q_{10} = \frac{k_{T+10}}{k_T} \quad (31)$$

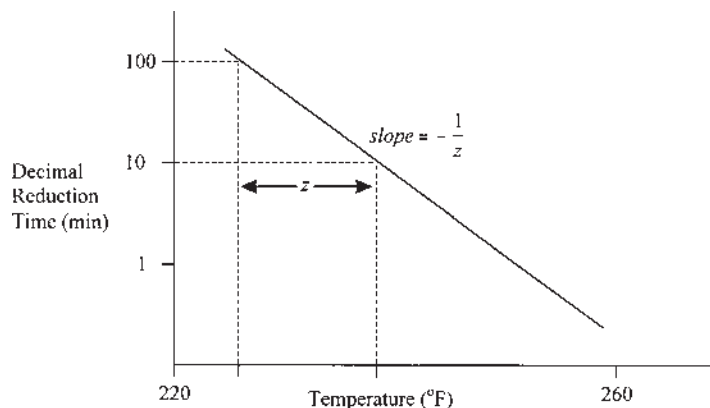


FIGURE 2.3 log decimal reduction time for inactivating microorganisms versus temperature.

where T is temperature in Celcius ($^{\circ}\text{C}$) or Kelvin (K). For many enzyme-catalyzed reactions Q_{10} is 2, meaning the reaction rate doubles for every 10°C rise in temperature. This will hold only up to temperatures at which the controlling enzymes begin to denature and lose their catalytic nature (usually less than 50°C).

VI. KINETIC PARAMETER VALUES IMPORTANT IN FOOD PROCESSING

Quantitatively describing time dependence and temperature dependence of rate processes using rate constants (or D -values) and activation energy, respectively, is commonplace especially in food processing and preservation. Furthermore, the model applies generally to describe physical phenomena such as diffusion coefficients (for example, mass transfer and heat transfer), physical properties (such as viscosity and crystallization rates), and, of course, chemical reactions (including inactivation of enzymes and microorganisms or their spores). It is not the purpose here to provide specific values of D and E_a for specific processes but rather to provide a sense of order of magnitude so that insight into design of food processes can be obtained. Table 2.3 provides values of D_{121} (decimal reduction time at 121°C) and E_a (activation energy) for various categories of rate processes [from Thijssen and Kerkhof (1977)].

From this table, several general but useful observations can be made. Remember that a large E_a means the process rate is highly temperature sensitive and a small E_a indicates the process rate is not very temperature sensitive.

TABLE 2.3 Decimal Reduction Times (D_{121}) and Activation Energy (E_a) for Physical and Chemical Processes Important in Food Science

| Chemical or physical process | D_{121} (min) | E_a (kJ/mol) |
|--|-----------------|----------------|
| Physical properties | — | 2–40 |
| Water vapor pressure | | 40 |
| Water diffusion coefficient | | 8–40 |
| Heat transfer coefficient | | 2–30 |
| Physical process rates (drying, crystallization) | Widely varying | 17–60 |
| Enzyme-catalyzed reactions | | 17–60 |
| Chemical reactions | | 6–210 |
| Hydrolysis | < 0.5 | 60–110 |
| Thiamin destruction | 40–400 | 80–110 |
| Chlorophyll destruction | 40–300 | 30–80 |
| Maillard browning | 0.4–400 | 100–200 |
| Protein denaturation | Widely varying | 350–700 |
| Destruction of microorganisms | 10^{-10} –10 | 200–700 |

Source: Thijssen and Kerkhof (1977).

For food process operations dependent on physical properties such as viscosity or transfer rates (heat or mass transfer coefficients or diffusion coefficients), increasing the temperature will increase the rate of the process, but there are probably better ways (e.g., agitation) to enhance process rate than increasing temperature (i.e., these parameters are not very temperature sensitive). In fact, increasing temperature to increase the rate may be counterproductive since the deteriorative reactions within the food will increase faster than the process rate-controlling variable (i.e., reactions are more temperature sensitive than physical properties or physical process rate constants).

For processes in which the primary function is inactivation of microorganisms or their spores, increasing temperature is a very effective way to increase the rate of the process (i.e., D_{121} values are very dependent on temperature). An important observation is that protein denaturation (i.e., enzyme inactivation) exhibits a temperature dependence on the same order and has led to the postulate that microbial inactivation is a result of denaturation of one or more key enzymes in the cell or spore. As we shall see in Chapter 6 on heat processing, however, there are heat-resistant enzymes that exhibit activation energies 2 to 4 times less than those for destruction of microorganisms.

Finally, one can observe that most chemical reactions including destruction of nutrients like thiamin are less temperature sensitive than destruction of microorganisms or their spores. This difference has attributed to the improvement of nutrient, color, and flavor retention in foods when higher

temperature, shorter time (HTST) thermal processes are used. Optimizing quality factor retention (color, flavor, nutrients, texture, etc.) using this principle is now commonplace in the food thermal processing industry and will be illustrated in Chapter 7 on thermal process design.

VII. ENZYME-CATALYZED REACTIONS

A. Introduction

Many reactions that occur in food systems in which intact or macerated foodstuffs are constituents are catalyzed by enzymes originating in the plant or animal tissue. Enzymes are biocatalysts primarily consisting of proteins that bind substrates stereospecifically so that the activation energy barrier to the reaction is decreased. Although enzymes are ubiquitous in biological systems, two of the more important with regard to food systems are hydrolases (enzymes that catalyze hydrolysis of compound molecules such as esters, proteins, complex carbohydrates, etc.) and oxidoreductases (enzymes that catalyze oxidation or reduction reactions such as peroxidase and lipoxygenase).

Since enzymes are so important in food processing as biocatalysts for both beneficial use (e.g., rennin in cheese-making) and food deterioration and decrease in quality (e.g., starch hydrolases), the kinetics of enzyme-catalyzed reactions have been widely studied. Furthermore, since most enzymes are very substrate specific, the kinetics of enzyme-catalyzed reactions can be easily determined qualitatively and quantitatively. For our purposes, we shall consider enzyme kinetics in general.

B. Michaelis–Menten Analysis

Michaelis and Menten (1913) proposed the theory of enzyme-substrate complex formation to describe enzyme kinetics. This is depicted in the following reaction scheme:



where E is the enzyme, S the substrate, ES the enzyme-substrate complex, and P the product. The rate constants for the forward and reverse reactions are k_1 , k_2 and k_{-1} , k_{-2} , respectively. Both reactions are reversible in the general case.

From this description, when the substrate concentration is very small, the forward reaction to form ES is first-order in S . At very large substrate concentration, the forward reaction is zero order in S since the reaction rate is only dependent on the concentration of enzyme. This is characteristic of enzyme-catalyzed reactions in foods. Figure 2.4 illustrates the dependence of initial velocity of the reaction on substrate concentration.

Michaelis and Menten (1913) applied steady-state kinetic analysis to Eq. (32) and derived the following equation to describe the velocity of an enzyme-catalyzed reaction as depicted in Fig. 2.4

$$v = \frac{-dS}{dt} = \frac{dP}{dt} = \frac{V_{\max}[S]}{K_m + [S]} \quad (33)$$

where v is the velocity, V_{\max} is the maximum velocity when enzyme is saturated with substrate, $K_m [= (k_{-1} + k_2)/k_1]$ is the substrate concentration at which $v = 0.5V_{\max}$, and $[S]$ is the substrate concentration at time t . In this analysis, k_{-2} is assumed to be zero. To eliminate complications that can arise when substrate concentration decreases or product concentration increases, most kinetic studies on enzymes are completed at very small conversion ratio ($[S]/[S]_0 \leq 0.05$), i.e., $<5\%$ conversion).

Determination of K_m and V_{\max} may be conveniently determined by linearizing Eq. (33). The resulting plot is called a Lineweaver-Burk plot (Lineweaver and Burk, 1934). Taking the reciprocal of both sides of Eq. (33) results in

$$\frac{1}{v} = \frac{1}{V_{\max}} + \frac{K_m}{V_{\max}[S]} \quad (34)$$

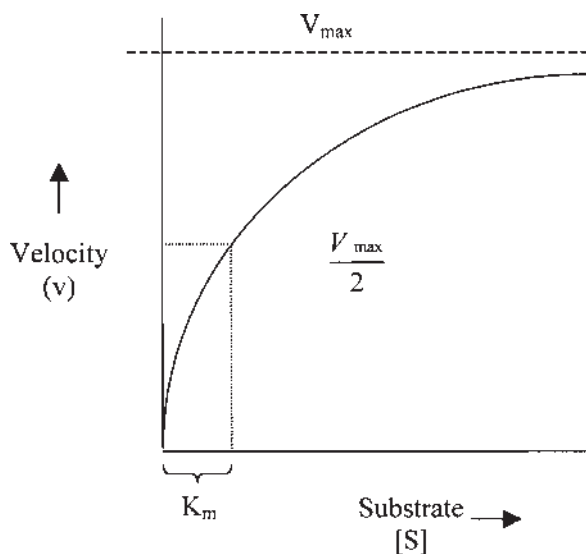


FIGURE 2.4 Enzyme-catalyzed reaction.

Thus a plot of $1/v$ versus $1/[S]$ results in a straight line with intercept $1/V_{\max}$ and slope K_m/V_{\max} .

One mechanism for inactivating or controlling the activity of enzymes is the use of inhibitors. An inhibitor is a compound that interacts with the enzyme reducing the activity of the enzyme. Inhibitors have found widespread use in treatment of microbially caused diseases. The inhibitor may compete competitively with substrates or cofactors for binding to active sites or the inhibitor may form a covalent bond with active site groups. Inhibitors are also used to control enzyme activity in plant and animal tissue after harvest. Other chemical and physical means of controlling enzyme activity include chelation or sequestration of metal cofactors, elevated temperatures for short periods (e.g., blanching), shifting the pH outside the range for enzyme activity, treatment with high pressure, and use of shear forces. Several of these treatments are covered elsewhere in this book.

Reversible inhibitors are distinguished from irreversible inhibitors by forming complexes with the enzyme that can be reversed by displacing the equilibrium by dialysis or gel filtration. Irreversible inhibitors, on the other hand, slowly form covalent bonds with enzyme, enzyme-substrate or enzyme-product complexes. Reversible inhibitors are identified by the nature of their interaction with the enzyme and consequently by their effect on the intercept and slope of a Lineweaver-Burk plot. The intercept and slope for three types of reversible inhibitors are given in Table 2.4.

Competitive inhibition occurs when the inhibitor binds reversibly with the enzyme competing with the substrate for active sites. Noncompetitive inhibition is observed when the inhibitor does not compete with the substrate for binding with enzyme but rather both inhibitor and substrate can bind to the enzyme simultaneously. Uncompetitive inhibition occurs when the inhibitor can only

TABLE 2.4 Slope and Intercept Values for Lineweaver-Burk Inhibitors^a

| Type of inhibition | Slope | y intercept | x intercept |
|--------------------|---|---|--|
| None | $\frac{K_m}{V_{\max}}$ | $\frac{1}{V_{\max}}$ | $\frac{1}{K_m}$ |
| Competitive | $\left[1 + \frac{I_o}{K_i}\right] \frac{K_m}{V_{\max}}$ | $\frac{1}{V_{\max}}$ | $\frac{1}{K_m \left[1 + \frac{I_o}{K_i}\right]}$ |
| Noncompetitive | $\left[1 + \frac{I_o}{K_i}\right] \frac{K_m}{V_{\max}}$ | $\left[1 + \frac{I_o}{K_i}\right] \frac{1}{V_{\max}}$ | $\frac{1}{K_m}$ |
| Uncompetitive | $\frac{K_m}{V_{\max}}$ | $\left[1 + \frac{I_o}{K_i}\right] \frac{1}{V_{\max}}$ | NA |

^a I_o = concentration of inhibitor; K_i = dissociation constant of inhibitor-enzyme complex.
Source: Whitaker (1996).

bind to the enzyme-substrate or one or more of the intermediate complexes. Finally, a more complex reversible inhibition occurs when the inhibitor binds to multi-subunit enzymes. Kinetically, this can be analyzed to produce the number of subunits to which the inhibitor can bind. Whitaker (1996) gives an analysis of the kinetics. Irreversible inhibitors, those that form covalent bonds with the enzyme or its substrate complexes, can be treated kinetically through rate equations and not through Lineweaver-Burk or Michaelis-Menton analysis.

The effect of temperature on enzyme activity and inactivation is generally treated by the Arrhenius equation. At temperatures well below that where protein denaturation occurs, the Arrhenius activation energy for the enzyme-catalyzed reaction is less than that for nonenzyme-catalyzed conversion. At higher temperatures at which enzyme inactivation can occur, the Arrhenius activation energy for enzyme inactivation is very large, as illustrated in Table 2.3. Large activation energy is indirect evidence that numerous hydrogen bonds must be broken to permanently alter the structure and destroy the active site of the enzyme. It has been demonstrated that some enzymes have heat-stable isozymes, proteins that perform the same function as the enzyme but are marginally different in conformation. For these isozymes, the Arrhenius activation energy for inactivation is usually much smaller than the heat-labile isozymes (i.e., less temperatures sensitive) indicating that perhaps only a few hydrogen bonds need to be broken to eliminate enzyme activity or perhaps one covalent bond such as a disulfide bond.

VIII. SUMMARY

To design food-processing operations and predict shelf life of foods it is essential to have quantitative data on rates of reaction and their dependence on macro- and microenvironmental variables. The literature is replete with studies on reactions important in foods. Unfortunately, control of process variables and quality of the data are not uniformly good. Consequently, when using literature values it is important to examine the original reference to make your own assessment of quality of the data. Points to observe include were the important variables identified, was the study properly conducted, were conditions consistent with those in your system (e.g., pH, presence of catalysts, temperature)? Were a sufficient number of half-lives traversed in the concentration range so that accurate rate constants could be determined? Did the concentration range cover that in which you are interested? For temperature dependence determination, were an adequate number of temperatures (generally more than four) used and does the temperature range cover your process conditions? As we shall see in later chapters these are important points to consider if food process operations are to be properly designed.

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3

Heat Transfer in Food

I. INTRODUCTION

Heat transfer is one of the most important unit operations in the food industry. Nearly every process requires either heat input or heat removal to alter the physical, chemical, and storage characteristics of the product. For example, in the storage of fresh fruits, vegetables, meats, and dairy products heat is removed to decrease temperature and thereby increase storage life. On the other hand, heat is temporarily added to achieve preservation by thermal means. Examples of heat input to change the characteristics of products include cooking to alter the texture of foods and heating to develop color and flavor in candy. Removal of heat is used to produce desirable physical changes (crystallization) in frozen desserts and some candies.

In all of these applications, transfer of heat is governed by physical laws. An understanding of these physical principles enables one to predict heating phenomena and to determine optimum operating conditions. In determining optimum operating conditions consideration must of course be given not only to the rate of energy transfer but also to food quality. This necessitates a working knowledge of both engineering and food science.

In this chapter the basic physical principles of heat transfer are presented with particular attention given to the nature of the material being heated.

II. MECHANISMS OF HEAT TRANSFER

Heat transfer is an energy-transfer phenomenon. Increased heat energy causes a product's molecules to move rapidly. That is, the kinetic energy of a molecule increases as heat energy is absorbed. Heat is transferred when a fast moving molecule collides with a slow-moving molecule, causing the fast moving molecule to lose kinetic energy and the slow moving molecule to gain kinetic energy. From this it is apparent that heat transfer involves a molecular mechanism.

One manifestation of the level of heat energy in a group of molecules is temperature, a substance's relative hotness or coldness. Several arbitrary "yardsticks" or scales have been developed for measuring temperature, but the two most common ones are the Celsius and Fahrenheit scales. However, if the energy level of atoms and molecules are compared to zero kinetic energy (i.e., no motion of the particles and consequently zero on an absolute temperature scale) the temperature is expressed in Kelvin or degrees Rankine. The relationships among these temperature scales are shown in Table 3.1.

The amount of heat energy is also measured in arbitrary units. In the System International (SI) the joule is the unit of heat energy, whereas in the fps system the Btu (British thermal unit) is the unit of heat energy. A joule (J) is 0.239 cal, and a calorie is the amount of heat necessary to raise the temperature of 1 g of water 1°C (from 14.5 to 15.5°C). A Btu is the amount of heat necessary to raise 1 lb of water 1°F (usually from 61 to 62°F).

Heat capacity (C_p , the p indicating constant pressure) is a term used to define the amount of heat energy necessary to cause a given mass of a substance to change 1°. In the SI system heat capacity is kJ/kg K. However, it is more convenient to define heat capacity in terms of calories. Then heat capacity is the calories required to raise 1 g of substance 1°C; in the fps system, it is the British thermal units required to raise 1 lb of substance 1°F.

TABLE 3.1 Relationships Among Various Temperature Scales

| Reference points for water | Celsius (°C) ^a | Fahrenheit (°F) | Kelvin (K) ^b | Rankine (°R) ^c |
|----------------------------|------------------------------|--------------------|----------------------------|------------------------------|
| Boiling point (1 atm) | 100 | 212 | 373 | 672 |
| Freezing point (1 atm) | 0 | 32 | 273 | 492 |
| Zero kinetic energy | -273 | -460 | 0 | 0 |

$$^{\circ}\text{C} = (5/9) (\text{F} - 32)$$

$$^{\circ}\text{K} = \text{C} + 273$$

$$^{\circ}\text{R} = \text{F} + 460$$

Since the definition of the calorie and of the Btu is based on water, the heat capacity for water is 1 cal/g°C (4.184 J/g K) or 1 Btu/lb°F. If the heat capacity of a substance is compared to that of water, the resulting ratio is called *specific heat*. Specific heat is a dimensionless ratio that is numerically equal to the heat capacity of the substance.

$$\text{Specific heat (sh)} = \frac{C_{p, \text{ substance}}}{C_{p, \text{ water}}} \quad (1)$$

The heat capacities of a variety of common foods are given in Table 3.2 (Rahman, 1995). Note that heat capacity is given with energy in units of joules (or kJ). One calorie is 4.187 J. Also, C_p usually has temperature unit K, and $1\text{K} = 1^\circ\text{C}$.

Since heat capacity is very dependent on water content and composition, some correlations for calculating heat capacity as a function of composition have been developed. Dickerson (1968) developed the following equation for heat capacity of meat products with moisture content greater than 26% and fruit juices with moisture content greater than 50%.

$$C_p = 1.675 + 0.025w$$

where w is water content (%). When the composition is known, heat capacity can be calculated from proximate composition of the food.

$$C_p = 1.42m_c + 1.549m_p + 1.675m_f + 0.837m_a + 4.187m_m \quad (2)$$

where m is mass fraction and the subscript are c , carbohydrate; p , proteins; f , fat; a , ash; and m , water.

When heat energy is added to or taken from a substance, either the temperature or the physical state of the substance changes. Heat input which causes a rise in temperature is called *sensible heat* since the heat can be “sensed.” Added heat that does not contribute to a temperature increase is called *latent heat*. Latent heat is the heat that is used to bring about a change of state of a substance without a change in temperature. If the substance goes from a solid to a liquid, the latent heat is called *heat of fusion*. If the changes is from liquid to a gas, it is called *heat of vaporization*. For the reverse process of gas to liquid or liquid to solid the latent heat is usually called *heat of condensation* and *heat of solidification* (heat of crystallization), respectively. Energy involved in a change of state is added or emitted as a result of changes in various forces of attraction among molecules.

For many heating and cooling applications in food, a change in the physical state of water is the primary objective. For example, changing liquid water to vapor is the primary objective in dehydration and evaporation, and changing liquid water to a solid is the objective of freezing foods that are to be consumed or stored in a frozen state.

TABLE 3.2 Heat Capacity of Food between 0 and 100°C

| Material | x_w^a | Heat capacity (kJ/kg K) |
|-------------------------|--------------|-------------------------|
| Fruit | | |
| Apples | 0.75–0.85 | 3.724–4.017 |
| Berries (fresh) | 0.84–0.90 | 3.724–4.100 |
| Berries (dried) | 0.30 | 2.134 |
| Fruits (fresh) | 0.75–0.92 | 3.347–3.766 |
| Fruits (dried) | 0.30 | 2.092 |
| Grape Marsh (fresh) | — | 3.703 |
| Lemon Eureka (fresh) | — | 3.732 |
| Orange Valencia (fresh) | — | 3.515 |
| Orange Naval (fresh) | — | 3.661 |
| Plums (Fresh) | 0.75 to 0.78 | 3.514 |
| Plum (dried) | 0.28 to 0.35 | 2.218–2.469 |
| Meat | | |
| Bacon | 0.50 | 2.008 |
| Fat (beef) | 0.51 | 2.887 |
| Beef (lean) | 0.72 | 3.431 |
| Beef (mincemeat) | — | 3.515 |
| Beef (boiled) | 0.57 | 3.054 |
| Bones | — | 1.674–2.510 |
| Goose (eviscerated) | 0.52 | 2.929 |
| Kidneys | — | 3.598 |
| Mutton | 0.90 | 3.891 |
| Fat (pork) | 0.39 | 2.594 |
| Pork (lean) | 0.57 | 3.054 |
| Sausages (fresh) | 0.72 | 3.431 |
| Veal | 0.63 | 3.222 |
| Veal cutlet | 0.72 | 3.431 |
| Veal cutlet (fried) | 0.58 | 3.096 |
| Venison | 0.70 | 3.389 |
| Miscellaneous | | |
| Bread (white) | 0.44–0.45 | 2.720–2.845 |
| Bread (brown) | 0.485 | 2.845 |
| Curd (cottage cheese) | 0.60–0.70 | 3.264 |
| Dough | — | 1.883–2.176 |
| Egg (dried) | 0.030 | 1.840 |
| Egg (dried) | 0.042 | 1.883 |
| Flour | 0.12–0.135 | 1.79–1.883 |
| Grains | 0.15–0.20 | 1.883–2.008 |
| Salt | — | 1.130–1.339 |
| Macaroni | 0.125–0.135 | 1.841–1.883 |

(continued)

TABLE 3.2 Continued

| Material | x_w^a | Heat capacity (kJ/kg K) |
|----------------------|-------------|-------------------------|
| Pearl barley | — | 2.803–2.845 |
| Porridge (buckwheat) | — | 3.222–3.766 |
| Raisins | 0.245 | 1.966 |
| Rice | 0.105–0.135 | 1.757–1.841 |
| Sugar | — | 1.25 |
| White of egg | 0.87 | 3.849 |
| Yolk of egg | 0.48 | 2.803 |
| Soups | | |
| Broth | — | 3.096 |
| Cabbage | — | 3.766 |
| Pea | — | 4.100 |
| Potato | 0.88 | 3.933 |
| Fish | | |
| Fried | 0.60 | 3.012 |
| Fresh | 0.80 | 3.598 |
| Dried (salted) | 0.16–0.20 | 1.715–1.841 |
| Fats | | |
| Butter | 0.14–0.155 | 2.050–2.134 |
| Margarine | 0.9–0.15 | 1.757–2.092 |
| Vegetable oils | — | 1.464–1.883 |
| Beverages | | |
| Cacao | — | 1.841 |
| Cream, 45–60%fat | 0.57–0.73 | 3.054–3.264 |
| Rich (cow) milk | 0.875 | 3.849 |
| Skim (cow) milk | 0.91 | 3.975–4.017 |
| Vegetables | | |
| Artichokes | 0.90 | 3.891 |
| Beet (dried) | 0.044 | 2.008 |
| Cabbage (dried) | 0.054 | 2.176 |
| Carrots (fresh) | 0.86–0.90 | 3.807–3.933 |
| Carrots (dried) | 0.044 | 2.092 |
| Carrots (dried) | 0.060 | 2.176 |
| Carrots (boiled) | 0.92 | 3.766 |
| Cucumber | 0.97 | 4.100 |
| Leek | 0.92 | 3.975 |
| Lentils | 0.12 | 1.841 |
| Mushrooms (fresh) | 0.90 | 3.933 |
| Mushrooms (dried) | 0.30 | 2.343 |
| Onions | 0.80–0.90 | 3.598–3.891 |
| Onion (dried) | 0.033 | 1.966 |

(continued)

TABLE 3.2 Continued

| Material | x_w^a | Heat capacity (kJ/kg K) |
|------------------------|-----------|-------------------------|
| Parsley | 0.65–0.95 | 3.180–4.058 |
| Peas (dried) | 0.14 | 1.841 |
| Potatoes | 0.75 | 3.515 |
| Potatoes (boiled) | 0.80 | 3.640 |
| Potatoes (dried) | 0.061 | 1.715 |
| Potatoes (dried) | 0.080 | 1.799 |
| Sorrel | 0.92 | 2.050 |
| Spinach | 0.85–0.90 | 1.925 |
| Spinich (dried) | 0.059 | 4.017 |
| Sweet potato (dried) | 0.076 | 2.050 |
| White cabbage (fresh) | 0.90–0.92 | 3.891 |
| White cabbage (boiled) | 0.97 | 4.100 |

^a x_w , mass fraction of water (wet basis).

Source: Rahman (1995).

The latent heat of vaporization is dependent on the pressure and boiling point of the aqueous phase. For pure water at 100°C (212°F), the latent heat of vaporization is 2259 kJ/kg or 540 cal/g (971 Btu/lb). Values of latent heat of vaporization as a function of pressure and temperature can be found in most handbooks of the physical sciences (e.g., Handbook of Chemistry and Physics). The latent heat of fusion for pure water at 0°C (32°F) is 335 kJ/kg or 80 cal/g (144 Btu/lb).

In many heat transfer processes it is necessary to know the total quantity of heat that must be transferred. Knowing this, the rate of the process can be estimated from process parameters of the heat transfer system. In assessing the total quantity of heat transferred, sensible heat, heat of vaporization, and heat of fusion all must be considered whenever appropriate. Sensible heat can be calculated from the relationship

$$Q_s = MC_p \Delta T \quad (3)$$

where Q_s is sensible heat transferred (kJ), M is mass of material (kg), C_p is heat capacity (kJ/kg K), and ΔT is temperature change of the product (°C). The heat of fusion or melting can be calculated from the relationship

$$Q_f = M_f \lambda_f \quad (4)$$

where Q_f is latent heat transfer (kJ), M_f is mass of material solidified or melted (kg), and λ_f is heat of solidification or melting (kJ/kg). Likewise, the heat

removed or supplied for condensation or vaporization can be calculated from the relationship

$$Q_v = M_v \lambda_v \quad (5)$$

where Q_v is latent heat transfer (kJ), M_v is mass of material evaporated or condensed (kg), and λ_v is heat of vaporization or condensation (kJ/kg).

The total heat required (or released) is then the sum of these three, i.e.,

$$Q_{\text{total}} = Q_s + Q_f + Q_v \quad (6)$$

Equation (6) can be used to calculate the total quantity of heat transferred but not the rate of heat transfer. To arrive at the rate of heat transfer the process must be expressed on a time basis. If it is known that the mass of material must undergo a change in sensible heat or a change of state in a given length of time, then the rate of heat transfer can be calculated. The rate of heat transfer is obtained by dividing Eq. (6) by the time involved. For example, if the process is to be completed in 1 h then Q_{total} would be in units of kJ/h. On a rate basis the change in sensible heat becomes

$$Q_s = WC_p \Delta T \quad (7)$$

where W is mass flow rate (kg/h), Q_s is heat transfer rate (kJ/h), and $C_p \Delta T$ is as defined in Eq. (3). Likewise, Eqs. (4) and (5) can be expressed on a time basis as follows:

$$Q_f = W_f \lambda_f \quad (8)$$

where W_f is the mass of material solidified or melted per unit time (kg/h) and

$$Q_v = W_v \lambda_v \quad (9)$$

where W_v is the mass of material evaporated or condensed per unit time (kg/h). The total rate of heat transfer is then

$$Q_{\text{total}} = WC_p \Delta T + W_f \lambda_f + W_v \lambda_v \quad (10)$$

Heat transfer is a dynamic process wherein heat is transferred from a hotter body to a colder body, the rate being dependent on the temperature difference between the two bodies. A temperature difference is therefore necessary for heat transfer, and this temperature difference is called the *driving force* for heat transfer. Without a temperature difference there is no heat transfer. For example, water cannot be boiled at 100°C by heating with steam at 100°C.

In transferring heat energy from one body to another resistance may be encountered. This resistance to heat flow can occur within or at the surface of the material. Expressions for these resistances are given in Sec. II. B and II. C. Like all rate processes, the rate of heat transfer is directly proportional to driving force

and inversely proportional to resistance. Thus,

$$\text{Rate of transfer} = \frac{\text{driving force}}{\text{resistance}}$$

There are three basic mechanisms by which heat transfer can occur: conduction, convection, and radiation. Conduction heat transfer occurs when thermal energy is transferred from one molecule (or atom) to an adjacent molecule (or atom) without gross change in the relative positions of the molecules. Molecular movement is limited to oscillation about a fixed position, allowing any given molecule to make contact with only its immediate neighbors. In heat transfer by convection, the molecules are free to move about, resulting in mixing of warmer and cooler portions of the same material. Convection is thus restricted to flow of heat in fluids, either gases or liquids. Transfer of heat by radiation occurs by means of an electromagnetic radiation. Electromagnetic radiation passes unimpeded through space and is not converted to heat or any other form of energy until it collides with matter. Upon collision the radiation can be transmitted, absorbed, or reflected. Only the absorbed energy can (but need not) appear as heat.

One final introductory concept should be discussed, namely the differences between steady-state and unsteady-state processes. The criterion of a steady state is that conditions at all points in the system do not change with time. If one of the conditions at any given point changes with time an unsteady state exists. An example will help illustrate the difference. Consider a pipe through which water is flowing at a constant inlet temperature and a constant rate while surrounded by a jacket in which steam is circulating at a constant temperature. Conditions in the water vary from one location to another throughout the length of the heat exchanger, but at any given point the conditions are constant with time. This system is said to be in steady state. Obviously there is a flow of energy from the hot fluid (steam) to the cold fluid (water), but the equations which describe the conditions at any point in the exchanger are independent of time. Now consider a tank of cold water in which a steam coil is immersed. In this situation, the mean temperature of the water increases, and there is no point in the mass of water where conditions are constant with time. This system is said to be in unsteady state. Generally, steady state is characteristic of continuous processes, whereas unsteady state is characteristic of batch or discontinuous operation. A steady-state system can be analyzed as unsteady state if the frame of reference is changed. For the example cited above for the tubular heat exchanger, if the frame of reference is a volume element of water flowing through the tube, then the temperature of the water changes with time as the volume element moves through the tube. This is the situation, for example, when the objective of heating is to inactivate microbial cells or spores and it is necessary to describe the time-temperature relationship. This will be demonstrated in Chapter 6 on thermal processing.

A. Conduction

The basic law of heat transfer by conduction is given by Fourier's law. Fourier's law states that the rate of heat transfer through a uniform material is directly proportional to the area for heat transfer, directly proportional to the temperature drop through the material, and inversely proportional to the thickness of the material. Stated mathematically, Fourier's law is

$$\frac{dQ}{dt} = -kA \frac{dT}{dx} \quad (11)$$

where dQ/dt is rate of heat transfer ($J/s = W$), A is area for heat transfer (m^2), dT/dx is temperature drop per unit thickness (C/m), and k is a proportionality constant.

The principles of Fourier's law are illustrated schematically in Fig. 3.1. In Eq. (11) the negative sign is included on the right-hand side of the equation because the term dT/dx is negative and therefore must be multiplied by the minus sign to yield a positive heat transfer rate, dQ/dt . If the temperature gradient does not vary with time, then the rate of heat flow is constant and Eq. (11) can be written

$$q = -kA \frac{dT}{dx} \quad (12)$$

where q is the rate of heat flow (W). For constant conditions of A , L , and k , Eq. (11) can be separated and integrated, resulting in

$$q = k \frac{A\Delta T}{L} \quad (13)$$

The proportionality constant k is called the *thermal conductivity* and it is a physical property of the material through which heat is transferred. The units of k may be

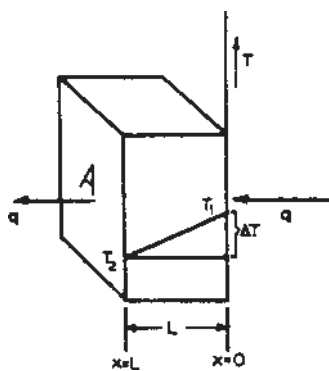


FIGURE 3.1 Heat transfer by conduction.

derived from Eq. (11) as $(\text{J/s m}^\circ\text{C}) = (\text{W/m}^\circ\text{C})$. Like most physical properties, k is dependent on temperature and the k in Eq. (13) is actually k between T_1 and T_2 . Thermal conductivity values of various materials are available in the literature [e.g., Rahman (1995)] and a few representative values are presented in Table 3.3.

The most notable feature of food products is their extremely low values of thermal conductivity compared to metals. This difference in thermal conductivity is due to differences in abundance of free electrons. In metals, electrons transmit most of the heat energy, whereas in foods, where water is the main constituent, the free electron concentration is low and the transfer mechanism involves primarily vibration of atoms and molecules. Therefore good electrical conductors are also good thermal conductors. Similarly, those materials which are good electrical insulators, such as air and glass, are also good thermal insulators (see Table 3.3).

Another striking feature in Table 3.3 is that the thermal conductivity of ice is nearly four times greater than that of water. This difference in thermal conductivity partly accounts for the difference in freezing and thawing rates of food tissues. During freezing, heat is conducted through an ice layer, a layer which has a higher conductivity than that of water and therefore offers comparatively little resistance to heat flow. During thawing, on the other hand, the frozen material becomes surrounded by a continually expanding layer of immobilized water and heat flow through this layer is comparatively difficult. In essence, the water is acting as an insulator compared to ice. Consequently the thawing process for foods that are not fluid in nature is inherently slower than the freezing process.

Sweat (1974, 1975) derived several equations to estimate thermal conductivity of food classes. Examples include the following:

TABLE 3.3 Thermal Conductivity of Various Materials

| Material | Temperature ($^\circ\text{C}$) | Thermal conductivity (w/mK) |
|----------------------|----------------------------------|-----------------------------|
| Ice | 0 | 2.22 |
| Water | 0 | 0.544 |
| Water | 93 | 0.677 |
| Air | 20 | 0.0256 |
| Peanut oil | 4 | 0.168 |
| Meats (average) | 0 | 0.502 |
| Fruits (average) | 0–27 | 0.38–0.50 |
| Vegetables (average) | 0–27 | 0.38–0.50 |
| Stainless steel | | 16.3 |
| Copper | | 398 |
| Pyrex glass | | 0.087 |

1. For fruits and vegetables with $m > 60\%$, $k = 0.148 + 0.0493w$, where w is water content (%).
2. For meats at $0 < T < 60\text{C}$ and $60\% < M < 80\%$ (w.b), $k = 0.08 + 0.0052w$
3. For foods of known proximate composition, $k = 0.25 m_c + 0.155 m_p + 0.16 m_f + 0.135 m_a + 0.58 m_m$

B. Convection

As pointed out earlier, convective heat transfer occurs as a result of bulk movement in a fluid. Obviously, heat transfer by conduction occurs simultaneously, but it is generally negligible compared to convective heat transfer. There are two types of convective heat transfer: natural (or free) convection and forced convection. In natural convection, bulk movement of the fluid occurs as a result of density gradients established during heating or cooling the fluid. With forced convection an external source of energy (such as a pump, stirrer, or fan) is used to move the fluid. In most processing applications with foods, forced-convection heat transfer is used since it is inherently much faster than free convection.

The rate of convective heat transfer is governed by Newton's law of cooling. This law states that the rate of heat transfer by convection is directly proportional to the heat transfer area and the temperature difference between the hot and cold fluid. The quantitative relationship is

$$q = hA\Delta T \quad (14)$$

where q is rate of heat transfer (W), A is heat transfer area (m^2), ΔT is temperature difference ($^{\circ}\text{C}$), and h is a proportionality constant ($\text{W}/\text{m}^2\text{C}$). The proportionality constant h is called the *heat transfer coefficient*.

The magnitude of h is dependent on properties of the fluid, nature of the surface, and velocity of flow past the heat-transfer surface. It can be regarded as the conductance of heat through a thin stagnant layer of fluid of thickness δ_f and is often referred to as the film heat transfer coefficient. Thus, $h = k/\delta_f$, where k is the thermal conductivity of the fluid. Some typical values of h are shown in Table 3.4.

A method for calculating individual film heat transfer coefficient must take into consideration properties of the fluid and the conditions of flow that affect heat transfer. Since there are so many factors affecting h , the most useful method for developing equations involves dimensional analysis. This method shows the relationship between variables in the form of dimensionless groups. Actual data are then used to establish the constants and exponents in a power function relating these dimensionless groups. Examples will be provided later in this chapter.

TABLE 3.4 Typical Film Heat Transfer Coefficients

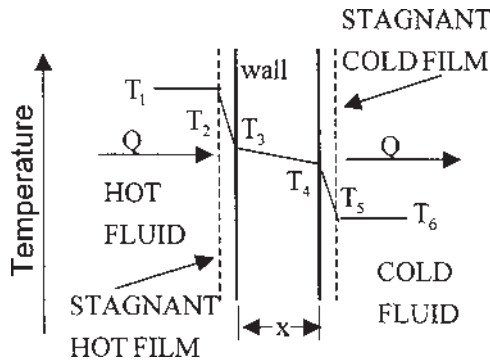
| Condition | h (W/m ² K) |
|------------------------------------|--------------------------|
| Gases, natural convection | 3–30 |
| Gases, forced convection | 10–100 |
| Viscous liquids, forced convection | 60–600 |
| Water, forced convection | 600–6000 |
| Boiling water | 1700–23000 |
| Condensing steam | 6000–18000 |

1. Overall Heat Transfer Coefficient

Most food heating applications involve indirect heating (i.e., heat is transmitted from a hot fluid, through a wall, into a cold fluid). Direct heating occurs when hot steam and cold fluids are mixed together.

The process of indirect heating is shown schematically in Fig. 3.2. In steady state, the rate of heat transfer across each physical boundary is constant. There is a heat transfer coefficient characterizing transfer of heat from the hot fluid to the wall, a thermal conductivity characterizing heat transfer through the wall, and finally a heat transfer coefficient for transfer of heat from the wall to the cold fluid. The resistance to heat transfer in each of these sections can be determined by rearranging Eqs. (13) and (14) as follows:

$$q = \frac{\Delta T_{\text{wall}}}{(L/kA)} = \frac{\Delta T_{\text{hot fluid}}}{(1/hA)_{\text{hot fluid}}} = \frac{\Delta T_{\text{cold fluid}}}{(1/hA)_{\text{cold fluid}}} \quad (15)$$

**FIGURE 3.2** Indirect heat transfer.

The term L/kA then represents the resistance of the wall to heat transfer, $(1/hA)_{\text{hot fluid}}$ is the resistance in the hot fluid, and $(1/hA)_{\text{cold fluid}}$ is the resistance in the cold fluid.

It can be shown that the overall resistance to heat transfer is the sum of the individual resistances. Thus,

$$R_{\text{total}} = (1/hA)_{\text{hot fluid}} + (L/kA)_{\text{wall}} + (1/hA)_{\text{cold fluid}} \quad (16)$$

The rate of heat transfer is then directly proportional to the overall driving force and inversely proportional to the total resistance

$$\begin{aligned} q &= \frac{\Delta T_{\text{overall}}}{R_{\text{total}}} \\ &= \frac{(T_1 - T_6)}{(1/hA)_{\text{hot fluid}} + (L/kA)_{\text{wall}} + (1/hA)_{\text{cold fluid}}} \end{aligned} \quad (17)$$

Since the total resistance to heat transfer is inversely proportional to the overall conductance, Eq. (17) can be expressed as

$$q = \frac{\Delta T_{\text{overall}}}{(1/UA)} = UA\Delta T_{\text{overall}} \quad (18)$$

where U is the overall heat transfer efficient ($\text{W/m}^2\text{C}$). Equation (18) is similar to Eq. (14), except U is substituted for h . Equation (18) indicates that the rate of heat transfer is the product of three factors: overall heat-transfer coefficient, temperature drop, and area of heating surface.

For cylindrical geometries, as we saw earlier, the area is dependent on r and the heat transfer must be referred to a specific dimension, usually either the inside or outside radius of the tube. Consequently, if U is referred to the inside radius, then

$$\frac{1}{U_i A_i} = \frac{1}{h_i A_i} + \frac{r_o - r_i}{k A_{\text{lm}}} + \frac{1}{h_o A_o}$$

and $q = U_i A_i (T_1 - T_6)$. A_{lm} is the log mean area. If the outside radius is chosen then, $q = U_o A_o (T_1 - T_6)$.

In every heating application it is necessary to establish the magnitude of U so that the equipment can be properly sized. By knowing the rate of heat transfer desired, the overall heat transfer coefficient, and the driving force for heat transfer, the required surface area can be calculated. In food applications, generally the major resistance to heat transfer is encountered in the food. Thus, U values are generally of the same order of magnitude as the h value for the food side of the heat exchanger.

Equation (16) is actually applied only when the temperature drop is constant for all parts of the heating surface. In reality the temperature of the hot fluid decreases as the fluid moves through the heat exchanger. Thus, ΔT is not constant over the length of the heat exchanger. The ΔT used in Eq. (18) must, therefore, represent a mean driving force for heat transfer. It can be shown that the mean ΔT should be a logarithmic mean. To illustrate this point, consider the heat-exchange system shown in Fig. 3.3. As the hot fluid moves through the heat exchanger its temperature changes from T_{1H} to T_{2H} and the cold fluid temperature changes from T_{1C} to T_{2C} . Obviously the ΔT between the two streams is constantly changing and heat is transferred more rapidly at the entrance than at the exit. Analysis of this system by means of heat energy balances shows that.

$$q = UA \frac{\Delta T_1 - \Delta T_2}{\ln(\Delta T_1/\Delta T_2)} = UA \Delta T_{\text{lm}} \quad (19)$$

where ΔT_{lm} is the log mean temperature difference. Equation (19) can be used to calculate the size of various heat transfer systems, such as tube-in-shell heat exchangers used for continuous heating of food slurries (e.g. confectionery manufacture, tomato paste processing, aseptic canning) and plate-type heat exchangers used for milk and beer pasteurization.

Although Eq. (19) was illustrated for a parallel-flow heat exchanger, it applies equally to counter-current flow (i.e., the streams going in opposite directions). Under these circumstances the ΔT is more uniform throughout the heat exchanger and the rate of heat transfer is greater than in parallel flow operation. Therefore, most heat exchangers are operated in counter-current flow.

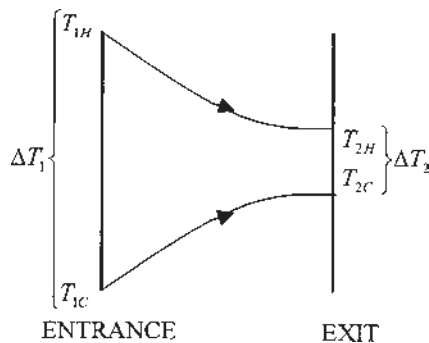


FIGURE 3.3 Temperature in a parallel-flow heat exchanger.

2. Fouling

When most biological fluids are heated or cooled, there is a tendency for some components to deposit on the surface. This phenomenon, known as fouling or burn-on, occurs because most food contact surfaces such as stainless steel have a large surface free energy. Since there are surface active components in foods such as fat, protein, carbohydrate polymers, and minerals, these constituents adhere to the surface decreasing the energy boundary between food product and surface.

In heating, these deposits undergo continuous change through reactions including polymerization, and the process of deposition continues until the deposit interferes with accomplishing the objective of the process, usually reaching some specific end-point temperature.

Fouling results in adding a further resistance to heat transfer and this is characterized by $h_f (= k_d / \delta_d)$ or $R_f (= 1/h_c = \delta_d / k_d)$. In practice, although there have been many investigations into fouling especially for pasteurization, sterilization, and evaporation of milk and fruit and vegetable purees and juices, there are very few predictive equations for estimating fouling resistance. In most cases, suppliers of heating and cooling equipment estimate fouling resistance in the design of the system based on their previous experiences with the specific product or type of product and heating or cooling specifications.

Factors important in fouling include fluid velocity, surface temperature, surface free energy, surface roughness, composition of the feed stream, pretreatment of the feed stream and temperature difference between the cold stream and the hot stream. Fouling is generally minimized by using counter-current flow with heat transfer coefficients approximately equal for both the hot and cold streams and, for streams with soluble protein, providing a preheat treatment at around 95°C for several seconds or even minutes to promote bulk denaturation (rather than denaturation at the wall).

Fouling is generally compensated by designing the heat exchanger to take into account the decrease in efficiency throughout the desired run (or processing) time. For severely fouling fluids, it may be necessary to have a stand by heating system so that one system is in operation while the other is being cleaned.

One final caution about fouling has to do with sensors. In heat transfer operations applied to foods, sensors are used to measure and record temperature as a function of time. The sensors themselves are also subject to fouling, and if this occurs and a resistance to heat transfer is deposited on the sensing unit, then the temperature that is sensed will be lower than the bulk fluid temperature. The consequence is that the heating system will respond by (1) increasing the temperature of the heating medium (to increase the ΔT for heat transfer and consequently overcome the added resistance) (2) decreasing the flow rate of the product stream (to provide a longer residence time in the heat exchanger),

or (3) increasing the flow rate of the heating stream (to provide a larger ΔT in the heat exchanger). Unfortunately, all of these action will serve to accelerate fouling resulting in a runaway situation.

To overcome this situation, most heating systems with control sensors also have stand by sensors plumbed into the system so that one sensor operates while the other is cleaned. In other situations, sensors are placed in the product flow stream where turbulence is maximized as in a constriction or an elbow in the flow system. Unfortunately, our quantitative knowledge on fouling is limited and so we have developed our ability to remove the deposit, a process called cleaning. Cleaning is a very important unit operation in food processing but is beyond the subject of this book.

C. Radiation

As stated in Sec. II. A, energy can be transferred in the form of electromagnetic waves emitted from one body and absorbed by another. Electromagnetic radiation travels at the speed of light and is characterized by its wavelength and frequency. The relationship between wavelength and frequency is

$$c = \lambda f \quad (20)$$

where c is velocity of light (3×10^{10} cm/sec), λ is wavelength (cm), and f is frequency (cps). The large ranges of wavelengths and frequencies for various types of electromagnetic radiation are shown in Table 3.5.

Radiation of wavelength 0.8–400 μm (infrared) is referred to as *thermal* radiation or heat rays since electromagnetic radiation with this wavelength is most readily absorbed and converted to heat energy. Since infrared radiation is transmitted rapidly to the surface of the material, it is used primarily for surface heating. Examples of use include (1) dehydration of fruits and vegetables, (2) roasting of cocoa beans and nut kernels, (3) dehydration of grain, (4) dehydration of tea, (5) freeze drying, and (6) baking.

All bodies emit electromagnetic radiation, the amount and wavelength being dependent on the physical state and temperature of the body. For comparative purposes it is desirable to define a body that emits the maximum possible amount of energy at a given temperature. This theoretical substance is called a *black body*. The energy emitted by a black body is given by the Stefan-Boltzmann law,

$$\frac{q}{A} = \sigma T^4 \quad (21)$$

where q/A is energy radiated per unit area (W/m^2), σ is the Stefan-Boltzmann constant ($5.669 \times 10^{-8} \text{ W}/\text{m}^2\text{K}^4$), and T is absolute temperature of the black body (K). Examination of Eq. (21) shows that the quantity of heat emitted is

TABLE 3.5 Electromagnetic Radiation

| Type of radiation | Major effect on matter | Wavelength (μm) ^a | Frequency (cps) |
|-----------------------|-------------------------------------|---|---|
| Cosmic rays | Transmitted | 1×10^{-6} | 3×10^{20} |
| γ rays | Absorbed, reflected, or transmitted | 1×10^{-6} – 140×10^{-6} | 3×10^{20} – 2×10^{18} |
| X rays | Strongly absorbed | 6×10^{-6} – $100,000 \times 10^{-6}$ | 5×10^{19} – 1×10^{15} |
| Ultraviolet rays | Absorbed, reflected, or transmitted | 0.014–0.4 | 2×10^{16} – 8×10^{14} |
| Visible or light rays | Absorbed, reflected, or transmitted | 0.4–0.8 | 8×10^{14} – 4×10^{14} |
| Infrared or heat rays | Strongly absorbed | 0.8–400 | 4×10^{14} – 8×10^{14} |
| Radio | Absorbed, reflected, or transmitted | 10×10^6 – $30,000 \times 10^6$ | 3×10^8 – 1×10^4 |

^a $1 \mu\text{m} = 1 \times 10^{-6}\text{m} = 0.001 \text{ mm}$.

highly dependent on temperature, varying as the fourth power of absolute temperature.

Since no real bodies behave as black bodies, Eq. (21) must be corrected. This is easily done by defining the emissivity of a body. *Emissivity* is the ratio of the energy emitted by a real body to that emitted by a black body at the same temperature, and its numerical value is always less than 1.0. Emissivity values for representative materials are given in Table 3.6. The radiation by any actual body is then

$$\frac{q}{A} = \epsilon\sigma T^4 \quad (22)$$

Bodies obeying Eq. (22) are called *grey bodies*.

If a body is in thermal equilibrium with respect to radiant energy, then it is absorbing as much radiation as it is emitting. For grey bodies the amount of energy absorbed is expressed by an equation similar to Eq. (22) except the term *absorptivity* (α) is used instead of emissivity. Thus,

$$\frac{q}{A} = \alpha\sigma T^4 \quad (23)$$

Absorptivity is defined analogously to emissivity in that it is the fraction of radiation absorbed by a real substance compared to a black body (a perfect absorber with $\alpha = 1.0$). For grey bodies it can be shown that $\alpha \cong \epsilon$.

The radiant energy transferred between two surfaces depends on the differences in surface temperatures, geometric arrangements, and emissivities. Although the effect of geometric variables on the heat transfer by radiation is too complex for treatment here, there are several applications in the food industry where simplifications can be made. In the case of a relatively small body completely surrounded by a surface at a uniform temperature, the net exchange of heat by radiation is given by

$$q = A\epsilon\sigma[T_1^4 - T_2^4] \quad (24)$$

TABLE 3.6 Emissivities of Solid Surfaces

| Surface | Emissivity |
|-------------------|------------|
| Polished iron | 0.14–0.38 |
| Rough steel plate | 0.94–0.97 |
| Asbestos board | 0.96 |
| Water | 0.95–0.96 |
| Foods | 0.50–0.97 |

where A is surface area of the body (m^2), ε is emissivity of the body, T_1 is absolute temperature of the body (K), and, T_2 is absolute temperature of the surroundings (K).

Equation (24) can be used to calculate rates of heat transfer in infrared ovens, radiation heat transfer in tunnels for freezing or drying, and in other similar situations. If one body is not completely surrounded by the other body, then the surface area that one body sees of the other body must be taken into account. This is done through shape factors which are dependent on the geometry of the system. Since this is beyond the subject of this book, there are several excellent references including Perry and Green (1997).

D. Dielectric and Microwave Heating

Electromagnetic radiation in the radio frequency range can be used to generate heat in substances which efficiently absorb these wavelengths. Substances containing water or other polar molecules absorb radio frequency (rf) energy efficiently; therefore, rf heating is applicable to foods.

There are two types of radio frequency heating. In one case heating is accomplished by placing the object between parallel electrodes (dielectric heating). In the other, the product is placed in a resonance cavity (microwave heating). In dielectric heating an electric field is established between two electrodes and the polarity is reversed millions of times per second. Dipolar molecules contained in the object to be heated attempt to align themselves in this field, and this molecular movement results in generation of heat. This may be thought of as capacitance heating since a relatively poor electrical conductor (the food) is situated between the electrodes. The heat developed in the product is a function of frequency, potential across the product (field strength), and the dielectric properties of the product (Zhang and Datta, 2001).

Since the frequencies used in rf heating are also used in communications, the Federal Communications Commission has ruled that only certain frequencies may be used for industrial, scientific, and medical (ISM) purposes. The four frequencies commonly used are 915, 2450, 5800, and 22,150 Mc/s. Of these, dielectric heating is generally accomplished at 915 Mc/s (1Mc/s = 1 MHz).

Microwave heating is a truly radiative process. Electromagnetic radiation is generated in special oscillator tubes, such as magnetrons or klystrons, and is radiated into a closed chamber containing the product. The chamber is constructed of highly reflective walls so the radiation reflects back and forth until it is absorbed by the product. There is usually a wave deflector located at the point where the radiation enters the oven (cavity) to distribute the radiation uniformly in the oven. Microwave radiation generally has a frequency of 2450 Mc/s.

The heat generated in microwave and dielectric heating is given by

$$P = 55.61 \times 10^{-14} E^2 f \epsilon'' \quad (25)$$

where P is power generated (W/cm^3), E is electric field strength (V/cm), f is frequency (cps), and ϵ'' is dielectric loss factor.

It can be seen that the power generated (this can be converted to thermal units because $1 \text{ W} = 14.43 \text{ cal}/\text{min}$) is directly proportional to the square of the field strength, the frequency, and the loss factor. The loss factor is an intrinsic property of the object and is a measure of the efficiency with which electromagnetic radiation is converted to heat. Thus a large loss factor indicates that the product would heat readily with dielectric or microwave heating.

From Eq. (25) it would appear that increasing the field strength would be the most effective way to increase the rate of heating. However, this approach is limited by the voltage breakdown strength of the product. If the breakdown strength is exceeded, an electrical discharge occurs resulting in localized burning.

The other means of increasing the rate of heating is to increase the frequency. However, since nearly 100% of the electromagnetic radiation is absorbed at frequencies between 1000 and 3000 Mc/s, commercial rf heating systems are designed to operate in this range. Since dielectric heating is usually accomplished at 915 Mc/s and microwave at 2450 Mc/s, the power generated from microwave heating is more than that of dielectric heating at constant field strength.

Radio frequency heating has been referred to as volume heating because the energy is absorbed within the product, in contrast to convection, conduction, and infrared heating, wherein the heat energy is absorbed at the surface of the product. As the electromagnetic wave is transmitted through a material that absorbs radiation at the selected wavelength (e.g., 2450 Mc/s), the power decreases. The penetration depth of the radiation can be calculated from

$$D_p = \frac{c}{4\pi f} \left(\frac{2}{\epsilon'_r [(1 + \tan^2 \delta)^{1/2} - 1]} \right)^{1/2} \quad (25a)$$

where c is the phase velocity in free space ($3 \times 10^8 \text{ m/s}$), f is frequency, ϵ'_r is the relative dielectric constant, and $\tan \delta$ is the loss tangent.

The depth at which the electric field strength is reduced to $1/e$ [and the power density to $(1/e)^2$] is twice the power penetration depth, $D_s = 2D_p$. The half-power depth is $D_{1/2} = 0.69D_p$.

From Eq. (25a), it can be seen that the degree of penetration increases as the frequency decreases. Thus dielectric heating penetrates better than microwave heating. Consequently, microwave heating is generally less uniform, particularly in large objects, than is dielectric heating.

Another important consideration in microwave heating is the behavioral differences between ice and water. Liquid water absorbs radio frequency energy much more efficiently than does ice. Thus if ice and pockets of liquid water exist together (as in frozen foods) the water pockets absorb energy much more rapidly than the adjacent frozen areas and large thermal gradients can result. Pulsed applications of rf energy can help overcome this problem.

Dielectric and microwave heating have been successfully applied in several situations in the food industry [e.g., to bake crackers, to accomplish the final drying of potato chips, and to precook chicken pieces (Schiffmann, 2001)]. The high initial cost of dielectric and microwave equipment and the failure to heat nonhomogeneous products uniformly are factors which tend to limit their use. Additional methods for quantifying the effects of heat transfer by microwave energy on temperature are found in Datta and Anantheswaran (2001).

III. STEADY-STATE HEAT TRANSFER

Since heat transfer is one of the most common unit operations in food processing, in this section we will examine several cases of steady-state heat transfer which have wide application in processing food. Recall from the earlier description of modes of heat transfer that steady-state heat transfer means that the temperature is constant (i.e., independent of time) at any given location in the system but may vary from location to location.

A. Conduction Heat Transfer in Series

Consider a situation in which a solid wall is composed of several layers of material of different thickness each with its unique thermal conductivity (Fig. 3.4). This situation would exist, for example, in the wall of a cold storage room. There, in steady state, the rate of heat transfer across the wall may be considered using Fourier's law of heat transfer by conduction.

$$\left(Q = k_i \cdot A \frac{dT_i}{dx_i} \right)_{i=1,2,3} \quad (26)$$

Since steady state exists, then the heat transfer through each material must be constant and equal. That is, $Q_1 = Q_2 = Q_3$.

For materials 1, 2, and 3, Eq. (26) can be rewritten as

$$\Delta T_1 = \frac{Qx_1}{k_1} \quad \Delta T_2 = \frac{Qx_2}{k_2} \quad \Delta T_3 = \frac{Qx_3}{k_3}$$

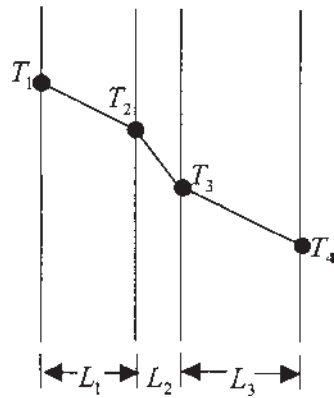


FIGURE 3.4 Composite rectilinear wall.

or

$$T_1 - T_2 = \frac{QAx_1}{k_1} \quad T_2 - T_3 = \frac{QAx_2}{k_2} \quad T_3 - T_4 = \frac{QAx_3}{k_3}$$

$$\begin{aligned} (T_1 - T_2) + (T_2 - T_3) + (T_3 - T_4) &= T_1 - T_4 \\ &= \frac{QAx_1}{k_1} + \frac{QAx_2}{k_2} + \frac{QAx_3}{k_3} \\ &= QA \left[\frac{x_1}{k_1} + \frac{x_2}{k_2} + \frac{x_3}{k_3} \right] \end{aligned}$$

Thus

$$QA = \frac{T_1 - T_4}{(x_1/k_1) + (x_2/k_2) + (x_3/k_3)} = \frac{T_1 - T_4}{(R_1 + R_2 + R_3)} = \frac{(T_1 - T_4)}{\sum_{i=1}^3 R_i} \quad (27)$$

This simple analysis illustrates the important principle of thermal resistances in series. That is, the total thermal resistance is the sum of the individual resistances. This also leads to the analogy with electrical systems in which rate = driving force/resistance ($I = E/R$). This analysis can be used to assess the value of insulating walls of processing equipment.

The previous discussion applies to objects which are rectilinear in which two dimensions are much larger than the third dimension. In the case of

cylindrical objects such as pipes, the analysis is more complex. Consider the tubular system in Fig. 3.5. Fourier's law for heat conduction in cylindrical coordinates is

$$q_r = -k_{12}A \frac{dT}{dr}$$

where q_r is the heat transfer in the radial direction and k_{12} is the thermal conductivity of material between r_1 and r_2 . The area for heat transfer is $A = 2\pi rL$ and boundary conditions across the inner most layers are

$$T = T_1 \quad \text{at} \quad r = r_1$$

$$T = T_2 \quad \text{at} \quad r = r_2$$

Then

$$q_r = -k_{12}(2\pi rL) \frac{dT}{dr} \quad \text{and} \quad \frac{q_r}{2\pi L} \int_{r_1}^{r_2} \frac{dr}{r} = \int_{T_1}^{T_2} -k_{12}dT$$

Integration for constant k_{12} yields

$$\frac{q_r}{2\pi L} \ln \frac{r_2}{r_1} = -k_{12}(T_2 - T_1)$$

and

$$q_r = \frac{2\pi L k_{12}}{\ln(r_2/r_1)} (T_1 - T_2) \quad (28)$$

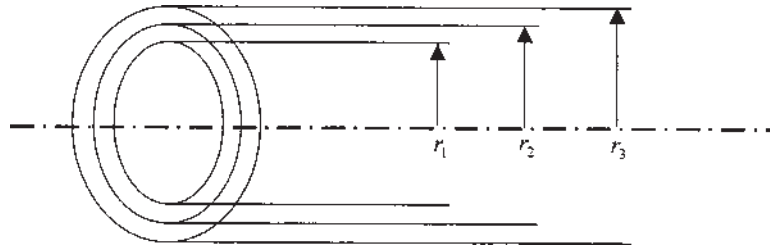


FIGURE 3.5 Cylindrical geometry for heat transfer.

Similarly, for the outer layer r_2 to r_3 ,

$$q_r = \frac{2\pi L k_{23}}{\ln(r_3/r_2)} (T_2 - T_3) \quad (29)$$

In a manner similar to that used for rectilinear thermal resistances in series, Eq.(28) and (29) can be solved for ΔT and summed yielding:

$$(T_1 - T_3) = \frac{q_r}{2\pi L} \left[\frac{\ln(r_2/r_1)}{k_{12}} + \frac{\ln(r_3/r_2)}{k_{23}} \right] \quad (30)$$

Since the area for heat transfer is dependent on r , define a logarithmic mean area such that

$$q_r = k A_{\text{lm}} \frac{(T_1 - T_2)}{(r_2 - r_1)}$$

where

$$A_{\text{lm}} = 2\pi L \frac{(r_2 - r_1)}{\ln(r_2/r_1)} \quad (31)$$

Substituting Eq. (31) into Eq. (30) for each layer yields

$$(T_1 - T_3) = q_r \left(\frac{r_2 - r_1}{k_{12} A_{\text{lm}}} + \frac{r_3 - r_2}{k_{23} A_{\text{lm}}} \right)$$

and

$$\begin{aligned} q_r &= \frac{T_1 - T_3}{[(r_2 - r_1)/k_{12} A_{\text{lm}}] + [(r_3 - r_2)/k_{23} A_{\text{lm}}]} \\ &= \frac{T_1 - T_3}{(\Delta r/k A_{\text{lm}})_{12} + (\Delta r/k A_{\text{lm}})_{23}} \end{aligned} \quad (32)$$

B. Convection Heat Transfer Coefficient

As mentioned earlier, the convective heat transfer coefficient h may be thought of as a heat transfer resistance caused by a film of immobile liquid of thickness δ and thermal conductivity k_f . Since it is not practical to measure δ in most convective heat transfer applications, empirical equations have been developed from experimental data using dimensional analysis. Dimensional analysis consists of identifying all the variables or parameters in a system that influence the value of another variable or parameter (e.g., h), combining those variables into dimensionless numbers [dimensionless numbers consist of a combination of multiplying and dividing variables so that the dimensions (mass, distance, time, and energy)

exactly cancel one another], and developing correlations which enable one to estimate the value of a parameter in a particular system.

The following section illustrates dimensionless correlations that can be applied to free and forced convection and are applicable for Newtonian fluids only (i.e., constant viscosity independent of shear rate).

C. Free or Natural Convection

Earlier it was pointed out that free or natural convection occurs when bulk movement of fluid occurs solely due to density gradients which are established when heating or cooling a fluid. These situations occur in food processing systems in which there are thermal gradients in the fluid (liquid, gas, or vapor). Examples include vegetables in brine in containers subjected to nonagitated thermal processing (still retorts), freezing or cooling ambient fruits and vegetables in still air (not a recommended practice), and heat gain or loss from sides of buildings and cold stores (warehouses) in still air.

The dimensionless numbers which are important include the Nusselt number, Grashof number, and Prandl number. The Nusselt number (Nu) is the ratio of convective to conductive heat transfer in the fluid and is given by

$$\text{Nu} = \frac{hD}{k_f} = \frac{\text{convective heat transfer}}{\text{conductive heat transfer}} \quad (33)$$

where h is the convective heat transfer coefficient ($\text{W/m}^2\text{C}$), D is the characteristic dimension of the system (m), and k_f is the thermal conductivity of the fluid ($\text{W/m}^\circ\text{C}$).

The Grashof number (Gr) represents the physical properties of the fluid and the temperature difference between the surface and the bulk fluid, one of the most important variables in the system.

$$\text{Gr} = \frac{D^3 \rho^2 g B \Delta T}{\mu^2} = \frac{\text{buoyancy forces}}{\text{viscous force}} \quad (34)$$

where D is the characteristic dimension (m), ρ is the fluid density (kg/m^3), g is the acceleration due to gravity (9.80665 m/s^2), B is the coefficient of thermal expansion ($1/T$) (K^{-1}), ΔT is temperature of the wall minus bulk fluid temperature ($T_w - T_b$) (C), and μ is viscosity (Pas)(kg/ms). The values of all properties are estimated at the average temperature [$T_f = (T_w + T_b)/2$].

The Prandl number (Pr) represents the relative magnitude of the thermal boundary layer to the momentum boundary layer.

$$\text{Pr} = \frac{\mu C_p}{k} = \frac{\text{viscous effect}}{\text{thermal diffusion effect}} \quad (35)$$

TABLE 3.7 Constants a and m for Free Convection

| Configuration | GrPr | a | m |
|---|--|------|-----|
| Vertical Plates and cylinders | | | |
| Length > 1 m | | | |
| Laminar | $< 10^4$ | 1.36 | 1/5 |
| Laminar | $10^4 < \text{GrPr} < 10^9$ | 0.55 | 1/4 |
| Turbulent | $> 10^9$ | 0.13 | 1/3 |
| Spheres and horizontal cylinders | | | |
| Diameter < 0.2 m | | | |
| Laminar | $10^3 < \text{GrPr} < 10^9$ | 0.53 | 1/4 |
| Turbulent | $> 10^9$ | 0.13 | 1/3 |
| Horizontal plates | | | |
| Heated plate facing up (Or cold plate facing down) | | | |
| Laminar | $10^5 < \text{GrPr} < 2 \times 10^7$ | 0.54 | 1/4 |
| Turbulent | $2 \times 10^7 < \text{GrPr} < 3 \times 10^{10}$ | 0.14 | 1/3 |
| Heated plate facing down (Or cold plate facing up) | | | |
| Laminar | $3 \times 10^5 < \text{GrPr} < 3 \times 10^{10}$ | 0.27 | 1/4 |

Source: Perry and Green (1997).

where μ is fluid viscosity (Pas) (kg/ms), C_p is heat capacity (kJ/kg°C), and k is thermal conductivity of the fluid (W/m°C).

The empirical correlations generally take the following form

$$\text{Nu} = a(\text{GrPr})^m \quad (36)$$

and a and m are functions of the geometry and magnitude of GrPr (sometimes identified as the Rayleigh number, Ra). Values for a and m for various conditions are illustrated in Table 3.7.

D. Forced Convection

In forced convection, the fluid is moved by the application of forces upon the fluid. Conventionally the forces are created by a pump, fan or stirrer. This is the most common type of convection in food processing since not only are the heating and cooling media moved (e.g., air, water, brine, refrigerant) but also the product is moved (e.g., milk, ice cream mix, vegetables or fruit in brine or syrup).

It is easy to imagine that forced convection will result in more rapid heat transfer than free convection because additional energy is used to cause bulk

TABLE 3.8 Correlation Equations for Convective Heat Transfer Coefficient

| Condition | Equation |
|---|--|
| Pipes | |
| a. $Re < 2100$ $Re \cdot Pr \cdot \frac{D}{L} < 100$ | $Nu = 3.66 + \frac{0.085 Re \cdot Pr \cdot (D/L)}{1 + 0.045 [Re \cdot Pr \cdot (D/L)]^{0.66}} \left(\frac{\mu_b}{\mu_w}\right)^{0.14}$ |
| $Re \cdot Pr \cdot \frac{D}{L} > 100$ | $Nu = 1.86 (Re \cdot Pr \cdot \frac{D}{L})^{0.33} \left(\frac{\mu_b}{\mu_w}\right)^{0.14}$ |
| b. $2100 \leq Re \leq 10,000$ | $Nu = 0.116 [Re^{2/3} - 125] Pr^{1/3} \left[1 + \left(\frac{D}{L}\right)^{2/3}\right] \left(\frac{\mu_b}{\mu_w}\right)^{0.14}$ |
| c. $Re > 10,000$ | $Nu = 0.023 Re^{0.8} Pr^{0.33} \left(\frac{\mu_b}{\mu_w}\right)^{0.14}$ |
| Flow passed immersed objects | |
| Single sphere | $Nu = 2.0 + 0.60 Re^{0.5} Pr^{0.33}$ |
| $1 < Re < 7000$ | |
| $0.6 < Pr < 400$ | |

Source: Perry and Green (1997).

mixing. Furthermore, the value of the convective coefficient should be a function of not only the physical properties of the fluid and the relative thermal and momentum boundary layers (i.e., the Prandl number) but also of the nature of the fluid flow [i.e., laminar or turbulent flow, represented by the Reynolds number (Re), the kinetic forces/viscous forces].

Correlations for forced convection generally take the form

$$Nu = a Re^n Pr^m \left(\frac{\mu_b}{\mu_w}\right)^p \left(\frac{D}{L}\right)^d \quad (37)$$

All properties are evaluated at the average temperature [i.e., $(T_w + T_b/2)$]. If T_b varies from inlet to outlet, then the average bulk temperature is used for T_b . Table 3.8 gives several equations for various geometric and flow conditions. Handbooks on chemical and mechanical engineering provide many more correlations for specific operating conditions [see, for example, Perry and Green (1997)].

IV. UNSTEADY-STATE HEAT TRANSFER

A. General Principles

In food processing, there are many situations where temperature at some point in a product is a function of time; i.e., unsteady-state heat transfer is occurring.

The most notable examples of unsteady-state heat transfer are heating or cooling of particulate materials, such as in blanching and aseptic thermal processing, or heating and cooling products in containers (canning). As we pointed out earlier, unsteady heat transfer also occurs when the frame of reference is changed to consider a volume element of fluid or solid moving through a process operating at steady state.

To illustrate the fundamental principles involved in unsteady-state heat transfer, consider the simple case of cooling a cylinder in air. Assume the cylinder is perfectly insulated at both ends so the only heat transfer is in the radial direction. Furthermore, assume (1) the cylinder is at an initial uniform temperature T_i , i.e., there are no thermal gradients in the cylinder, (2) the heat is convected away from the cylinder uniformly with a surface heat transfer coefficient h , (3) the air temperature is constant T_a , (4) the cylinder is uniform in composition with a thermal conductivity k_s , and (5) all of the heat is transferred from the center of the cylinder. The system is represented diagrammatically in Fig. 3.6.

The rate of heat transfer by conduction must equal the rate of heat transfer by convection.

$$\frac{dQ}{dt} = hA(T_s - T_a) = \frac{k_s A}{R}(T_c - T_s) \quad (38)$$

Rearranging Eq. (38) yields

$$\frac{hR}{k_s} = \frac{T_c - T_s}{T_s - T_a} \quad (39)$$

The ratio hR/k_s is a very important dimensionless number in unsteady-state heat transfer and is called the Biot (Bi) (pronounced Bee-oh) number. The Biot number represents the convective transport (h) relative to conductive transport k/R . A large Bi, therefore, means large convection compared to smaller conduction, and conversely for small Bi (i.e., small convection compared to large conduction).

From Eq. (39) the Bi number also represents the relative temperature drop in the solid compared to the temperature drop in the convective transport fluid. Thus, a large Bi means the temperature drop in the solid is very large compared to the temperature drop from the surface to the cooling or heating medium. Conversely, a small Bi means the temperature drop in the solid is very small compared to the temperature drop in the convective medium.

It is important to note that the Bi number looks very similar to the Nusselt (Nu) number (hD/k_f) [Eq. (33)], but they pertain to very different situations. Bi number pertains to unsteady-state heat transfer with an external convective heat transfer coefficient and an internal conductive heat transfer to an object of characteristic dimension R . Nu number pertains only to convective heat transfer in

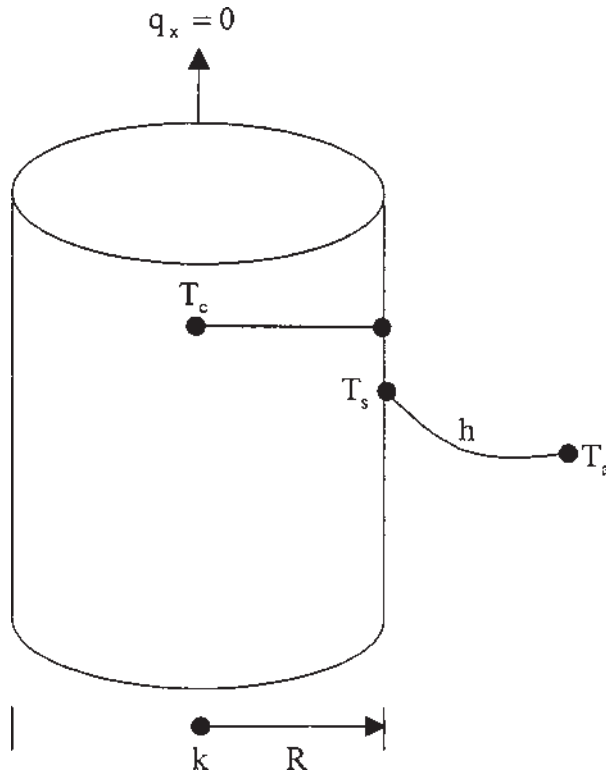


FIGURE 3.6 Unsteady-state heat transfer model.

which the convective heat transfer coefficient is related to the thermal conductivity of the convective fluid k_f , and the characteristic dimension of the system, D .

Proceeding with the example, since we assumed all the heat was transferred from the center of the cylinder, this means that there is very little temperature drop across the solid cylinder ($T_c - T_s$) compared to the temperature drop from the surface to the bulk of the cooling air ($T_s - T_a$). For the convective transport term in Eq. (38), the ordinary differential equation can be solved by separating variables and establishing boundary conditions.

$$\frac{dQ}{dt} = hA(T_s - T_a)$$

$$dQ = hA(T_s - T_a)dt \quad (40)$$

Furthermore, the heat convected away from the cylinder lowers the temperature of the cylinder by the equation describing the effect of changing sensible heat on

temperature.

$$Q = mC_p\Delta T$$

Since $m = \rho V$ and $\Delta T = T_i - T_s$, then

$$Q = \rho VC_p(T_i - T_s) \quad (41)$$

Eq. (41) uses the fact that the ΔT across the solid cylinder ($T_c - T_s$) is very small and the temperature of the cylinder is approximated by the surface temperature (i.e., small Bi). Differentiating Eq. (41) and setting it equal to Eq. (40) yields

$$dQ = \rho VC_p dT_s = hA(T_s - T_a)dt \quad (42)$$

Equation (42) can be solved by separating variables and integrating for boundary conditions $T_s = T_i$ at $t = 0$ and $T_s = T_2$ at $t = t$,

$$\int_{T_1}^{T_2} \frac{-dT}{T_s - T_a} = \int_0^t \frac{hA}{\rho VC_p} dt; \ln\left(\frac{T_2 - T_s}{T_1 - T_a}\right) = \frac{hAt}{\rho VC_p} \quad (43)$$

For a cylinder, $A = 2\pi RL$ and $V = \pi R^2 L$. Substituting in Eq. (43) yields

$$\frac{hAt}{\rho VC_p} = \frac{h(2\pi RL)t}{\rho(\pi R^2 L)C_p} = \frac{2ht}{\rho RC_p} \quad (44)$$

Multiplying and dividing Eq. (44) by k_s and R yields

$$\frac{2ht}{\rho C_p R} \frac{k_s R}{k_s R} = 2 \frac{hR}{k_s} \frac{k_s}{\rho C_p} \frac{t}{R^2}$$

Note that hR/k_s is the Bi number and $kt/\rho C_p R^2$ is also a dimensionless number called the Fourier number. The combination $k/\rho C_p$ is called thermal diffusivity and generally given the symbol α . Thus

$$\left(\frac{k}{\rho C_p}\right) \frac{t}{R^2} = \frac{\alpha t}{R^2} = \text{Fourier number (Fo)}$$

Finally, Eq. (43) becomes

$$\ln\left(\frac{T_2 - T_a}{T_1 - T_a}\right) = -2\text{BiFo}$$

$$\frac{(T_2 - T_a)}{(T_1 - T_a)} = \exp(-2\text{BiFo}) \quad (45)$$

For this simple example, with small Bi, temperature difference as a function of time can be described by Fig.3.7.

This example can serve to emphasize several principles in unsteady-state heat transfer. First, the change in temperature is a function of convective to conductive heat transfer (Bi number). Second, the temperature change is also

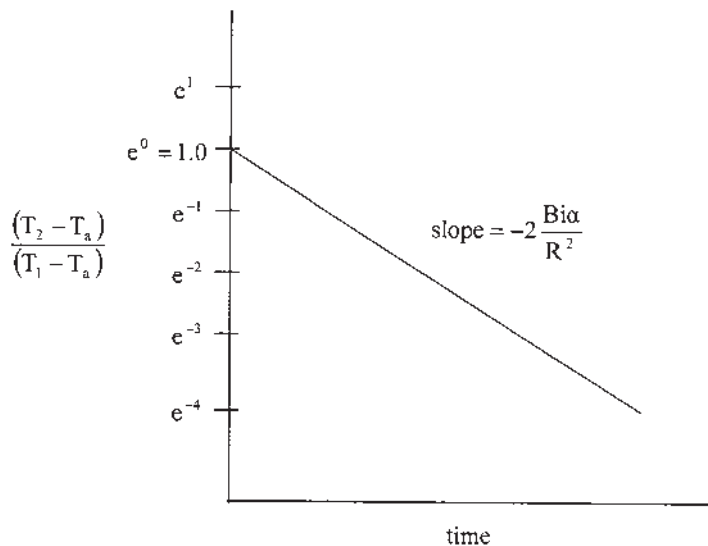


FIGURE 3.7 Unaccomplished temperature-time curve.

a function of time described through the Fo number. Third, if the Bi is not sufficiently small, then the temperature in the object will be a function of both time and position (r/R or x/L). Finally, the example suggests that the temperature ratio $(T - T_a)/(T_i - T_a)$ is appropriate to represent dimensionless temperature in unsteady-state heat exchange processes.

B. Unaccomplished Temperature Change

Before proceeding with further procedures for calculating temperature-time relationships in unsteady state, it is appropriate to reintroduce the concept of unaccomplished change. From Fig.3.7 and Eq. (45), T is a semilogarithmic function of time. A plot of temperature versus time for cooling is represented in Fig. 3.8. The total temperature change is $T_1 - T_a$, the accomplished temperature change is $T_1 - T_2$, and the unaccomplished temperature change is $T_2 - T_a$. The ratio $(T_2 - T_a)/(T_1 - T_a)$ is the unaccomplished fraction temperature change, usually referred to as *unaccomplished temperature* and given the symbol ΔT_{unacc} .

The similarity between ΔT_{unacc} as a function of time and first order chemical reactions is striking in that both are first-order processes in which $\log \Delta T_{\text{unacc}}$ or $\ln \Delta T_{\text{unacc}}$ and $\log (c/c_o)$ or $\ln (c/c_o)$ are linear functions of time. By analogy, time constants which are used to quantify time dependence of chemical reactions (D -value and τ_c) can also be used to quantify time dependence

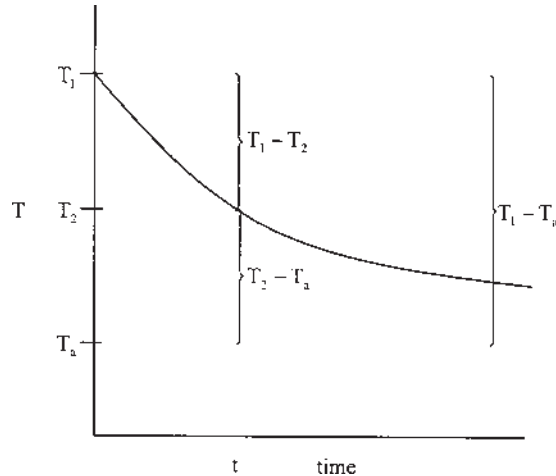


FIGURE 3.8 Temperature versus time for cooling.

of temperature in unsteady-state processes. This shall be used extensively when we examine procedures for calculating thermal processes for food products.

C. Generalized Solution for Unsteady-State Heat Transfer

The previous example served to introduce unsteady-state heat transfer. In general, the temperature is a function of time and location, and the consequence mathematically for the one-dimensional case is a second-order partial differential equation:

$$\frac{\partial T}{\partial t} = \frac{k}{\rho C_p} \frac{\partial^2 T}{\partial x^2} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (46)$$

where T is temperature ($^{\circ}\text{C}$), t is time (s), and x is location (m). $k/\rho C_p$ is the thermal diffusivity (m^2/s).

This partial differential equation has been solved for the three geometries in one dimension, the infinite slab [Eq. (46)], the infinite cylinder, and the sphere. An infinite slab is an object in rectilinear coordinates (x , y , z) where two dimensions (for example, y and z) are considered infinite compared to the third (x). An infinite cylinder is an object in cylindrical coordinates in which the length (x) is infinite compared to the radius (r) and the object is symmetrical about the third coordinate (θ). Obviously a sphere is unidimensional in r since it is symmetrical about the two angle coordinates (θ and ψ).

The specific solutions to the partial differential equations for unsteady-state heat transfer are beyond the scope of this book. They are presented for a variety of one- and two-dimensional cases with numerous boundary conditions in reference books on heat transfer [e.g., Carslaw and Jaeger, (1959)]. For our purposes we can utilize solutions obtained with simplifying assumptions and graphical or empirical equations which give unaccomplished temperature as a function of Bi number, Fo number, and r/R (or x/L) location.

D. Negligible Internal Resistance to Heat Transfer (Well-Mixed Fluid) ($Bi < 0.1$)

From the simple example presented earlier, it was assumed that the Bi was very small. This can be the case when $Bi < 0.1$. Recall that this means the convective transfer is less than 10% of the conductive transport.

$$Bi = \frac{hR}{k} \leq 0.1 \quad \text{and} \quad h \leq 0.1 \frac{k}{R}$$

This also means that the temperature drop in the conduction heating solid is only 10% of the temperature drop in the convective medium.

$$Bi = \frac{hR}{k} = \frac{T_s - T_c}{T_s - T_a} \leq 0.1$$

$$(T_s - T_c) < 0.1(T_s - T_a)$$

The solution is thus

$$\frac{T_2 - T_a}{T_1 - T_a} = e^{-(hA/\rho C_p V)t} \quad (47)$$

where T_2 is the temperature at the time t ($^{\circ}\text{C}$), T_1 is initial temperature ($^{\circ}\text{C}$), h is the convective heat transfer coefficient ($\text{W}/\text{m}^2\text{C}$), A is area for heat transfer (m^2), ρ is solid density (kg/m^3), C_p is heat capacity ($\text{kJ}/\text{kg}^{\circ}\text{C}$), V is volume (m^3), and t is time (s).

There are several examples in food processing in which Eq. (47) applies. For indirect heating (i.e., a wall separates the product from the heating or cooling medium) if the food contents of a container or vessel are well mixed and the heating or cooling medium exhibits a large convective heat transfer coefficient as in condensing steam or turbulently agitated water, then the temperature of the food fluid may be independent of location except for a thin film of food product at the surface of the vessel. Then Eq. (47) may be used. This is referred to as the *Well-mixed fluid* situation in heat transfer.

The situation may also apply in which the convective coefficient of the heating or cooling medium is not so large but the contents of the vessel are very well mixed. This may be the case with a scraped-surface kettle when relatively viscous food product is heated (e.g., a sugar solution for making candy or a fruit or vegetable puree). In this case, the overall heat transfer coefficient is substituted for h in applying Eq. (47)

A simple matter of checking the applicability of this condition to a particular situation is to estimate the magnitude of the operating variables and physical properties.

$$\text{Bi} \leq 0.1 \text{ or } \frac{hR}{k} \leq 0.1$$

If the solid is a food product with significant water content, then $k_{\text{product}} \cong k_{\text{water}} = 0.0597 \text{ W/m}^\circ\text{C}$. Substituting into the Bi number results in

$$(0.1)k = (0.1)(0.0597) = 0.0597 \text{ W/mC} \geq hR$$

Then any combination of h and R (half-thickness or radius) $< 0.0597 \text{ W/mC}$ will satisfy the condition of negligible internal resistance to heat transfer (well-mixed model). For example, if the heating or cooling medium is forced convection air with a maximum $h = 200 \text{ W/m}^\circ\text{C}$, then the maximum container size to assure uniform temperature in the product is

$$R \leq \frac{0.0597}{h} \text{ m} = \frac{0.0597}{200} = 3 \times 10^{-4} \text{ m} = 0.3 \text{ mm}$$

If still air is used to heat or cool a product and the convective coefficient (h) is $5 \text{ W/m}^\circ\text{C}$, then

$$R \leq \frac{0.0597}{h} \text{ m} = \frac{0.0597}{5} = 0.012 \text{ m} = 12 \text{ mm}$$

This example clearly illustrates that a uniform temperature in a food product will only occur when the package dimension is very small (for example, less than 12 mm, 0.5 about in radius or half-thickness).

E. Finite Internal Resistance to Heat Transfer ($\text{Bi} > 0.1$)

For this situation, the solutions to the partial differential equations for each of the one-dimensional geometries are presented as unaccomplished dimensionless time (Fo) charts with Bi number and location as variables, as shown in

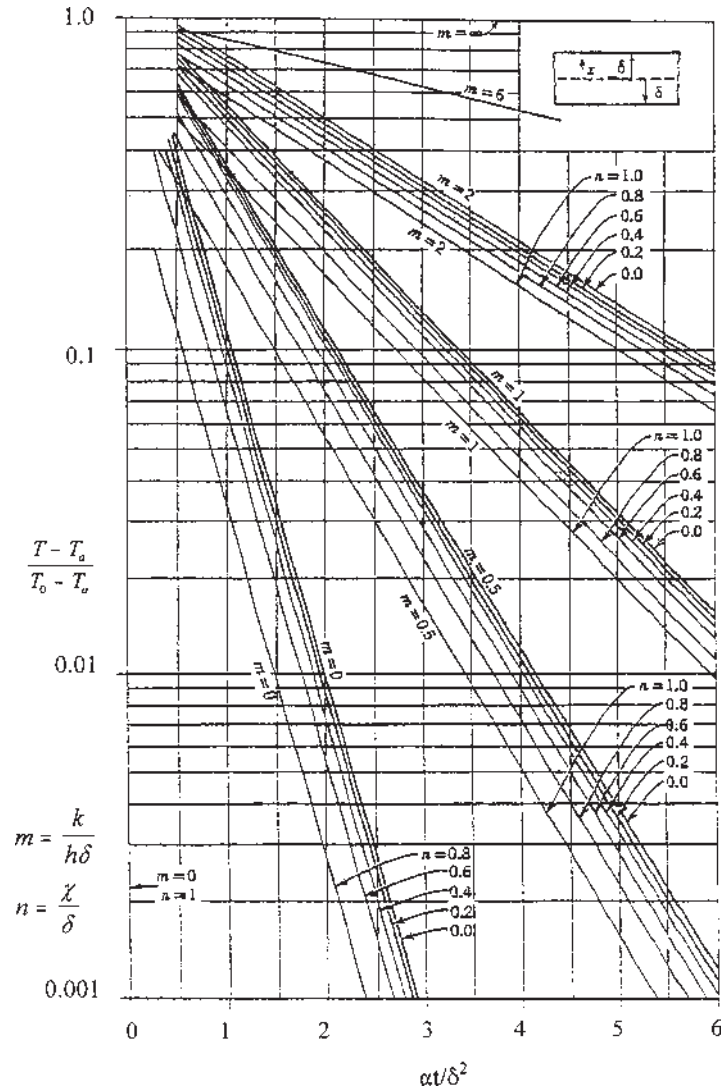


FIGURE 3.9 Unaccomplished temperature–Fourier number for the infinite slab.

Fig 3.9, 3.10, and 3.11 for the infinite slab, infinite cylinder, and spheres, respectively. In these charts, often referred to as Gurnie-Lurie or Heisler charts, ΔT_{unacc} is plotted against Fourier numbers with $1/\text{Bi}$ as a variable and x/L , r/R , and r/R as the location variable for the infinite slab (L is the half-thickness of the slab),

infinite cylinder (R is the radius of the cylinder), and sphere (R is the radius), respectively.

For $1/Bi = 0$, the set of lines represent ΔT_{unacc} versus Fo for negligible convective or surface heat transfer resistance. This is assumed to be the case for $Bi > 40$. Applying the same analysis as was applied for negligible internal

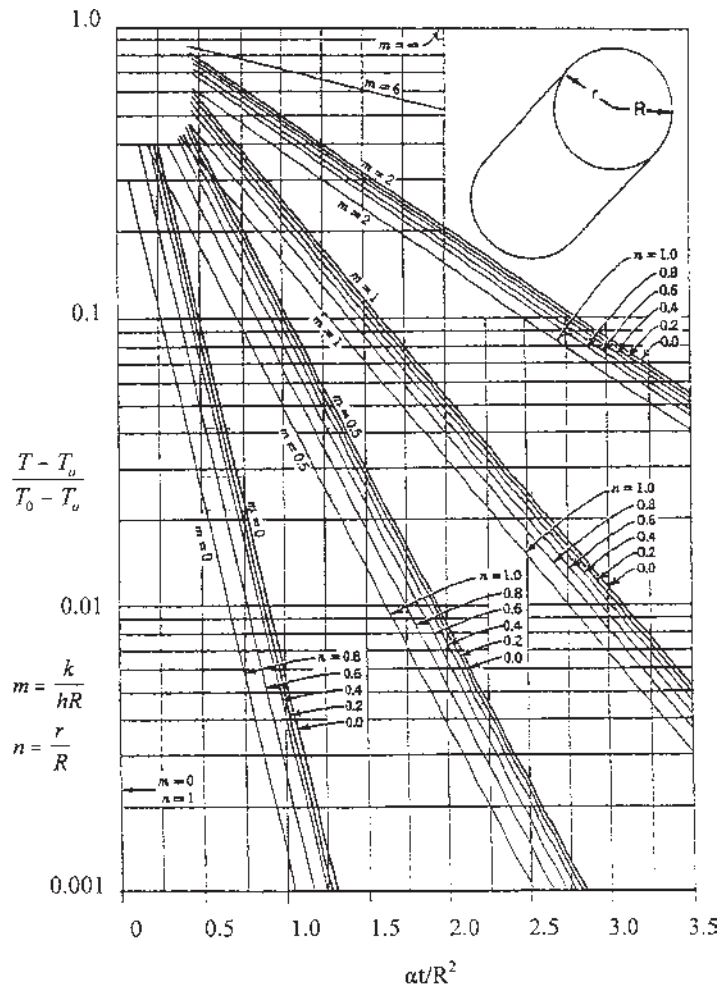


FIGURE 3.10 Unaccomplished temperature–Fourier number for the infinite cylinder.

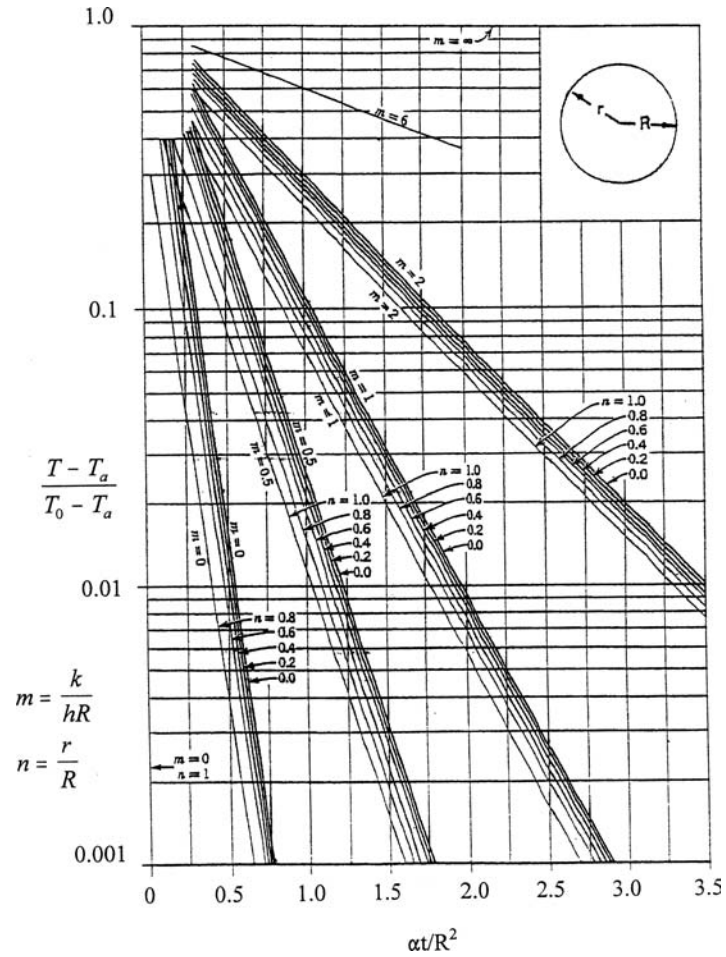


FIGURE 3.11 Unaccomplished temperature-Fourier number for the sphere.

resistance, then

$$\text{Bi} \geq 40 \geq \frac{hR}{k}$$

for water $k = 0.597 \text{ W/m}^\circ\text{C}$ and

$$(40)(0.597) > hR > 24 \text{ W/m}^\circ\text{C}$$

For condensing steam, $h = 10,000 \text{ W/m}^2\text{C}$ and

$$R \geq \frac{24}{10^4} = 0.0024 \text{ m} = 2.4 \text{ mm}$$

For forced convection water, $h = 1000 \text{ W/m}^2\text{C}$; then

$$\text{Bi} \geq 40 \geq \frac{hR}{k}$$

$$(40)(0.597) > hR = 24 \text{ W/m}^2\text{C}$$

$$R \geq \frac{24}{1000} \text{ m} = 0.024 \text{ m} = 2.4 \text{ cm}$$

This illustrates that for containers of food heated in steam, the half-thickness or radius need only be greater than approximately 2.4 mm (0.1 in) to assume negligible external heat transfer resistance. Consequently, heating nearly any size or shape container in condensing steam will be characterized by $\text{Bi} = 40$ or $1/\text{Bi} = 0$. For forced convection heating or cooling in water, the container need be no larger than approximately 5 cm in diameter or total thickness [about the size of a 0.4-kg (1-lb) conventional can].

F. Example

A canning company was packing and thermal processing sliced table beets. They had changed their operation slightly and noticed the appearance of dark centers in some of the sliced beets. They suspected that the dark centers were the result of tyrosinase, a polyphenoloxidase in beets which polymerizes tyrosine to dark brown pigments. Normally blanching to an internal temperature of 60°C (145°F) will inactivate the enzyme. As a food processing specialist you are asked to analyze the heat transfer occurring in the blanching process and assessing the adequacy of the blanch. The blanching conditions are $T_{\text{water}} = 100^\circ\text{C}$ initial temperature of beets (T_i) = 15°C , residence time $t = 15 \text{ min}$, $h = 6000 \text{ W/m}^2\text{C}$, 2.54 cm (1 in) < Diameter of beets < 7.6 cm (3 inches). Properties of beets:

$$C_p = 3.8 \text{ kJ/kg}^\circ\text{C} \quad \rho = 1100 \text{ kg/m}^3 \quad k = 0.070 \text{ W/m}^\circ\text{C}$$

1. Will tyrosinase be inactivated by the blanching process?

$$Fo = \frac{kt}{\rho C_p R^2} = \frac{0.7 \text{ W}}{\text{m}^\circ\text{C}} \frac{15 \text{ m}}{\text{m}} \frac{60 \text{ s}}{1100 \text{ kg}} \frac{\text{m}^3}{3.8 \text{ kJ}} \frac{\text{kg}^\circ\text{C}}{1000 \text{ W s}} \frac{\text{kJ}}{R^2} = \frac{1.507 \times 10^{-4}}{R^2}$$

$$Bi = \frac{hR}{k} = \frac{6000R}{0.7} = \frac{8571}{R}$$

| 2.54 cm diameter | 7.6 cm diameter beet |
|---------------------|----------------------|
| $Fo_{2.54} = 0.233$ | $Fo_{7.6} = 0.026$ |
| $Bi_{2.54} = 218$ | $Bi_{7.6} = 651$ |

From the Gurnie-Lurie chart

$$T_{\text{unacc}, 2.54} \leq 0.20 \quad \Delta T_{\text{unacc}, 7.6} = 1.0$$

$$\frac{T_s - T}{T_a - T_i} \leq 0.20 \quad \left(\frac{T_a - T}{T_s - T_i} \right) = 1.0$$

| | |
|------------------------------|-----------------------------|
| $T = T_a - 0.20 (T_a - T_i)$ | $T = T_a - 1.0 (T_a - T_i)$ |
| $T = 100 - 0.20 (100 - 15)$ | $T = 100 - 1.0 (100 - 15)$ |
| $T = 100 - 0.20 (85)$ | $T = 100 - 85$ |
| $= 100 - 17$ | $T = 15^\circ\text{C}$ |
| $T = 83^\circ\text{C}$ | |
| Tyrosinase inactivated | Tyrosinase active |

2. Where will the dark center occur?

For the 7.6 cm beet,

$$Fo = 0.026, 1/Bi = 0, \text{ and } \frac{T_a - T}{T_a - T_i} = \frac{100 - 60}{100 - 15} = \frac{40}{85} = 0.47$$

From the Gurnie Lurie chart, $r/R = 0.6$.

Therefore, the dark center will occur at $r/R = 0.6$; $r = 0.6 R = 0.6 (3.8) \text{ cm}$;
 $r = 2.3 \text{ cm}$.

G. Finite Objects

The preceding discussion presented solutions for unsteady-state heat transfer to objects which can be approximated as unidimensional (one-dimensional). In the real world, objects are often two- or three-dimensional. It can be shown that the solution to the partial differential equations for heat transfer to or from objects which are two- or three-dimensional is the product of the solution for each dimension. Thus,

$$\Delta T_{\text{unacc finite cylinder}} = \Delta T_{\text{unacc, infinite cylinder}} \\ \times \Delta T_{\text{unacc infinite slab}}$$

and

$$\Delta T_{\text{unacc finite brick shape}} = \Delta T_{\text{unacc, x}} \times \Delta T_{\text{unacc, y}} \times \Delta T_{\text{unacc, z}}$$

The finite cylinder is thus the perpendicular intersection of an infinite cylinder with an infinite slab, and the finite brick-shaped object is the perpendicular intersection of the infinite slab in the x , y , and z directions (Fig. 3.12).

General rules of thumb may be used to assess if a real object can be approximated as an infinite object. For cylinders, if $x/r > 5$, then the object may be approximated as an infinite cylinder. If $x/r < 0.15$, then the object can be approximated as an infinite slab (flat plate).

For brick shaped objects, if the ratio of the longer sides to the shortest side is > 8 , then the heat transfer in the longer dimension can be neglected and the ΔT_{unacc} in that direction is assumed to be 1.0, i.e., no temperature change as the result of heat transfer in that direction.

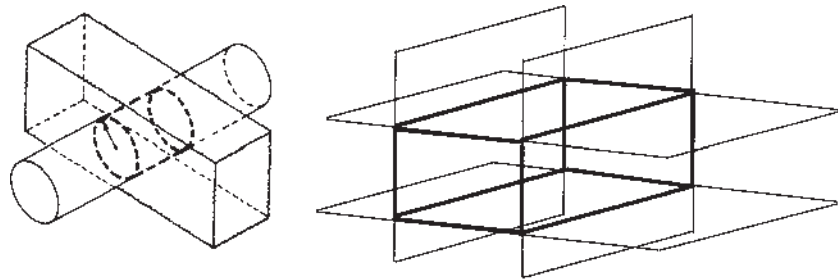


FIGURE 3.12 Finite cylinder and finite brick.

H. Other Conditions

The previous presentation was developed for heating and cooling processes in which the temperature of the heating or cooling medium is constant, the surface heat transfer coefficient is constant and all physical properties and dimensions of the product are constant. Obviously, in industrial processes applied to real products, these conditions do not necessarily apply. Although textbooks such as Carslaw and Jaeger (1959) present solutions to some of these situations, the more commonly accepted practice today is to apply finite-difference and finite-element analyses to solve these problems.

SYMBOLS

| | |
|-----------------|--|
| A | heat-transfer area (m^2) |
| c | velocity of light (CM/sec) |
| C_p | heat capacity (kJ/kg C) |
| E | electric field strength (V/cm) |
| f | frequency (cps) |
| h | film heat-transfer coefficient (W/m^2C) |
| k | thermal conductivity (W/mC) |
| L | characteristic length or half-thickness (m) |
| M | mass (kg) |
| P | power (W/cm^3) |
| Q or q | heat transferred (kJ or W) |
| R | thermal resistance (C/W) or radius (m) |
| t | time (s) |
| T | temperature ($^{\circ}C$, $^{\circ}F$, R, K) |
| ΔT | temperature difference ($^{\circ}C$) |
| ΔT_{lm} | logarithmic mean temperature difference |
| U | overall heat-transfer coefficient ($W/m^2^{\circ}C$) |
| W | mass flow rate (kg/s) |
| X_f | fictitious film thickness (m) |
| α | absorptivity |
| ϵ | emissivity |
| ϵ'' | dielectric loss factor |
| λ | latent heat (kJ/kg) or wavelength (cm) |
| σ | Stefan-Boltzmann constant (W/m^2K^4) |
| ρ | density (kg/m^3) |

Subscripts

| | |
|-----|--------------------------------------|
| f | solidification or melting process |
| s | sensible heat |
| v | vaporization or condensation process |

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4

Mass Transfer in Food Preservation Processes

I. INTRODUCTION

Mass transport is involved in many, if not most, food processes. In the present book we are concerned with food preservation processes, and mass transfer features significantly in many of them. Mass transfer is a key feature of processes that preserve foods by lowering the availability of water for microbial activity and for deteriorative reactions. The role of mass transfer in lowering water activity is discussed in Chapter 5, and Chapters 8, 9, and 10 are devoted to processes that achieve the lowering of water activity by freezing, concentration, and dehydration. Control of mass transfer is also the dominant feature of protective packaging of foods, which is discussed in Chapter 12. Mass transfer has in common with other transport processes the general dependence of its rate on a driving force and on resistance: Rate of mass transfer is proportional to driving force divided by the resistance.

In dehydration, concentration, and freezing the driving force is provided by the difference in partial pressure of water. Partial pressure of water is also a key driving force in protective packaging of moisture-sensitive foods. Other aspects of protective packaging involve other gases and vapors, and in these cases the partial pressure differences of the gas in question across a packaging barrier provides the driving force for transfer.

In each of the above preservation processes mass transfer of various food components other than water may be involved and contribute to the complexity of the given operation. Thus, as will be discussed later, transport of solutes may result in local changes in water activity, transport of flavors concomitant with the preservation processes may affect the quality of the processed food, and transport of antioxidants and biocidal agents may be important in stabilization of preserved foods. The driving forces for mass transport depend on equilibria between phases and are often proportional to the “distance from equilibrium.”

The resistance to mass transport depends on the transport mechanism. In most cases *diffusion* is the mechanism by which transport occurs, and the resistance is inversely proportional to the *diffusion coefficient* (D). Where bulk flow is involved, the driving force is usually related to total pressure (rather than partial pressure) difference, and the resistance is often proportional to viscosity.

II. PHASE EQUILIBRIA

A. The Phase Rule

In Chapter 1, we introduced a useful equation relating the number of intensive variables which can be varied independently, (F) to the number of components (Γ) and the number of phases (ϕ) is

$$F = \Gamma + 2 - \phi \quad (1)$$

An intensive variable of one which does not depend on the total amount of each phase (a physically independent homogeneous portion of a system). For instance, temperature, pressure, and composition are intensive variables. The phase rule is useful in predicting the number of variables which can be varied independently.

Consider, for instance, an aqueous solution of sucrose in equilibrium with water vapor above the solution: ($\Gamma = 2$ (water and sucrose), $\phi = 2$ (gas and liquid)). Accordingly, $F = 2$, and it is possible to vary independently any two of the three pertinent variables of temperature, pressure, and concentration. Thus, if concentration and temperature are fixed, the pressure at which equilibrium is achieved between water vapor and solution is determined as well.

B. Gas-Liquid Equilibria

A relationship useful in consideration of gas-liquid equilibria is Dalton's law, which states that the total pressure in a gas phase is equal to the sum of partial pressures of the components.

$$P_{\theta} = p_A + p_B + \cdots \quad (2)$$

where p is partial pressure, P_θ is total pressure, and A, B, \dots , are subscripts referring to components A, B, \dots , respectively.

In many situations, especially at moderate pressures, it is possible to approximate the behavior of gases by the ideal gas law,

$$PV = NRT \quad (3)$$

where P is pressure, V is volume of the gas phase, N is number of moles of gas phase, R is the gas constant, and T is absolute temperature.

When Eqs. (2) and (3) are combined, a relation is obtained between concentration of a given component in the gas phase and its partial pressure at a given constant temperature. Let

$$n_A \equiv N_A/V = P_A/RT \quad (4)$$

where n_A is the molar concentration of component A (moles per unit volume). Let

$$y_A \equiv n_A/n_\theta \quad (5)$$

where y_A is the mole fraction of A in the gas phase and n_θ is the molar concentration of all components. Then

$$y_A = p_A/P_\theta \quad (6)$$

The dependence of vapor pressure on temperature is well approximated by the Clausius-Clapeyron equation:

$$\frac{dp^\circ}{dT} = \frac{\Delta H_v}{T(\Delta V)} \quad (7)$$

where ΔH_v is the Latent heat of vaporization, ΔV is the volume change in vaporization, and p° is the vapor pressure.

If the ideal gas law is assumed applicable, then this equation may be approximated by:

$$\frac{dp^\circ}{p^\circ} = \frac{\Delta H_v}{RT^2} dT \quad (8)$$

Integration of this equation between any two given temperatures (T_1) and (T_2) yields Eq. (9), which allows the calculation of pressures.

$$2.3 \log_{10} \left(\frac{p_2^\circ}{p_1^\circ} \right) = \frac{-\Delta H_v}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (9)$$

A plot of the logarithm of vapor pressure vs the reciprocal temperature gives a straight line, provided the ideal relations mentioned above apply and ΔH_v does not vary with temperature.

C. Solutions

1. Raoult's Law

The partial pressure of water in equilibrium with an aqueous solution is lower than the vapor pressure of pure water. An estimate of the pressure of solvent over a solution is given by Raoult's law:

$$y_A = \frac{p_A}{P_\theta} = \frac{P_A^\circ}{P_\theta} x_A \quad (10)$$

where x_A is the mole fraction of solvent.

Raoult's law is accurate only in predicting vapor-liquid equilibria for ideal solutions in equilibrium with ideal gases. It is most applicable to dilute solutions. At moderate and high concentrations substantial deviations may occur.

2. Henry's Law

In certain systems where Raoult's law does not apply, the relation between partial pressure and composition of the liquid phase may be estimated by Henry's law:

$$p_A = S_A x_A \quad (11)$$

where S_A is a constant. (When $S_A = P_A^\circ$ Henry's law is identical with Raoult's law.)

D. Representation of Equilibrium Relationships for Binary Systems with Two Volatile Components

In a binary mixture, the component with the higher vapor pressure at a given temperature is referred to as the more volatile component, and the ratio of its vapor pressure to that of the less volatile component is called *relative volatility*. When Raoult's law is applicable, relative volatility is independent of concentration of the components in the binary mixture.

The relationship between partial pressure, composition, and temperature may be represented graphically in different ways, each of which is useful for particular purposes.

At constant temperature, the partial pressure of one component (usually the more volatile component) may be plotted against its mole fraction in the solution. A directly related plot is that of the "activity" of the component against its mole fraction in solution. The activity (a) is defined in Eq. (12) and a typical plot is shown in Fig. 4.1

$$a_A = p_A/P_A^\circ \quad (12)$$

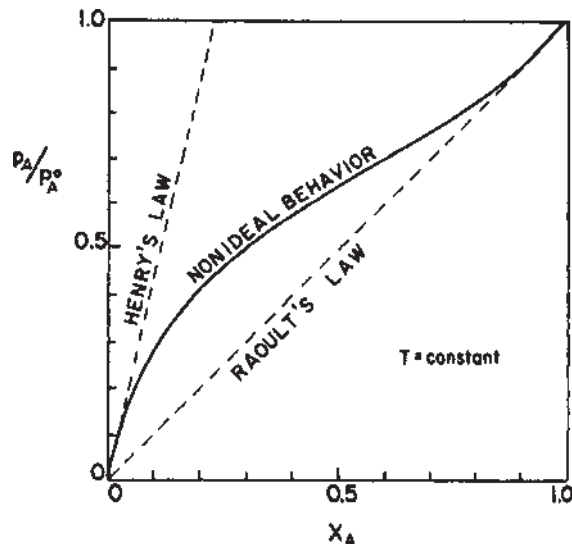


FIGURE 4.1 Dependence of partial pressure of a component on its mole fraction in a liquid.

This representation is useful for isothermal processes and for evaluating relative humidity in equilibrium with solutions.

In evaluating evaporation and distillation, it is often more convenient to evaluate the relationships between gas phase and liquid phase composition at the boiling point, that is, at a temperature at which the sum of partial pressures of the two volatile components equals atmospheric pressure, usually arbitrarily taken as 760 mm Fig. A diagram relating boiling point to composition of gas and liquid phases of a binary mixture is shown in Fig. 4.2. A diagram relating x_A to y_A at the boiling point for a binary mixture is shown in Fig. 4.3.

Most of the solutions of importance in food show nonideal behavior at high concentration and some behave nonideally even in relatively dilute systems. The solid curve shown in Fig. 4.4 is typical of deviations from ideal behavior and represents “positive deviation” from Raoult’s law.

Equation (13) is suitable for correlation of properties of nonideal solutions:

$$a_A = x_A \gamma_A \quad (13)$$

where γ_A is an activity coefficient dependent on concentration.

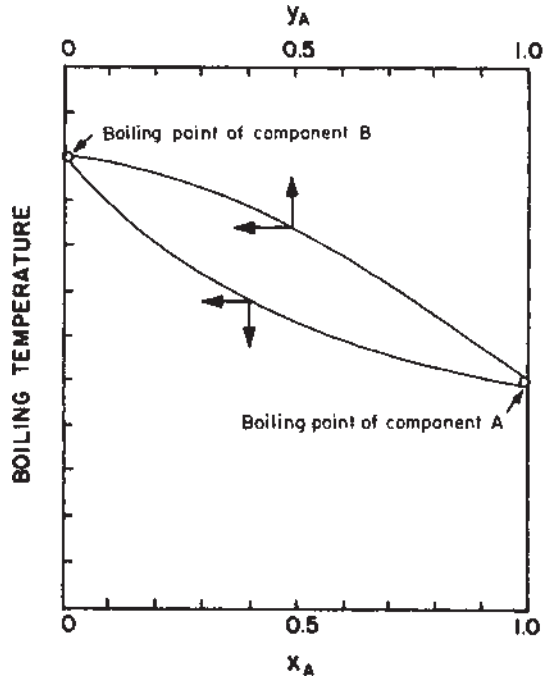


FIGURE 4.2 Boiling point diagram for a binary system.

E. Colligative Properties Related to Vapor Pressure

We have noted that the presence of solute results in depression of partial pressure of a solvent below its vapor pressure. Depression of vapor pressure and freezing point and elevation of boiling point and osmotic pressure belong to a group of properties referred to as *colligative*. These properties depend on the number of kinetic units in solution (that is, the number of molecules, ions, and particles) and not on the concentration by weight. In the ideal case, all of the above properties can be linearly related to solute concentration.

Thus vapor pressure depression may be written

$$P^\circ - p = P^\circ(1 - x) = P^\circ x_a \quad (14)$$

where P° is the vapor pressure of pure solvent, p is the partial pressure of solvent over solution, x is the mole fraction of solvent, and x_a is the mole fraction of solute.

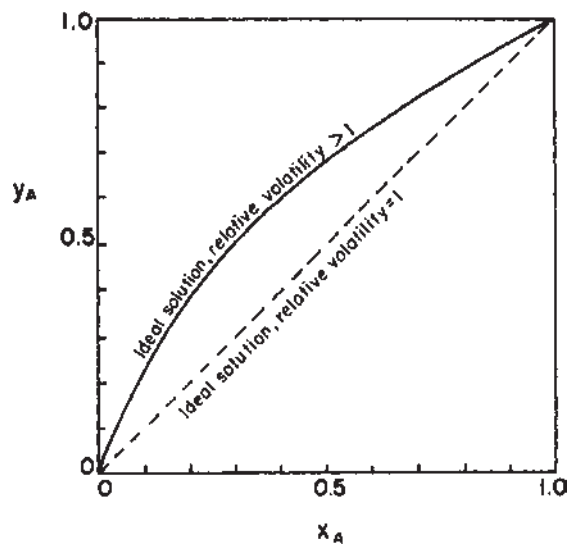


FIGURE 4.3 Relation of mole fraction in vapor phase (y) to mole fraction in liquid phase (x).

Depression of freezing point and elevation of boiling point are usually approximated by

$$\Delta T = \text{const} \times \text{molality of solute} . \quad (15)$$

Osmotic pressure in dilute solutions of nonelectrolytes is well approximated by

$$\Delta \pi = n_s RT \quad (16)$$

where $\Delta \pi$ is osmotic pressure and n_s is solute concentration.

F. Liquid-Liquid Equilibria

Consider a component A soluble in two mutually immiscible liquids L and ℓ . The two liquids, when brought into contact, constitute two phases and component A is transported from one phase to the other until the concentrations of A in phases L and ℓ reach equilibrium levels defined by

$$C_{A(L)} = K_{A(L/\ell)} C_{A(\ell)} \quad (17)$$

where $C_{A(L)}$ is the concentration of A in liquid L , $C_{A(\ell)}$ is the concentration of A in liquid ℓ , and $K_{A(L/\ell)}$ is the partition coefficient.

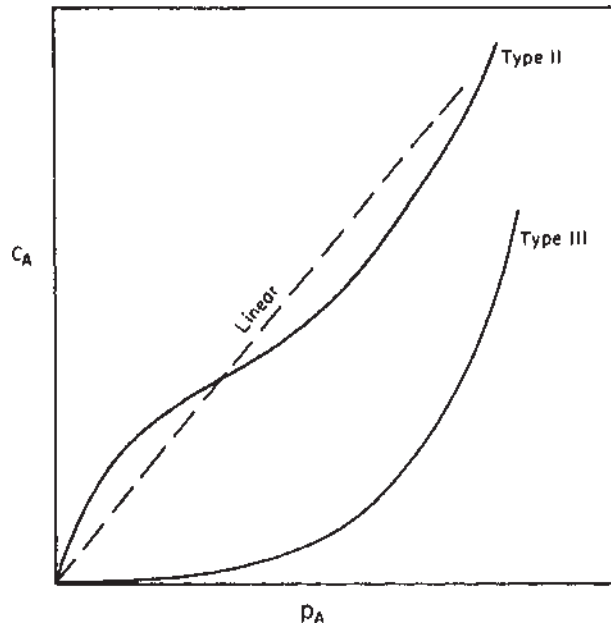


FIGURE 4.4 Sorption isotherms. Several other isotherms are known and described by Adamson (1960).

Equation (15) is analogous to the idealized situation for gas-liquid equilibria represented by Henry's law, Eq. (16). The partition coefficient may depend on concentration, especially in concentrated solutions, in which case Eq. (17) requires modification.

G. Gas-Solid Equilibria

Gas-solid equilibria are usually presented in the form of relations between partial pressure of a given component in the gas phase and its concentration in the solid phase. Four representations are often made, of which the isotherm is the most common. These representations are as follows.

1. Isotherms

Isotherms are analytical or graphical representations of partial pressure of a component in equilibrium with its concentration in a solid, at constant temperature:

$$p_A = f(C_A) \quad T = \text{const} \quad (18)$$

where C_A is the concentration of component A in the solid phase.

The simplest case is one in which Henry's law applies. In most cases, however, isotherms are nonlinear, and in the case of water held by foods, the isotherms are of type II or of type III of the five types commonly considered in analyses of adsorption (Adamson, 1960). Isotherms of type II and III as well as the linear isotherm, which is the form represented by Eq. (18), are shown in Fig. 4.4.

2. Isobars

Isobars represent relations between concentration and temperature while partial pressure of a component is held constant as shown in Fig. 4.5 and Eq. (19)

$$C_A = f(T) \quad P_A = \text{const} \quad (19)$$

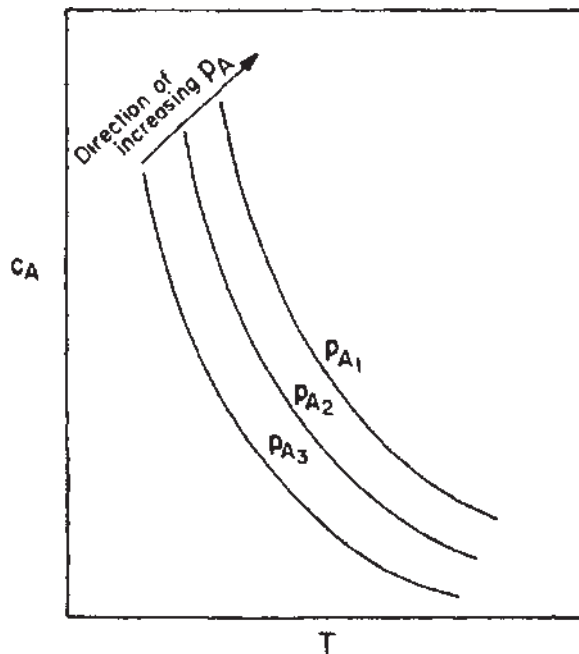


FIGURE 4.5 Sorption isobars.

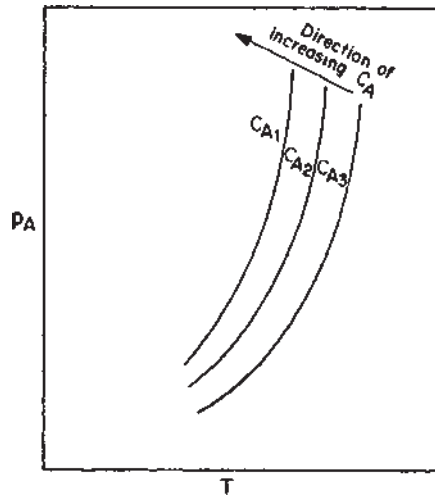


FIGURE 4.6 Sorption isosteres.

3. Constant Activity Curves

Constant activity curves are similar to isobars except that their activity is held constant, as shown in Eq. (20):

$$C_A = f(T) \quad P_A/P_A^\circ = \text{const} \quad (20)$$

4. Isosteres

Isosteres are curves or functions relating equilibrium pressure of an adsorbed component to temperature when the amount adsorbed is held constant, as shown in Fig. 4.6 and Eq. (21):

$$P_A = f(T) \quad C_A = \text{const} \quad (21)$$

III. MASS TRANSFER BETWEEN PHASES

A. Interface Between Phases

Phases in contact are usually assumed to be in equilibrium at the plane of contact, that is, the interface. This assumption means that the controlling factor in transfer of components from one phase to another is the rate of transport to and from the interface. The analysis of transfer between phases therefore requires that primary consideration be given to transport in each phase.

The following pages deal with transport of diffusing components in gases, liquids, and porous solids. Water is the substance usually transferred in processes for food preservation, but the same general principles apply to flavor components, preservatives, and other chemical species.

B. Diffusion Within a Homogeneous Phase

Within a homogeneous phase (gas, liquid, or solid) the mass transfer of a molecular species occurs primarily by diffusion. The driving force for diffusion is the difference in the chemical potential of the diffusant, when the chemical potential is constant the system is at equilibrium. At constant temperature the condition of equilibrium is given by constancy of activity of the diffusant and in most cases is approximated by equality of concentrations. Figure 4.7 represents the concentration gradient of a diffusing chemical species during approach to equilibrium. The mathematical formulation is given by the well-known *Fick's first law* shown in Fig. 4.8. Fick's law is analogous to the equation for steady-state heat transfer equation presented in Chapter 3.

Diffusion may be considered as the result of a very large number of small steps in random directions and the diffusion coefficient (D) has been related to the length of individual steps, and the time for each step by the classic Einstein-Smoluchowski equation (Fig. 4.9).

As in the case of heat transfer, it is possible to derive a differential equation for unsteady transfer by conducting a balance on a differential element in the space in which the transfer occurs. In the case of heat transfer the balance considered is energy balance, in diffusion mass balance. In fact Fick derived both of his laws on the basis of analogy to heat transfer relation.

The equation for unsteady-state diffusion is the *Fick's second law* shown in Fig. 4.10. The solutions to this differential equation for various boundary conditions (geometry, initial concentrations as a function of spatial coordinates) has well-known solutions analogous to those available for unsteady heat transfer (Treybal, 1968; Sherwood et al., 1975; Crank, 1956). Figure 4.11 shows a general solution for an infinite slab and approximations which are useful for specified time periods (short times and long times), Figure 4.12 shows graphically the conformance and deviation of the approximations from the general solutions. In addition to slab geometry, solutions have been developed for other geometric shapes including cylinders and spheres. Computer software is available for obtaining these solutions, and there are examples in literature of their application to food engineering problems (Barnard and Quintero, 1998). A useful approach is the graphical presentation of solutions of the equation analogous to those for heat transfer, such as the well-known Guernie-Lurie charts, the use of which for heat transfer calculations was explained in Chapter 3.

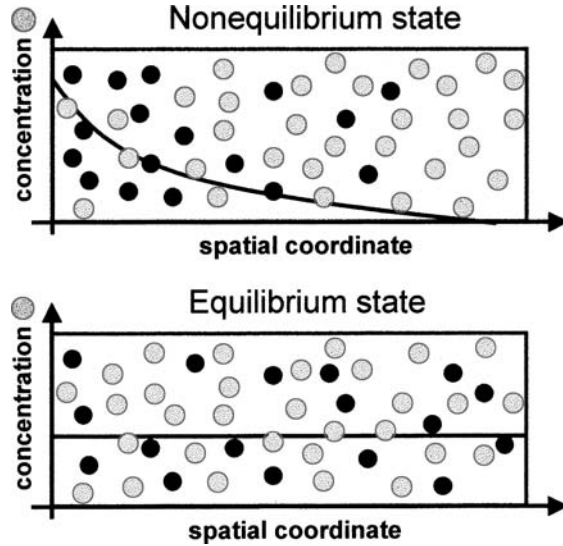


FIGURE 4.7 Schematic representation of the approach to equilibrium in diffusion process. General condition for equilibrium with respect to molecular species A. The chemical potential of A = μ_A is constant.

The analogy with heat transfer presentations can be recognized by consideration of the following dimensionless numbers used in these graphs. The unaccomplished change is often given the symbol Y and represents $(T - T_a)/(T_i - T_a)$ for heat transfer and $(c - c_a)/(c_i - c_a)$ for mass transfer. The subscripts a and i stand for initial and ambient conditions, respectively. In these charts

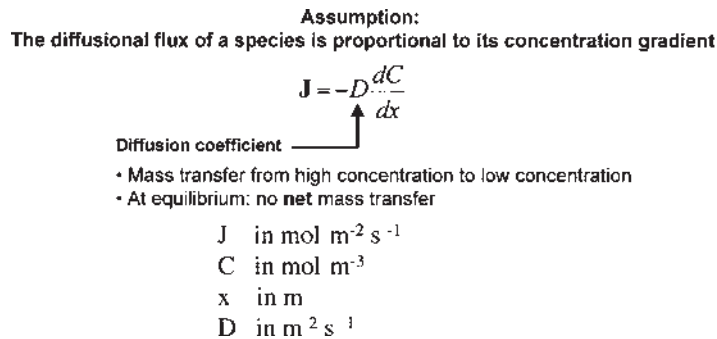
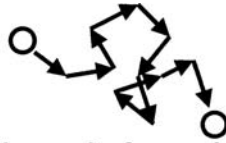


FIGURE 4.8 Fick's first law of diffusion.



Diffusion is the result of a very large number of very small steps in *random* directions

Einstein-Smoluchowski relation:

$$D = \frac{1}{2} \frac{d^2}{\tau}$$

Diffusion coefficient \uparrow

d = hopping length
 τ = hopping time

Illustration:

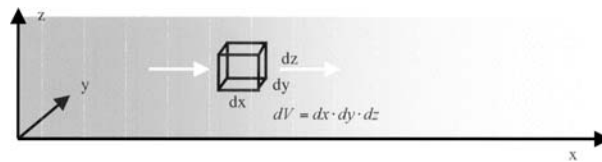
SO_4^- in water:
 $D = 10^{-9} \text{ m}^2/\text{s}$
 (at 25 °C)



Time to jump one diameter:
 $\tau = 8 \times 10^{-11} \text{ s}$

FIGURE 4.9 Statistical representation of diffusion.

the symbol X representing the abscissa stands for the quantity $\alpha t/l^2$ in heat transfer and in mass transfer for Dt/l^2 . α is the thermal diffusivity, D the (mass) diffusivity, t is time and l is a characteristic length for the geometric shape considered.



Change in concentration in box =
 (what comes in - what goes out) / volume of box

$$\frac{dC}{dt} = D \cdot \frac{d^2C}{dx^2}$$

\uparrow 1st derivative \uparrow 2nd derivative

FIGURE 4.10 Fick's second law of diffusion.

Full solution for the slab:

$$\frac{M(t)}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \cdot \pi^2} \exp\left(-\frac{D(2n+1)^2 \pi^2}{4l^2} t\right)$$

Approximate solutions for the slab:

'short times'

$$\frac{M(t)}{M_\infty} = \frac{2}{\pi} \left(\frac{Dt}{l^2}\right)^{\frac{1}{2}} - t^{\frac{1}{2}} \quad \frac{Dt}{l^2} \ll 1$$

'Long times'

$$\frac{M(t)}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{D^2}{4l^2} t\right) \quad \frac{Dt}{l^2} \gg 1$$

| Dimensionless diffusion number: | |
|---------------------------------|---|
| $\frac{Dt}{l^2}$ | > |

FIGURE 4.11 Some solutions to the differential equation of Fick's second law.

As in the case of heat transfer the graphs show solutions for specified locations within the object and for specified surface resistance ratios. Similar charts may be constructed for specific applications in mass transfer, such as infusion of compounds into foods. Infusion is used in *curing*, which is a set of processes in which microbial activity is inhibited by infused compounds such as salts and sugars, which lower water availability to microorganisms and may also have direct bacteriostatic effects.

Figure 4.13 shows *accomplished* concentration change, i.e., fraction of the total change attained if equilibrium is reached. If we use previously cited

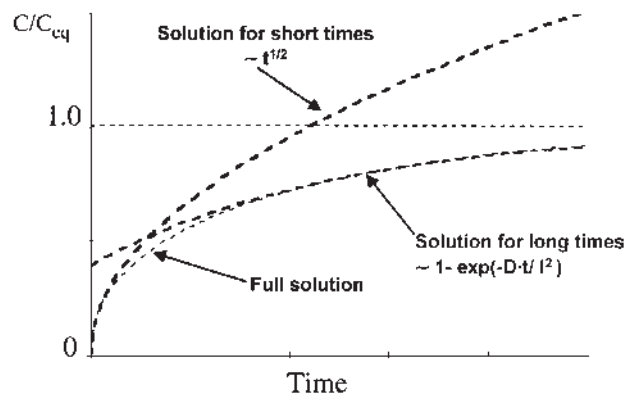


FIGURE 4.12 Graphical comparison of some solutions to Fick's second law.

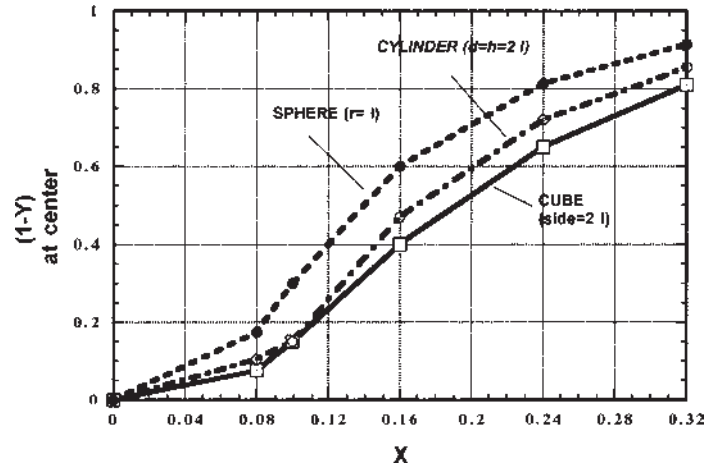


FIGURE 4.13 Accomplished concentration change ($1 - Y$) as a function the diffusion number (X) for some geometric shapes. Curves are for the center of each shape.

definition of Y , the accomplished change is equal to $(1 - Y)$. The curves in Figure 4.5–13 refer to conditions in the center of these geometric shapes. Similar curves may be obtained for other locations.

Another set of solutions may be developed for the *average* concentration in given geometric shapes. Figure 4.14 shows a set of such curves for spheres, slabs, and cylinders. The use of mathematical models for process design calculations in various leaching and diffusion processes important in preservation is reported in numerous reviews and research papers (Schwartzberg and Chao, 1983; Califano and Cavelo, 1983; Liu 1992; Wand and Sastry, 1993; Luna and Chavez, 1992).

We can illustrate the applicability of above solutions to food technology by considering the process for curing Parma Ham (Prosciutto). This rather expensive delicacy is produced by a very well controlled operation both in terms of raw materials and process conditions. The process involves trimming 12 to 14 kg hams to a weight of about 8 to 10 kg and covering them with solid sodium chloride. This results in the existence of a saturated salt solution on the surface of the hams, which are placed in refrigerated rooms at a relative humidity of 85% at 1 to 4°C for an initial equilibration period of approximately days, after which the remaining visible salt crust is removed and the ham are stored for an additional 15 to 18 days at the same temperature, but at somewhat lower temperature. The purpose of this two-step salt infusion period is to achieve a local salt concentration adequate to prevent microbial growth. Following this equilibration

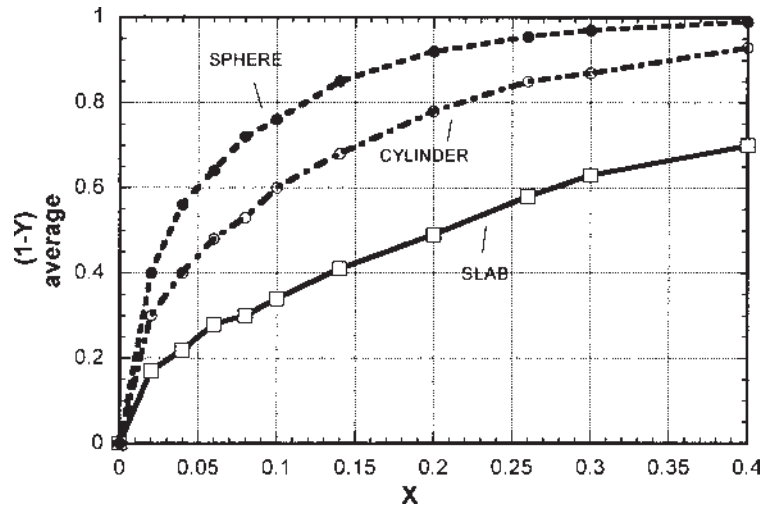


FIGURE 4.14 Accomplished average concentration change ($1 - Y$) as a function of the diffusion number (X) for the following spheres, infinite slabs, and infinite cylinders.

the surface is cleaned of remaining salt, and the hams are placed for several months in a room at 38°C to develop the desired characteristic flavor.

The composition of the cured Parma ham is water 62% proteins 27%, salt 6%, and fat 4%. The periods of initial equilibration are adjusted on the basis of extensive experimental data relating weight of the ham to the time needed for salt penetration.

The problem we shall consider is the estimation of the equilibration period on the basis the known salt/water diffusion coefficient, an assumed geometric shape of the ham, and the graphical solutions of Fick's second law.

We make the following "rough" approximations:

Geometric shape: Cylinder 18 cm in diameter and 36 cm in length. This gives the characteristic length $l = 9$ cm or 0.09 m. Assuming a density of ham of 1070 kg/m^3 (Lewis, 1987), the weight of the cylinder is approximately 9.8 kg.

Diffusion coefficient: We estimate D of sodium chloride in the meat as 4×10^{-10} (Saravacos and Maroulis, 2001).

Accomplished concentration change ($1 - Y$): We approximate the surface concentration of salt (saturated salt solution) as 240 kg/m^3 and assume that a post-equilibration concentration in the center of the ham of 50 kg/m^3 is adequate to assure microbial safety. Compare this with the equilibrium composition for the cured ham reported above, where salt content is 6%. We obtain a value of $1 - Y$ of $50/240 = 0.208$.

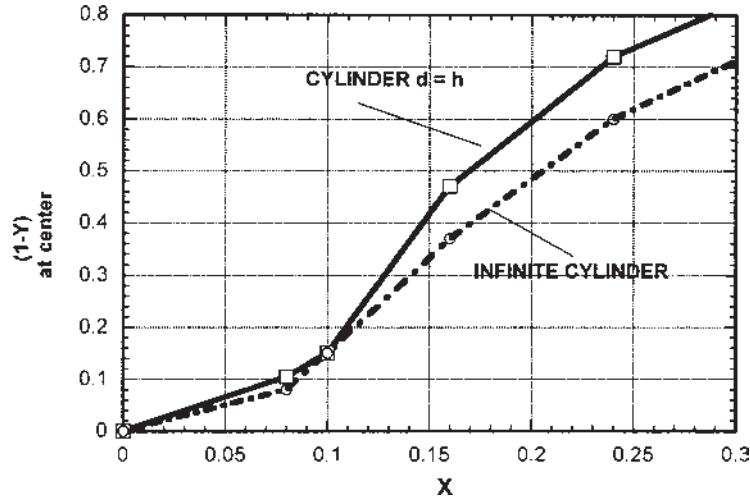


FIGURE 4.15 Accomplished concentration change $(1 - Y)$ at the center of two cylinders: infinite cylinder and cylinder with height equal to diameter.

To evaluate the diffusion behavior, we consult an accomplished concentration change chart for the center of a cylinder (Fig. 4.15). Note that at low values of $1 - Y$, the difference between cylinders with diameter equal to length and infinite cylinders is not significant. We obtain a value of $X = Dt/l^2$ by consulting the chart as equal to 0.11. We can now estimate equilibration time t : $t = (Xl^2)/D$. Therefore $t = 0.11 \times 0.09^2 / (4 \times 10^{-10}) = 6.2 \times 10^{-6} \text{ s} = 26 \text{ days}$.

We note that the estimated time required is in remarkably good agreement with the 22 to 25 days used according to literature description of the process. Given the large number of approximations we made, this close agreement is probably fortuitous. Nevertheless, estimations of this type are useful as guides to process design but must be confirmed by experiment or in cases where very good data on geometry and on physical properties are available by computer-aided solutions of Fick's Second Law.

C. Nonideal Diffusion Behavior

The diffusion equations described above constitute a description of so-called Fickian, or ideal behavior. The prerequisites for such behavior are

1. Diffusion constant independent of concentration of diffusant.
2. Absence of geometric changes in the matrix (absence of shrinkage or swelling).

3. Temperature dependence of D may be described by the Arrhenius equation.

In many materials, in particular in glassy polymers, and in foods which in many cases are composed of glassy polymers, significant deviations from Fickian behavior are observed (Crank and Park, 1968). The primary causes of such behavior of foods are swelling or shrinkage. Water is the universal plasticizer in foods, and since plasticization increases molecular mobility of polymer chains and often results in swelling, it is in the diffusion of water that nonideal behavior is most common in foods. The effect of polymer mobility on diffusion is expressed by the *Deborah Number*, De shown in Fig. 4.16.

In Fig 4.17 are shown schematically the effects of De on diffusion behavior as a function of diffusant (in this case water) concentration and temperature. When the rate of relaxation of the matrix (due to polymer segment mobility) is very much slower than the rate of diffusion, $De \gg 1$.

The matrix geometry does not change significantly during the diffusion and the regime of diffusion is ideal or *Fickian*. This occurs when the diffusant does not plasticize the matrix, or when the concentration and temperature condition limit such plasticization and the polymer remains in the glassy state. When the value of De is very much lower than 1, mechanical relaxation dominates the process (Peppas and Brannon-Peppas, 1994).

A special case observed in diffusion is the so-called Case II diffusion in which the initial sorption of the diffusant shows a linear dependence on time (Fig. 4.18). It will be recalled that the expected Fickian behavior gives a linear dependence on the square root of time (Fig. 4.11). There have been many attempts to model Case II behavior, and the most widely accepted model

Measure of the relative importance of diffusional processes and mechanical relaxation processes (e.g., matrix flow) in the sorption behavior

Matrix flow may result in collapse (porous dehydrated systems) or in swelling (hydrated systems)

$$De = \frac{\lambda}{\theta}$$

Where: θ = characteristic diffusion time = l^2/D
 l = characteristic sample dimension
 D = diffusion coefficient
 λ = mechanical relaxation time

FIGURE 4.16 The diffusional Deborah number De .

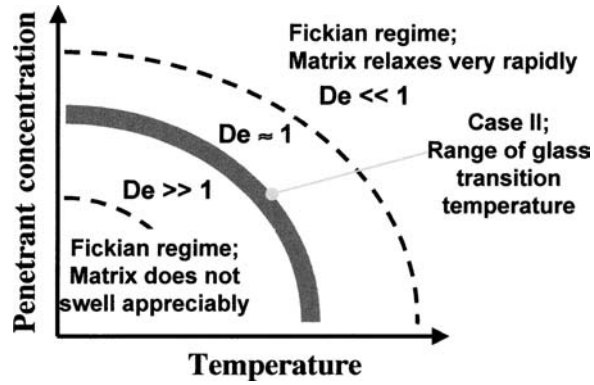


FIGURE 4.17 Case II diffusion in swellable polymers. (From Peppas and Brennon-Peppas, 1996.)

postulates a coupling of the diffusion process with viscoelastic effects. The viscoelastic properties of the polymers change as the diffusant plasticizes the matrix. Food polymers are known to behave in this manner. A recent study using nuclear-magnetic-resonance imaging reported the diffusion behavior of water in starch and found Case II behavior in diffusion into amylose pellets (Hopkinson et al., 1997).

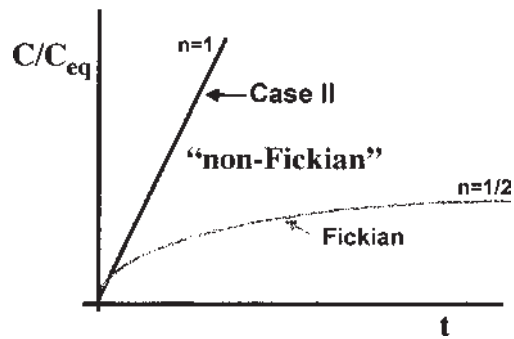


FIGURE 4.18 The initial portion of sorption curves in two types of diffusion. $C/C_{eq} = k t^n$; C , concentration; C_{eq} = C at equilibrium; t = time.

D. Film Coefficients for Mass Transfer

In analyzing mass transfer between phases, it is convenient to express rates in terms of coefficients incorporating various resistances to mass transfer and relating fluxes to gradients of concentration or pressure.

For instance, consider a liquid phase in contact with a gaseous phase, as shown in Fig. 4.19. Assume that a component is transferred from liquid to gas. In the bulk of the liquid, the concentration of the component is uniform and equal to C . The gradient of concentration is assumed to occur in a film adjacent to the gas-liquid interface. At the interface, the concentration (C_i) is in equilibrium with the partial pressure (p_i) of the component at the interface. The partial pressure in the bulk of the gas phase is also considered uniform and equal to p , with all the gradient in partial pressure occurring in a gaseous film adjacent to the interface. Given steady-state conditions, the following equation gives the rate of transfer in the liquid:

$$J = k_L(C - C_i) \quad (22)$$

where k_L is a film transfer coefficient in the liquid in units consistent with those

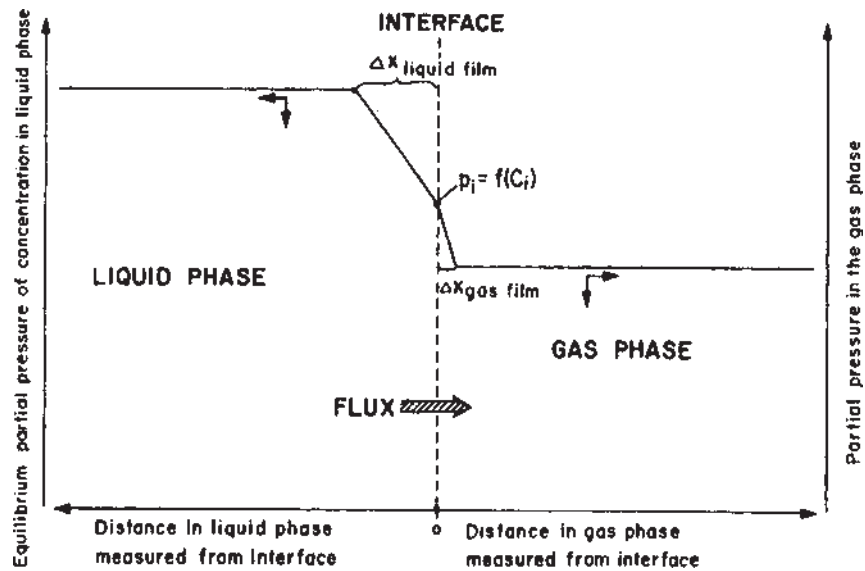


FIGURE 4.19 Schematic representation of mass transfer from a liquid to a gas phase.

of J and C . If for instance J is in mol/s cm² and C is in mol/cm³, then k_L is in

$$\frac{\text{mol}}{(\text{cm}^2)(\text{s})(\text{mol}/\text{cm}^3)} = \text{cm}/\text{s}$$

Note that Eq. (23) relates k_L to the diffusion coefficient

$$k_L = \frac{D}{\Delta X_{\text{liq film}}} \quad (23)$$

where $\Delta X_{\text{liq film}}$ is the thickness of the liquid film. Of course, under usual conditions $\Delta X_{\text{liq film}}$ is not known and k_L cannot be simply related to D .

The rate of transfer in the gas phase is given by

$$J = k_G(p_j - p) \quad (24)$$

where k_G is the film transfer coefficient in consistent units. For instance, if J is in mol/s⁻¹ cm² and p is in atmospheres, then k_G is in mol/s⁻¹ cm⁻² atm⁻¹. Note that k_G may be related to D by Eq. (25) if the following assumptions hold: (1) $\Delta X_{\text{gas film}}$ is known, and (2) partial pressure of the component transferred in the gas is very much less than the total pressure.

$$k_G = \frac{D}{RT(\Delta X_{\text{gas film}})} \quad (25)$$

where $\Delta X_{\text{gas film}}$ is the thickness of the gas film. Under conditions of steady state, the flux from the bulk of the liquid to the interface equals the flux from the interface to the bulk of the gas phase, and we can write

$$k_L(C - C_i) = k_G(P_i - P) \quad (26)$$

In the usual situation, the actual concentrations and partial pressures at the interface are not measured and the need arises to relate flux to concentrations and partial pressures in the bulk phase. If a function relating gas partial pressures in equilibrium with concentration in liquid is known, as symbolized in Eqs. (27) and (28) then overall transfer coefficients can be defined as shown in Eqs. (29) and (30)

$$C' = f(p) \quad (27)$$

$$p' = f(C) \quad (28)$$

where C' is the concentration in equilibrium with partial pressure p and p' is the partial pressure in equilibrium with concentration C .

$$J = K_L(C - C') \quad (29)$$

where K_L is the overall transfer coefficient defined in terms of concentrations in liquid.

$$J = K_G(p' - p) \quad (30)$$

where K_G is the overall transfer coefficient defined in terms of partial pressures. It follows that in steady state,

$$K_L(C - C') = K_G(p' - p) \quad (31)$$

If Henry's law can be applied to the equilibrium situation, Eq. (27) may be rewritten:

$$C = p/s' \quad (32)$$

where S' is the Henry's law constant in suitable units. Equation (31) can then be written:

$$K_L(p - p') = S'K_G(p' - p) \quad (33)$$

and it follows that

$$K_L = S'K_G \quad (34)$$

E. Transport in Porous Solids

In many of the operations performed on foods for purposes of preservation, water is removed from porous solids. Details of transport mechanisms in dehydration are discussed in another chapter and here the subject is introduced only in its most general aspects.

Transport in solids may occur by diffusion in the solid itself, in which case Fick's law can be used.

In porous solids, however, various mechanisms may be involved including

1. Diffusion in the solid itself
2. Diffusion in gas-filled pores
3. Surface diffusion along the walls of pores and capillaries
4. Capillary flow resulting from gradients in surface pressure
5. Convective flow in capillaries resulting from differences in total pressure

As discussed in a subsequent chapter, transport in porous solids can be related to various properties, such as porosity, internal surface area, and tortuosity of pores.

F. Simultaneous Heat and Mass Transfer

Often, when mass is transferred, heat also must be transferred. When a component is transformed from a liquid to a gas phase, latent heat of vaporization must be supplied. The same amount of heat must be removed when mass transfer occurs in the opposite direction. In every instance the temperature of the interface and transfer rate adjust themselves so that at steady state the rate of heat transfer and rate of mass transfer is balanced.

In some operations, heat transfer is of minor importance is controlling the overall rate of transport from one phase to another. This situation is true of operations in which latent heat affects are small. In liquid-liquid extraction and in leaching, for instance, the overall transfer rate may be considered as limited only by resistances to mass transfer. In other operations, including evaporation and crystallization, heat transfer is the controlling mechanism. Both heat and mass are transferred in large amounts, but the rates at which both occur can be determined by considering only the rate of heat exchange with an external sources.

In still other operations, particularly humidification, drying, and freeze drying, both heat transfer and mass transfer must be considered and balanced in determining overall rates. The methods used for that purpose are discussed in the chapters which follow.

SYMBOLS

| | |
|------------|--|
| a | activity |
| C, c | concentration |
| C' | equilibrium concentration |
| D | diffusion coefficient |
| De | Deborah number |
| d | diameter |
| d | hopping length (Defined in Fig. 4.9.) |
| F | number of intensive variables |
| h | height |
| J | flux |
| K | overall coefficient of mass transfer |
| k | constant |
| k_L, k_G | mass transfer coefficients in the liquid and gas phases respectively |
| l | characteristic length |
| N | number of moles in gas phase |
| p | partial pressure |
| P° | vapor pressure |
| R | gas constant |

| | |
|---------------------------------|--|
| r | radius |
| S, S' | constants |
| T | temperature |
| t | time |
| V | volume |
| v | molar volume |
| W | weight fraction |
| X | diffusion number = Dt/l^2 X_L mole fraction in liquid |
| x | distance |
| Y | unaccomplished concentration change |
| y | mole fraction in gas phase |
| ΔH_v | latent heat of vaporization |
| $\Delta X_{\text{Liquid Film}}$ | Liquid film thickness |
| $\Delta X_{\text{Gas Film}}$ | Gas film thickness |
| α | Thermal diffusivity |
| θ | Characteristic diffusion time (Fig. 4.15) |
| Γ | number of components |
| γ | activity coefficient |
| ΔH_v | latent heat of vaporization |
| ΔH_v | volume change |
| λ | mechanical relaxation time |
| ϕ | number of phases |
| η | viscosity |
| μ | chemical potential |

Subscripts

| | |
|----------|----------------|
| a | ambient |
| G | gas phase |
| i | initial |
| L | liquid phase |
| θ | all components |

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5

Water Activity and Food Preservation

I. INTRODUCTION

Food preservation has as its goal the extension of shelf life of foods to allow storage and convenient distribution. The most dangerous source of limitation of shelf life is due to the activity of microorganisms. The first aim of food preservation is therefore to eliminate the danger of spoilage due to microbes and to avoid their health-threatening activities. Several food preservation processes have a common basis in achieving this aim by limiting the availability of water to microorganisms. These processes include concentration, dehydration, and freezing. Concentration (Chapter 9) and dehydration (Chapter 10) reduce availability of water by reducing the total water content. Freezing (Chapter 8) results in crystallization of most of the water and consequently in a much reduced water content in the unfrozen portion of the food. Other preservation processes are based on adding solutes, such as sugars or salt, which reduces water availability. The present book does not include these processes since they are not considered physical methods of preservation.

In addition to controlling microbial activity water has a profound influence on the physical and chemical processes which influence shelf life. Water management is therefore a key aspect of food technology, and has been the

subject of intensive research and of numerous international conferences and workshops. A series of symposia was held under the title International Symposium on the Properties of Water (ISOPOW). The proceedings of the first of these symposia was published in 1975, the year of publication of the first edition of the present book (Duckworth, 1972). Great progress has been achieved, and while some aspects of the emerging theories remain controversial, our understanding of the relation between properties of foods and water has been greatly enhanced since the writing of the first edition (Reid, 1998). The present chapter attempts to present the reader with an up-to-date account of this understanding.

II. WATER ACTIVITY

Extensive studies on food properties and on reactions in foods have established that water content per se is not an adequate predictor of food stability. Early work in the field focused on describing the water effects in terms of the existence of “bound” and “free” water. The current consensus view is that broad definition of such “states” of water is not possible without specification of properties by which distinction between the two states is established. The present author prefers to discuss the role of water in determining some of the properties critical to food preservation without invoking the concepts of bound and free water.

A very successful concept, which in spite of some limitation has dominated the technology of shelf life extension for the past 40 years, is that of *water activity*. After an initial period of relative obscurity and a period of a somewhat euphoric expectation that all stability problems could be related to water activity, we have achieved a fairly comprehensive understanding. Water activity provides an excellent, possibly unique stability factor in situations in which equilibrium considerations dominate the processes. This is particularly true in the case of microbial growth because the creation of an osmotic pressure difference between the optimally hydrated microbial cell and the surrounding medium (food) leads to cessation of microbial growth through several mechanisms, which are now fairly well understood. Water activity is also a very useful factor in assessing mobility controlled processes in foods because it controls the water content in the various food components, and the water content (because of plasticizing action) has a dominating effect on mobility of hydrophilic food components (Fennema, 1996).

Water activity (a) is defined by Eq. (1)

$$a = p/p^{\theta} \quad (1)$$

where p = partial pressure of water in food at a given temperature and p^{θ} = vapor pressure of food at the same temperature.

The condition of equilibrium for any component in a system is the constancy of its *chemical potential* (μ). At constant temperature μ is constant

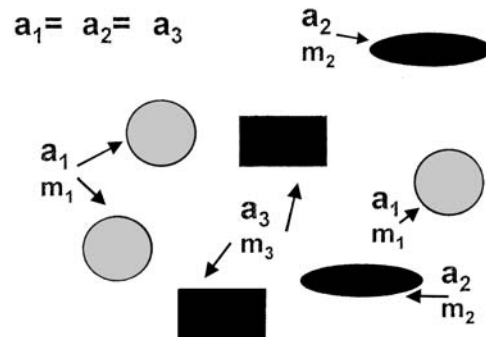


FIGURE 5.1 Water activity and equilibrium. Equilibrium with respect to water is established in systems with several components when their water activities are equal.

when activity is constant, and for water the relevant activity is the *water activity*. The situation is represented schematically in Fig. 5.1. Water activity is an equilibrium parameter; however, the concept is quite useful even when the equilibrium is not achieved. In fact it is particularly useful in calculating quantities of importance in processes in which we disturb or approach an equilibrium. For instance, in dehydration or in extraction we are often concerned not only with local concentration gradients but also with local activity gradients since they control the fluxes. Furthermore activities determine the local water concentrations which in turn determine local mobility, local rates of reaction, and local transition temperatures (e.g., freezing point and glass transition temperature).

The utility and relevance of the water activity concept resulted in development of an enormously useful knowledge base. Components of that knowledge base include the following:

1. Extensive compilations of water activities of food products as a function of water content and temperatures (Iglesias and Chirife, 1982)
2. Dozens of equations allowing the prediction of water activity as a function of water content and temperature, and several widely used equations estimating water activity as a function of composition (Van den Berg and Bruin, 1981)
3. Methodology for measuring water activity leading to successful laboratory as well as industrial on-line instrumentation (Wiederhold, 1995)
4. Extensive compilations of critical activities for growth of different microorganisms, and a scientific basis for understanding the reasons for the existence of such critical water activities (Chirife and Buera, 1996)

5. An extensive literature relating physicochemical properties of food components to water activities (Leung, 1986; Simatos and Multon, 1985)

The enthusiastic expectation of early researches in this field was that a range of water activities guaranteeing maximum stability could be established for most, if not all, foods. However the problem of food stability is complex. As the mechanisms controlling deteriorative processes in foods became better understood, it became clear that a single factor optimization could not lead to maximum stability but that an understanding of controlling mechanisms allows appropriate approaches to optimization based on consideration of multiple factors.

A particularly active phase involved development of models. Various stability maps based on water activity were developed, and the water relations themselves as well as the food stability as a function of water activity were among the early application of computer-aided prediction of food behavior. The models were found to have excellent applicability in real-life applications. Control of many processes in the drying and other preservation industries is often based on the water activity concept, and instrumentation for its on-line measurement is an important part of sensor development in food technology.

III. SORPTION OF WATER BY FOODS

The equilibrium relation between a component present in different phases and in particular between a solid and a gaseous phase can be represented by several types of curves. These include isotherms, isobars, and isosteres (curves representing equilibria at constant temperature, constant pressure, and constant water contents, respectively). These curves represent relations among three key variables; partial pressure of water in gas phase, water content, and temperature. Isotherms of food materials are usually obtained by one of the two basic methods shown in Fig. 5.2.

In the first method (Fig. 5.2a) a sample of known constant water content is allowed to come into equilibrium with a headspace and the partial pressure of water, or relative humidity is measured. The headspace must be small to assure that the water transferred from sample to headspace is negligible. The equilibrium relative humidity (ERH) in the headspace is numerically equal to water activity multiplied by 100. A number of instruments with good accuracy and precision are available for measuring ERH. A detailed discussion of these is beyond the scope of this book for more information the reader is referred to the monograph by Bell and Labuza (2000). It is useful, however, to be aware of the paradigm by which they operate: The partial pressure of water in the headspace comes to equilibrium with the food sample, a sensor component of the relative

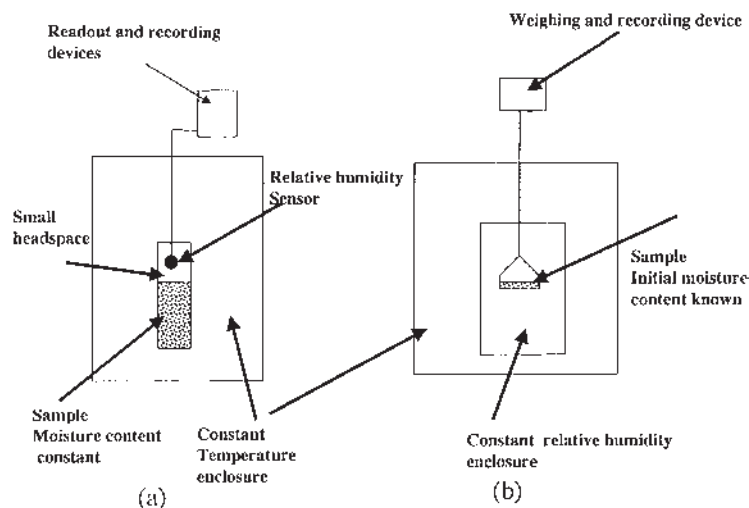


FIGURE 5.2 The basic paradigms for determining water sorption isotherms.

humidity instrument changes its water content by equilibrating with the headspace and a water-sensitive property of the sensor is used to measure the relative humidity. Thus an accurate method requires that the equilibria (food–headspace and headspace–sensor) are achieved. It is also critical that the sensor, headspace, and food sample remain at constant temperature during the measurement.

A second basic method (Fig. 5.2b) for preparing isotherms is the exposure of a small sample of food to various constant relative humidity atmospheres. After equilibrium is reached, the water content of the sample is determined gravimetrically or by other methods. Constant relative humidity is usually produced by using saturated salt solutions. Typical food isotherms are S-shaped as shown in Fig. 5.3, and they may be described by a number of mathematical relations. Two relations have been particularly significant in the study of sorption isotherms, namely the Brunauer–Emmet–Teller (BET) equation and the GAB equation of Guggenheim and co-workers (Van den Berg and Bruin, 1981). They are shown in Fig. 5.4.

The BET equation has two constants C and m_1 ; the GAB equation has the same general form but has an additional constant C' . The constant m_1 is called the *monolayer value* because under the assumptions of the BET model it corresponds to water content due to water molecules covering the surface as a monolayer. It is now widely agreed that this interpretation is not valid for water sorption in foods, but there is some evidence that m_1 may be related to the primary adsorption on

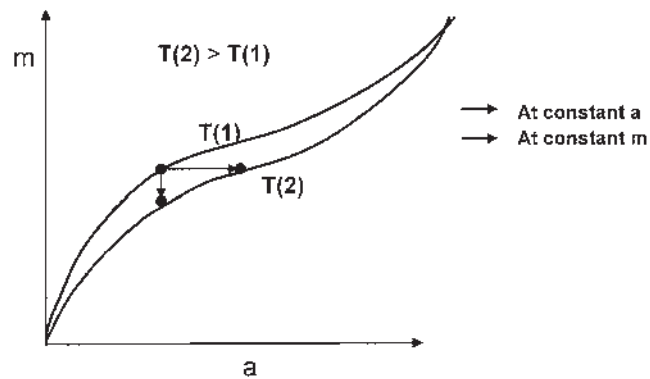


FIGURE 5.3 Effect of temperature change on isotherms. m , moisture content; a , water activity; T , temperature.

specific polar sites in the food. Therefore, in this book we will continue using this terminology for this constant. The BET equation is valid in most instances in the range of activities between 0 and 0.5. A linear transformation of this equation, in this activity range, allows the calculation of the two constants from the intercept and slope of a straight line fitted from experimental data (Fig. 5.5).

Isotherms of foods and food components are compiled in several modern books, and several of these list values of BET and GAB constants allowing the reader to calculate isotherms of these materials.

An important theoretical and practical consideration is the effect of temperature on sorption. As shown previously in Fig. 5.3, an increase in temperature (T) at constant water activity (a) results in decrease of water content (m). The relations between T , m , and a are expressed by the Clausius–Clapeyron

BET equation

$$m/m_1 = C a \{ (1-a) [1 + C a - a] \}^{-1}$$

GAB equation

$$m/m_1 = K' C a \{ (1-C a) [1 + K' C a - C a] \}^{-1}$$

FIGURE 5.4 The BET and the GAB equations for describing sorption isotherms. m = water content, a = water activity, m_1 = parameter (monolayer value), K' , C = parameters.

$$a / [(1-a)m] = 1/(m_1 C) + a(C-1)/(C m_1)$$

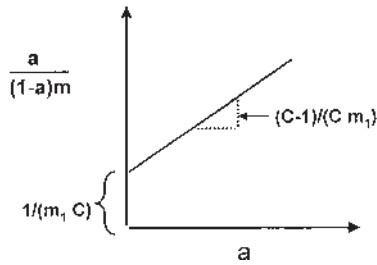


FIGURE 5.5 Plot of the BET isotherm. a = water activity, m = water content, m_1 = "monolayer" value, c = parameter.

equation applied to sorption [Eq. (2)].

$$a_m = a_o \exp - \frac{\Delta H_A}{RT} \tag{2}$$

where a_m is a at a given water content m , a_o is a constant, and ΔH_A is isosteric heat of sorption.

Plots of $\ln(a_m/a_o)$ against the reciprocal of the absolute temperature T , at constant values of m , yield straight lines with the slope of $-\Delta H_A/R$ and allow the calculation of the isosteric heat of sorption (Fig. 5.6).

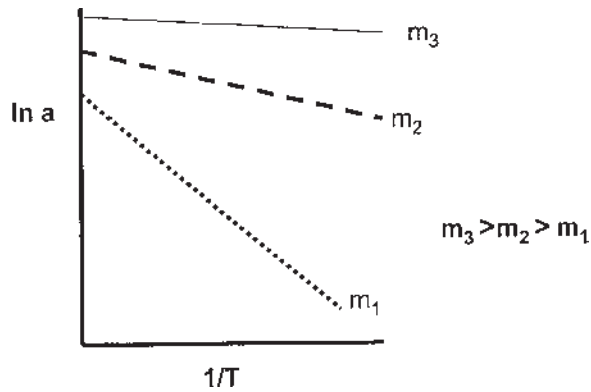


FIGURE 5.6 Temperature dependence of water activity. The Clausius–Clapeyron equation applied to water sorption.

$$a_m = a_o \exp - \Delta H_A / RT$$

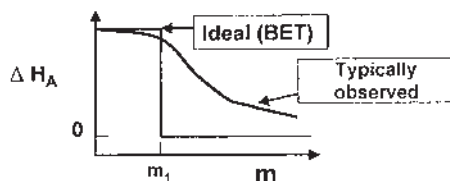


FIGURE 5.7 The dependence of the isosteric heat of sorption on moisture content. m_1 = "monolayer value"; $a_m = a$ at a given water content m ; $a_o = a$ constant; ΔH_A = isosteric heat of sorption.

ΔH_A may be considered as the additional energy (above the latent heat of vaporization of pure water) required of transfer 1 mol of water from the food at a given moisture content to the vapor state as given by

$$\Delta H_T = \Delta H_V + \Delta H_A \quad (3)$$

where ΔH_T is total heat of vaporization of water in food at a give water content and ΔH_V is latent heat of vaporization of water.

The BET model assumes that ΔH_A is constant up to the monolayer value, and above it drops to zero. The model assumes that water sorbed beyond the monolayer the same latent heat as pure water. Actual experiments on food systems show that this assumption is not realistic. ΔH_A below m_1 is in fact larger than at higher values of m , but the transition is gradual rather than abrupt, as assumed in this model (Fig. 5.7).

IV. INDICATORS OF THE STATE OF WATER IN FOODS

We have stated previously that a categorical division of water in foods into bound and free states is not feasible. Nevertheless there exist indicators, which reflect the availability of water for specific processes important in food technology. Two of these have been described above: ΔH_A is high at low water contents and indicates the higher energy requirement for water removal at these moisture contents. The monolayer value calculated using the BET equation seems to be related to the number and kind of polar groups binding water. The water molecules at the binding sites freely exchange with other water molecules, as indicated by the sticking time, or average time of residence at the binding site (Table 5.1). Since the polar sites bind water by physical adsorption these times are of the order of 0.1 ms (Adamson, 1968).

TABLE 5.1 Sticking Time (τ) and Heat of Sorption (ΔH_A)

| $\tau = 10^{-13} \exp(\Delta H_A/RT)$ | Approximate magnitudes | | |
|---------------------------------------|------------------------|----------------------------|--------------------------|
| | τ (s) | ΔH_A (kcal/mol) | ΔH_A (kJ/mol) |
| No adsorption | 10^{-13} | 0.1 | 0.42 |
| Physical adsorption | 10^{-7} | 7.5 | 31 |
| Chemisorption | 10^{17} | 40 | 167 |

Two additional indicators used in the literature (Duckworth, 1972) may be mentioned here:

1. "Non-freezing" water (NFW)
2. "Non-solvent" water (NSW)

The measurements of these indicators is simple in principle. A sample is dehydrated and is then hydrated in steps to higher water contents. In the case of NFW at each step a measurement is made to indicate whether ice is present. This measurement is usually carried out using differential scanning calorimetry (DSC).

In the case of NSW an indicator solute is added to the dehydrated sample, mixed well, and after stepwise hydration, tests are carried out to determine if some of the solute is dissolved in the water. While simple in principle, both measurements are complicated in practice. NFW measurement is complicated by kinetic considerations since the occurrence of freezing is often limited by the very high viscosity of any aqueous solution existing at low water contents. NSW presents experimental difficulties in determining the existence of an indicator solution.

Nevertheless a comparison of values of these indicators available in the literature is instructive. Table 5.2 shows the values of four indicators for some food polymers. The value of NSW is shown for two indicator solutes. A comparison of the values shown in Table 5.2 shows certain trends, which are significant.

The crystalline polysaccharide cellulose has lower values of monolayer water, as well as of NFW and of NFS than the amorphous starch, which has the same chemical composition. This is due to the unavailability of most of the hydroxy groups in cellulose. The ionic polysaccharide agar has still higher values of the water contents at the indicator values, perhaps due to greater affinity of charged groups for water. In general also the ionic polymers show higher maximal values of ΔH_A .

TABLE 5.2 Indicators of State of Water in Food

| Indicator | Cellulose | | Starch | | Agar | |
|--------------------|-----------|----------|----------|----------|----------|----------|
| | <i>m</i> | <i>a</i> | <i>m</i> | <i>a</i> | <i>m</i> | <i>a</i> |
| m_1 | 0.03 | 0.01 | 0.11 | 0.3 | 0.13 | 0.31 |
| ΔH_A (max) | | | ~14 | | | |
| NFW | 0.13 | 0.85 | 0.30 | 0.85 | 0.41 | 0.85 |
| NSW (sucrose) | 0.11 | 0.82 | 0.24 | 0.82 | 0.34 | 0.82 |
| NSW (urea) | 0.04 | 0.45 | 0.14 | 0.45 | 0.19 | 0.45 |

m = g water/g solids.

ΔH_A = kJ/mol.

V. CAUSES OF WATER VAPOR PRESSURE DEPRESSION IN FOODS

The water activity in foods is less than 1.0. The causes of this depression of vapor pressure of water vary with the water content. At low water contents the activity is almost certainly depressed due to binding of water at specific polar sites. Water at these values of m shows a decreased molecular mobility, and the ΔH_A magnitudes are significant. These low water contents are generally in the magnitude estimated by the BET monolayer, although as already indicated, the BET assumptions are not fully valid. Since the polar groups in proteins and their distribution throughout the surface of soluble proteins are well known, it has been possible to analyze the hydration of proteins in terms of the polar group contributions. Protein chemists starting with Linus Pauling (Pauling, 1945) showed that in many proteins a count of accessible polar groups (and some simple assumptions concerning the number of water molecules bound at each site) yields sorbed water values comparable to those given by the BET monolayer calculation.

One of the proteins studied most extensively is lysozyme. Molecular modeling has produced maps of distribution of water over the protein surface, which show considerable variation between different portions of the protein globule surface, corresponding to the location of polar group. A proposed scheme of hydration of lysozyme as the water content increases from 0 to 0.38 g of water per g of protein is shown in Table 5.3. At a lysozyme hydration level of 0.38 g/g the water activity is well over 0.8.

At high water activities the most appropriate model of water vapor depression is the Raoult's law shown in Fig. 5.8. This relation works best in dilute solutions and for small molecules, but in other cases it often requires the use of a correction factor (k , the so-called activity coefficient) resulting in a corrected

TABLE 5.3 Effect of Progressive Protein Hydration on Water Mobility

| m | Water location | Water mobility |
|-----------|------------------------------|---|
| 0–0.05 | Charged groups | Very low (H exchange 1000 lower than in solution) |
| 0.05–0.08 | Polar groups | Low |
| 0.08–0.15 | Clusters around polar groups | Mobility below solution level |
| 0.2–0.25 | Water “patches” | Enzyme activity detectable indicating enzyme and substrate mobile |
| 0.3–0.38 | Loose “monolayer” | Solution level mobility reached |

m = water content (g/g).

equation:

$$a = Xk \quad (4)$$

It is important to note that the mole fraction of water must be calculated by counting solute units actually in solution, in the case of dissociating ionic compounds the calculation must consider each ion as a unit in solution. Thus a 1 molal solution of NaCl would result in a 2 molal solution of ions.

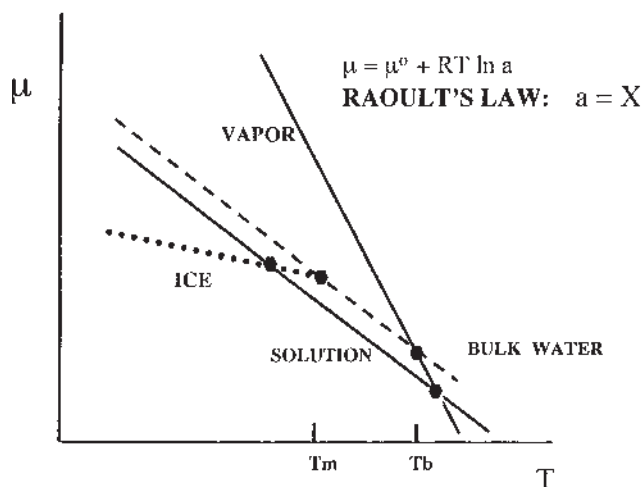


FIGURE 5.8 Depression of water activity in ideal solutions: Raoult's law. μ = chemical potential of water (KJ/mole); X = mole fraction of water; T_m = melting point; T_B = boiling point.

In the case of a 1 molal solution of a hypothetical compound ZY with a dissociation level of 50%, the kinetic units in solution will be 0.5 mol of ZY, 0.5 mol of Z, and 0.5 mol of Y, or an effective molal concentration of 1.5.

Deviations from ideal solution behavior may result from several causes:

1. Not all the water in food may be capable of acting as solvent.
2. Not all of the solute is actually dissolved. (Some may, for instance, be bound to other food components, as is often the case with salts bound to proteins.)
3. Interactions between solutes may cause deviations.

It is important to note here that small polar molecules are normally fully surrounded by water molecules, and in this case solute–solute interactions occur only at very high concentration, in fact often close to the solubility limit. Figure 5.9 shows the hydrogen bonding between molecules of *N*-methyl acetamide in various solvents. This very polar compound forms hydrogen-bonded dimers readily in organic solvents, but such dimers occur in water only at extreme concentrations.

Of more interest in food technology is the formation of intramolecular and intermolecular bonds in sucrose solutions (Starzak et al., 2000). At concentrations up to 1/3 of saturation level sucrose is hydrated with 5–6 water molecules per sucrose molecule (hydration number of 5–6). There are no intramolecular or intermolecular sucrose–sucrose bonds. As the concentration increases toward 2/3 of saturation level, some intramolecular

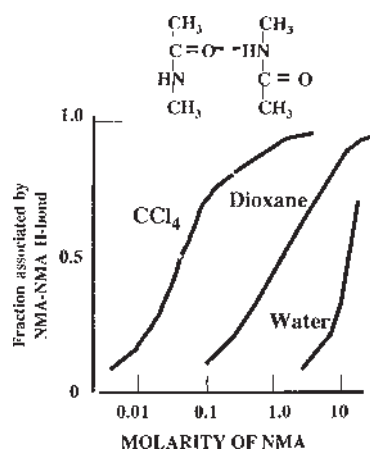


FIGURE 5.9 Formation of solute–solute hydrogen bonds by polar solutes in nonpolar solvents and in water. (From Klotz and Franzen, 1962.)

TABLE 5.4 Molality and Water Activity (a) of Selected Solutes

| Solute | $a = 0.9$ | $a = 0.8$ |
|--------------|-----------|-----------|
| Ideal solute | 6.17 | 13.9 |
| NaCl | 2.83 | 5.15 |
| Sucrose | 4.11 | — |
| Glycerol | 5.6 | 11.5 |

H bonds are formed, the hydration number decreases, but there are still no intermolecular sucrose–sucrose bonds. Above this concentration as the saturation level is approached, an average of two intramolecular H bonds occur in sucrose, and intermolecular sucrose–sucrose bonds begin to occur in competition with sucrose–water bonds. In supersaturated solutions sucrose clusters appear, and it has been suggested that formation of sucrose hexamers precedes nucleation and crystallization of this sugar.

The behavior of *polymer* solutions is often quite complex, and these solutions show often deviations from Raoult's law. Table 5.4 compares the molalities of several solutes at given water activities with those of an ideal, nondissociating solute.

The solute depression of water activity is limited by solubility. Solutes with high solubility can depress a to a much lower level than less soluble solutes, as shown in Table 5.5.

It may be useful at this point to stress that the vapor-pressure-depressing solute effect is not due to reduction of area available for evaporation, but is due to depression of the chemical potential of water. Insoluble particles on the surfaces of water or of aqueous solution can reduce the rate of attainment of equilibrium between the water and a headspace but do not change the equilibrium value of the water activity. These effects are shown schematically in Fig. 5.10.

TABLE 5.5 Minimum Water Activities of Some Solutions at Room Temperature

| Solute | Solubility (% w/w) | Minimum activity |
|------------------------------------|--------------------|------------------|
| Sucrose | 67 | 0.86 |
| Glucose | 47 | 0.91 |
| Invert sugar | 63 | 0.82 |
| Sucrose + Invert sugar (37.6:62.4) | 75 | 0.71 |
| NaCl | 27 | 0.74 |

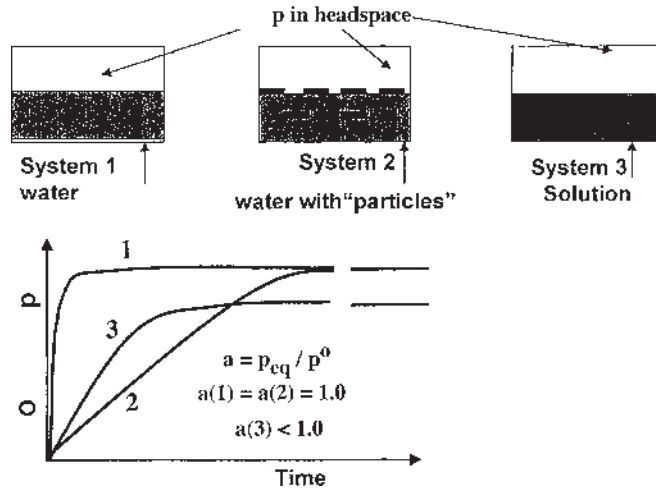


FIGURE 5.10 Vapor pressure over solutions contrasted with vapor pressure over water with insoluble particle in the surface. p = partial pressure; p° = vapor; $p_{eq} = p$ at equilibrium; a = water activity.

VI. SORPTION HYSTERESIS

In the preceding discussion we considered sorption isotherms in which a given material at a given water activity had at equilibrium a defined invariant water content. The history of the sample was assumed to have no effect on the isotherm.

In many cases, however, the very process of sorbing or desorbing water may change the sorbent (e.g., food components such as proteins) and affect subsequent sorption behavior. Well-known examples of such cases in food technology include starch gelatinization and retrogradation and crystallization of sugars.

An often observed behavior pattern is represented schematically in Fig. 5.11. A dry sample is exposed to increasing water activities, and the resulting adsorption of water is shown in the curve labeled "1st adsorption." The water in the sample is then desorbed by exposure to lower water activities. The desorption curve is labeled "desorption." It is evident that the adsorption and desorption paths diverge, giving a so-called hysteresis loop. In many cases a subsequent re-adsorption of water may then follow a path located within the hysteresis loop, as shown by curve labeled "2nd adsorption." The following are the major causes of hysteresis described in the sorption literature:

1. Changes in folding and orientation of polymers including proteins
2. Phase changes (in particular crystallization)

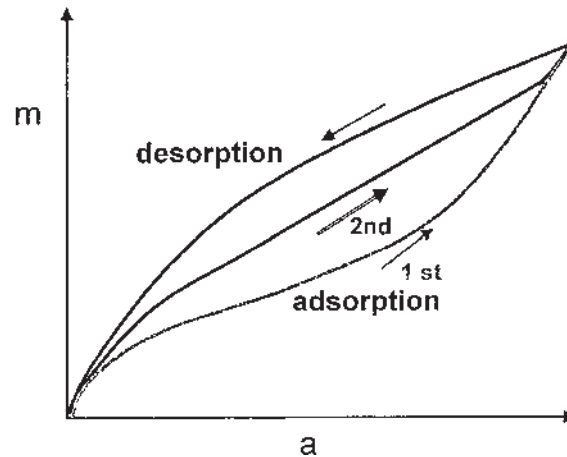


FIGURE 5.11 Typical hysteresis behavior in food sorption isotherms.

3. Effects of capillarity in microporous materials

The first two situations are common in food technology, the last case is more often encountered in inorganic materials but may contribute to hysteresis in food powders or microporous freeze dried materials.

Figure 5.12a shows a schematic representation of hysteresis due to unfolding of polymer chains, which may be required to accommodate sorption of water. The additional energy required to separate the chains and introduce the water between them results in a higher water activity for sorbing water than the activity at which water is desorbed.

The case shown here assumes that upon desorption the chains refold. If that occurs, the hysteresis loop persists through repeated sorptions and desorptions.

Figure 5.12b represents a case in which polymer chains once unfolded remain in this state through subsequent adsorptions and desorptions. The hysteresis loop is apparent only during the first adsorption–desorption cycle. The subsequent cycles follow the curve of the first desorption.

This ideal case does in fact approximate the behavior of some polymers, which once swollen, remain in this state, if not permanently, then at least for significant periods of time. However a more common situation is one in which the hysteresis loop persists, but its magnitude decreases with each sorption cycle as shown in Fig. 5.11. The ideal cases shown above give an excellent qualitative insight into the causes and manifestation of sorption hysteresis in polymers.

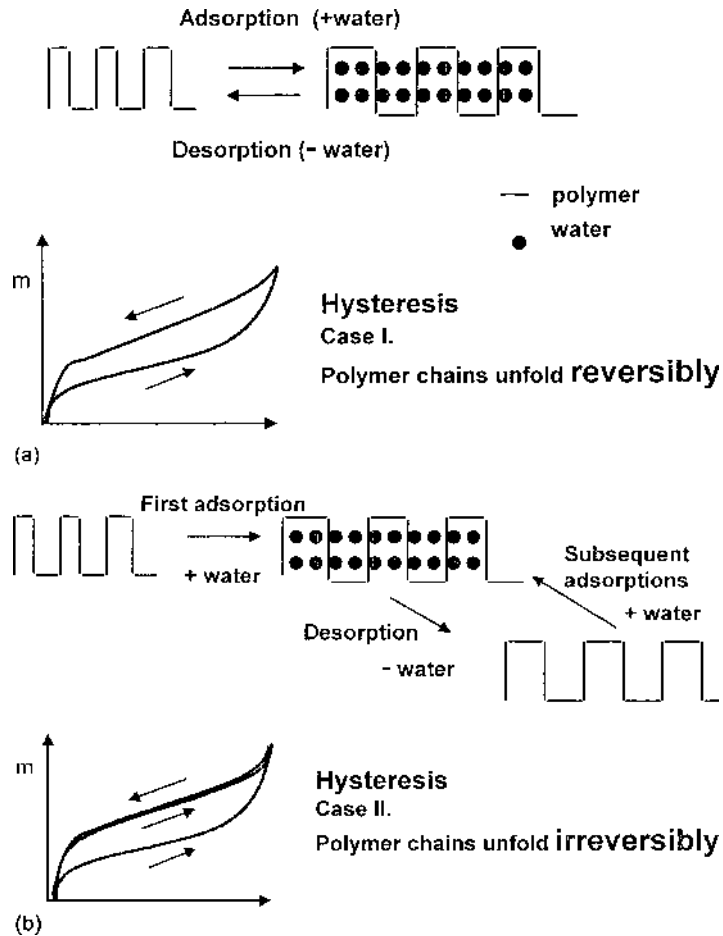


FIGURE 5.12 Causes of hysteresis: (a) irreversible unfolding of polymers, and (b) reversible folding of polymers.

The second type of effects causing sorption hysteresis occurs in materials containing crystallizable component. In foods such effects are primarily due to sugars. Figure 5.13 illustrates typical differences between sorption of water by crystalline and amorphous sugars. In crystalline sugars the sorption occurs only on crystal surfaces, and the capacity for water sorption is very limited, even when the crystals are small and have a high surface to volume ratio. The water content

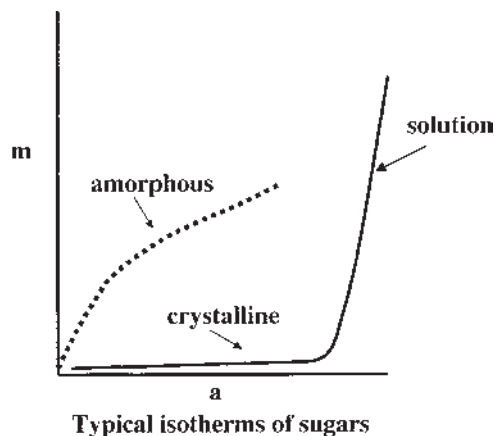


FIGURE 5.13 Causes of hysteresis: differences between sorption of crystalline and amorphous materials.

increases sharply only when the sugar begins to dissolve at a specific water activity, characteristic for each sugar. In amorphous sugars the polar hydroxy groups are accessible and substantial capacity for sorbing water (*hygrocapacity*) is evident. Therefore crystallization results in decreases in water sorption and is a common cause of hysteresis in sugar-containing foods.

Powders and porous materials with a system of small capillaries with different radii may show hysteresis due to capillarity. The Lord Kelvin equation applied to capillaries predicts a depression of vapor pressure of a liquid in capillary, the magnitude of which depends on capillary radius, and on the surface tension of the liquid. If a zero contact angle between the liquid walls and the liquid is assumed, then the equation shown in Fig. 5.14 applies. The figure shows schematically the depression of water activity and the water content for a capillary with a very narrow neck, entering a voluminous reservoir, a so-called ink bottle capillary. It is evident that the water activity in the reservoir is higher than in the neck. On adsorption a small amount of water would condense in the neck at activity a_1 corresponding to that expected for the neck radius r_1 . The reservoir however does not fill until the much higher activity corresponding to its radius is reached. On desorption the emptying of reservoir, however, must be delayed until the “threshold activity” of the neck, namely a_2 is reached. For a single capillary the hysteresis would be as indicated in Fig. 5.13. In a system of capillaries of varying neck and reservoir sizes a hysteresis loop similar to that shown in Fig. 5.11 could be anticipated.

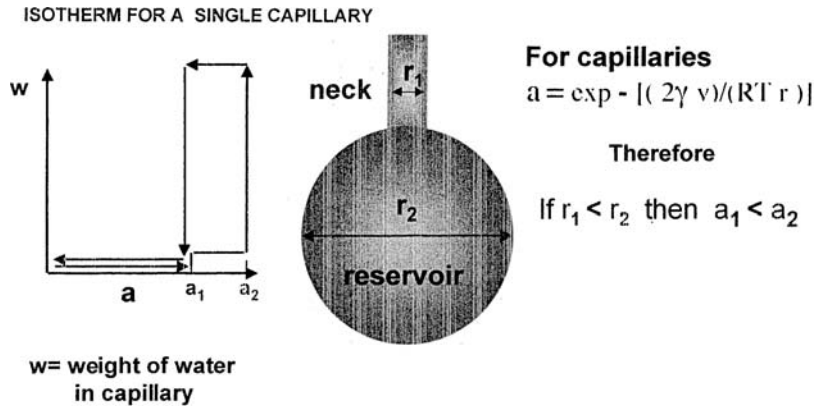


FIGURE 5.14 Causes of hysteresis: "ink bottle capillaries." Adsorption into the "reservoir" of the capillary starts at a_2 , but the desorption does not occur until the water activity of the "neck" a_1 is reached.

VII. WATER ACTIVITY OF MIXTURES

A task frequently of importance in practical food technology is the calculation of equilibrium water activity of a mixture of components with known initial moisture contents and the calculation of the water content of each component when that water activity is reached.

When all of the components are solutes, and the water content is relatively high, Raoult's law may be applied as a first estimate. In this case the mole fraction of water is calculated by subtracting the sum of the mole fractions of all the solutes from 1.0 and the resulting fraction is an approximate estimate of the water activity.

For example, consider 3 g of NaCl and 10 g of sucrose dissolved in 100 g of water. Given the molecular weights (water = 18, NaCl = 58.4, and sucrose = 342.3).

The molar amounts of each components are:

$$\text{Water} = 5.55 \quad (\text{Na}^+ + \text{Cl}^-) = 2 \times 0.051 = 0.102 \quad \text{sucrose} = 0.029 \quad (5)$$

The mole fraction of water is 0.976, which is also the assumed value of the water activity. In many situations, however, the mixture contains both soluble and insoluble components, for which Raoult's law does not apply. Calculations of resultant water activity may be performed if the isotherms of individual components are known or if they can be approximated.

Ross Equation

$$a = (a_1)(a_2) \dots (a_n)$$

a = water activity of mixture

a_1, \dots, a_n water activities of components if each is associated with the total water in the mixture

Modified GAB equation

$$m/m_1 = K'C a / \{(1-C a)[1+(K'-1)C a]\}$$

m = water content of mixture

a = water activity of mixture

m_1 = parameter (monolayer value)

K', C = parameters

Let ϕ represent any of the parameters (m_m, K', C)

Approximate ϕ of mixture of components 1, ..., n

$$\phi = \phi_1 w_1 + \phi_2 w_2 + \dots + \phi_n w_n$$

w_n = weight fraction based on solid

FIGURE 5.15 Equations for calculating water activity of mixtures.

Ross Equation

$$a = (a_1)(a_2) \dots (a_n)$$

a = water activity of mixture

a_1, \dots, a_n water activities of components if each is associated with all the water in the mixture

Example:

Composition (w/w): water 15 %, starch 70%, glucose 15 %

Obtain a_s for a mixture of 70 parts starch, 15 parts water:

water content ~ 21% dry basis

$$a_s \sim 0.90 \text{ (Iglesias and Chirife, 1982)}$$

then get a_G for a solution of 15 parts glucose in

15 parts water (i.e glucose concentration of 50%,

water content of 100% dry basis

$$a_G \sim 0.91 \text{ (Bell and Labuza, 2000)}$$

$$a = (a_s)(a_G) \sim (0.90)(0.91) = \underline{\underline{0.82}}$$

FIGURE 5.16 Example of calculation of water activity of a mixture.

Figure 5.15 shows two equations useful for performing these calculations, namely, the Ross equation (Ross, 1975) and a modification of the GAB equation.

Figure 5.16 shows an example of applying the Ross equation to a mixture of starch, water, and glucose using isotherms of the two solids published in the literature. In the case of insoluble components once the water activity at equilibrium is established, their individual water contents can be obtained from the individual isotherms.

The equilibrium water activity of the mixture is of paramount importance in assessing the susceptibility of the mixture to microbial growth; on the other hand, the water content of the individual components in a mixture is equally important since it controls the physical properties of these components and in particular their glass transition temperature. These considerations will be discussed next.

VIII. WATER AND GLASS TRANSITIONS IN FOOD MATERIALS

The physical state and physicochemical properties of food components affect food behavior in processing and storage. Many of the food components can exist in the amorphous state, especially at low temperatures, and/or low moisture contents. Amorphous materials may exist in a solid-like, *glassy* state, or in a viscous or *rubbery* state (Slade and Levine, 1995).

The transitions in materials, which can exist as crystalline solids, as glasses and “rubbers,” as molten liquids, and in solution, are shown schematically in Fig. 5.17. The glassy state is not an equilibrium state but is determined by kinetic considerations, such as rates of cooling or dehydration. However once established, the glasses are stable until the temperature exceeds the glass transition temperature T_g . It should be noted that T_g is not a first order transition that is a discontinuity in the enthalpy (H) or molar volume (v) of a substance but a second order transition in which there is a discontinuity in the rate of change of H and v with temperature. These relations are illustrated in Fig. 5.18. The discontinuity in the dH/dT which is of course the specific heat c_p is used experimentally to determine the glass transition temperature T_g by DSC.

T_g is a very strong function of the water content. A plot of T_g as a function of fractional water content (w) or of concentration (which, of course, is equal to $1.0 - w$) provides the basis for the so-called state diagram showing the transitions in specific materials. A typical state diagram is shown in Fig. 5.19 (Roos and Karel, 1991). It is evident that the T_g decreases very rapidly with decreasing solid concentration (or increasing water content). The diagram shows in addition to the T_g the T_m line, that is, the equilibrium melting point of water as

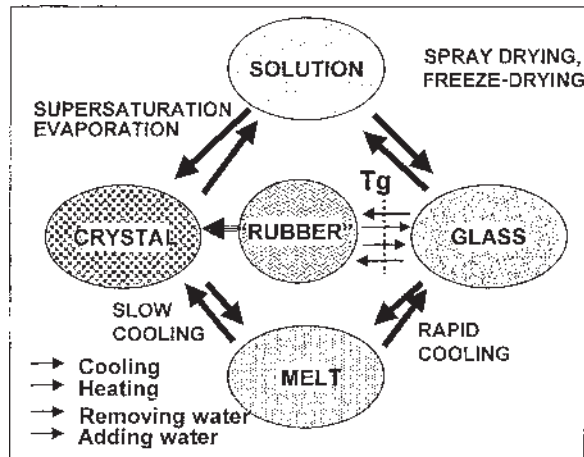


FIGURE 5.17 Phase transitions occurring in food components.

a function of concentration (liquidus line). The point (T'_g, C'_g) is also shown and represents that maximum concentration achievable by freezing and the corresponding glass transition temperature. The theoretical position of T'_g is based on the assumption that freezing ceases due to kinetic effect at T_g that is,

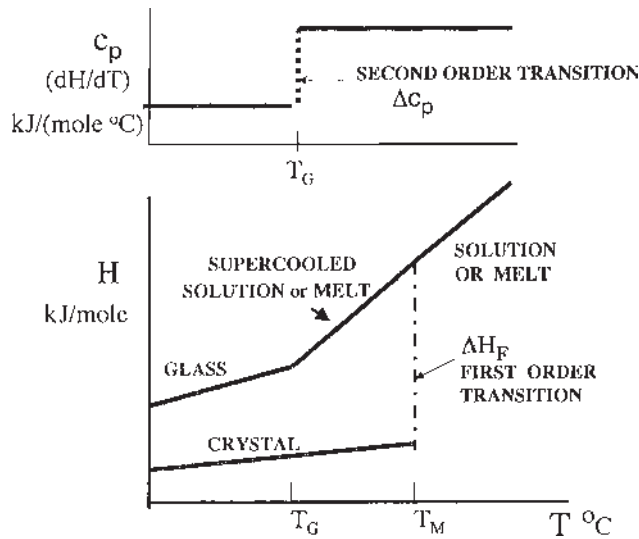


FIGURE 5.18 Glass transitions.

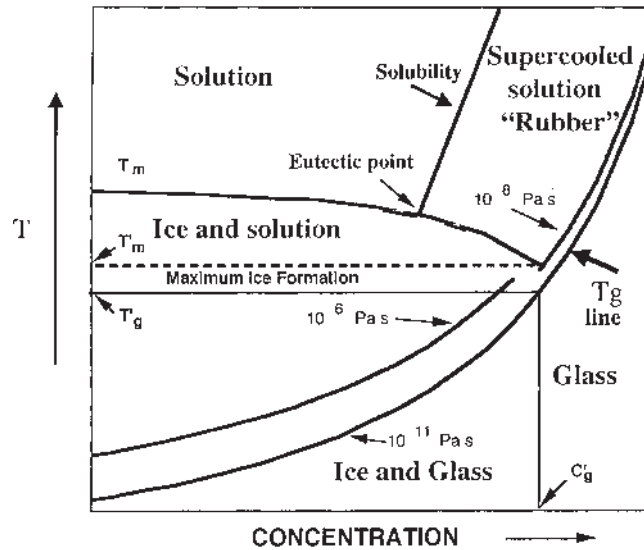


FIGURE 5.19 State diagram for an amorphous food component.

at T_g there is a depression of the mobility below the level necessary for nucleation and crystallization. In real situations T'_g and C'_g are very difficult to reach experimentally.

Also indicated in Fig. 5.19 are the solubility line and the eutectic point, at which, theoretically, the concentration of the still unfrozen solution remains constant. However this is almost never the case in freezing of sugars because the solutions become supersaturated without immediate crystallization of the solute. Above the glass transition temperature the viscosity of the supercooled solution, or *rubber* drops very rapidly. The state diagram also presents isoviscosity lines of 10^6 and 10^8 Pa s, based on an often assumed value of 10^{11} to 10^{12} Pa s at T_g , and calculated using the Williams–Landel–Ferry (WLF) equation.

$$\ln \eta = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \quad (6)$$

where η is viscosity, T is absolute temperature, T_g is glass transition temperature, and C_1 and C_2 are constants.

Figure 5.20 shows the viscosity of glucose above T_g calculated using the WLF equation and the Gordon-Taylor equation, which can be used to estimate the T_g of mixtures, in this case mixture of water and glucose. The calculation was

Calculation of T_g using the Gordon and Taylor Equation

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2}$$

Calculating the viscosities using the Williams-Landel-Ferry (WLF) Equation

$$\ln\left(\frac{\eta}{\eta_g}\right) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)}$$

$$\begin{aligned} C_1 &= 17.44 & T_g \text{ water} &= -135^\circ\text{C} \\ C_2 &= 51.6 & T_g \text{ glucose} &= 31^\circ\text{C} \\ \eta_g &= 10^{12} \text{ Pas} \end{aligned}$$

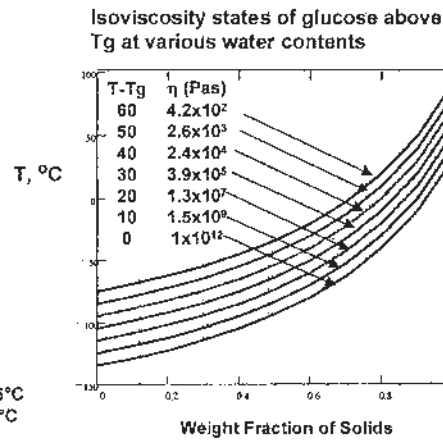


FIGURE 5.20 Viscosity of amorphous glucose above the glass transition temperature (T_g).

done using the so-called universal values of the two WLF constants ($C_1 = 17.44$ and $C_2 = 51.6$), which apply to many materials and are sometimes used as an approximation when the actual constants are not determined. A reasonable prediction of viscosity using the WLF equation, however, requires the experimental determination of the two constants. It should be noted that the equation assumes that the viscosity is determined solely by the quantity $T - T_g$ and is dependent on concentration and temperature only in as far as they affect $T - T_g$. The WLF equation predicts an extremely rapid drop in the temperature range just above T_g . For $T - T_g = 10^\circ\text{C}$ the viscosity is predicted to decrease by a factor of approximately 700 (Roos, 1995).

Because of the strong plasticizing effect of water on the hydrophilic food components glass transition of food components is strongly dependent on water content. The effect of water content on glass transition temperature of several carbohydrates calculated using the Gordon-Taylor equation is shown in Fig. 5.21. The Gordon-Taylor equation constants (k) for each water-carbohydrate system which were obtained experimentally are also shown in Fig. 5.21. The position of the point of maximum freeze concentration (C_g^f, T_g^f) is also indicated in this figure. Within the range of carbohydrates shown it should be evident that T_g increases with molecular weight. Within a homologous series the glass transition temperature is often inversely proportional to molecular weight as illustrated in Fig. 5.22.

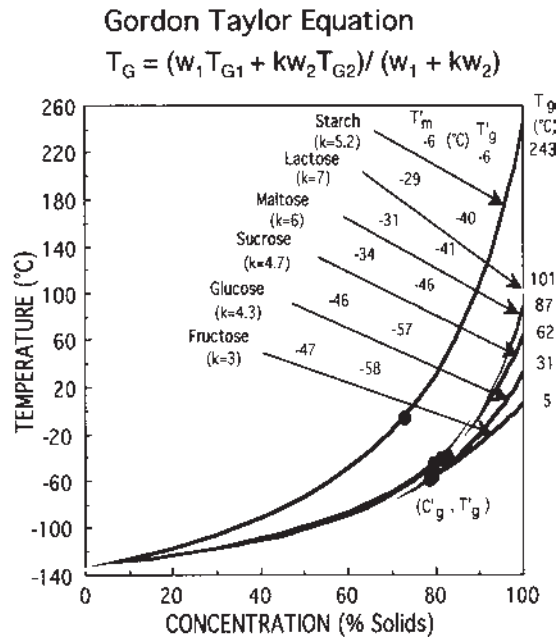


FIGURE 5.21 Glass transition temperature of carbohydrate solutions.

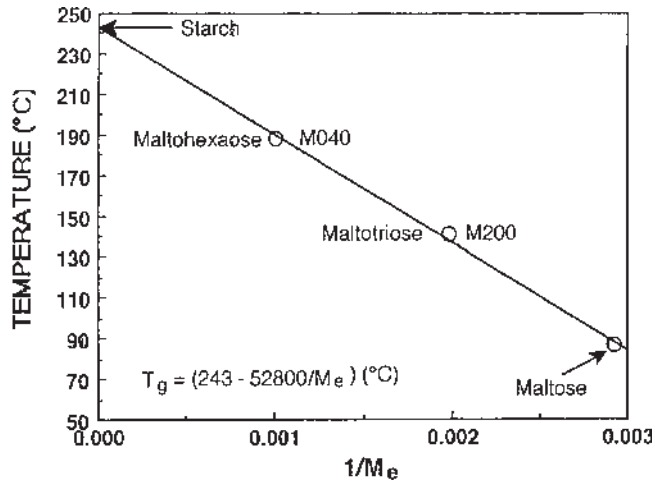


FIGURE 5.22 Effect of molecular weight on T_g in a homologous series of carbohydrates.

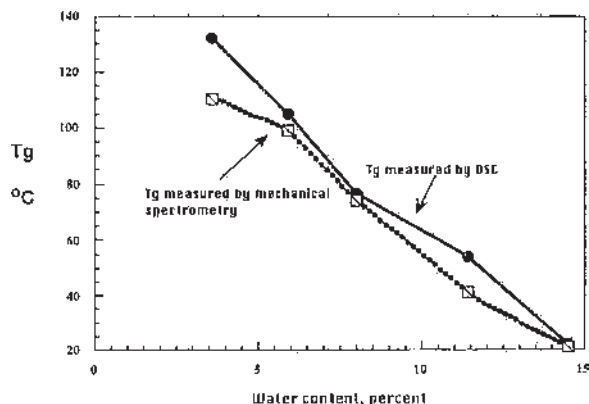


FIGURE 5.23 Glass transition of a protein as a function of water content.

Polymers have high T_g values, and some of them undergo thermal degradation without undergoing a glass transition. The T_g in the dry state is therefore often estimated by extrapolation of data obtained on polymers plasticized with water by using the Gordon Taylor equation, which has been shown to be applicable in many studies on polymers and proteins. Cereal proteins and milk proteins were studied extensively and found to have anhydrous T_g values in the range of 130 to 165 °C. They are readily plasticized by water (as shown in Fig. 5.23) for the wheat protein glutenin, and at moisture contents of

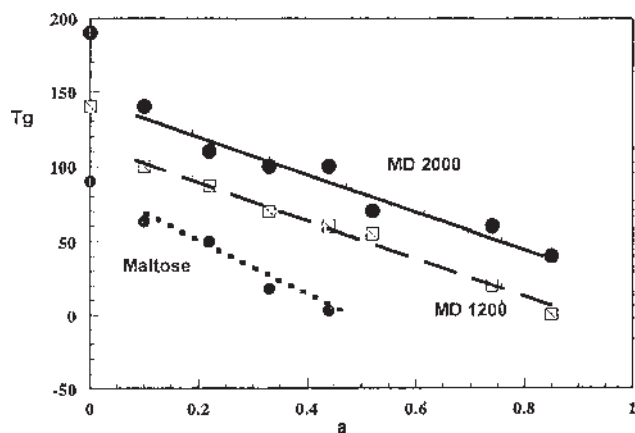


FIGURE 5.24 Water activity and glass transition temperature.

15 to 20% the value of T_g falls below room temperature for the wheat proteins gluten, gliadin, and glutenin (Cocero and Kokini, 1991).

A useful relationship results from the empirical observation that T_g is often a linear function of water activity in the range above water activity of 0.1 and up to activities at which T_g falls below the freezing point, as shown for several carbohydrates in Fig. 5.24.

The viscosity of some amorphous materials is less sensitive to temperature change above T_g . It is useful to mention the classification of liquids forming amorphous solids into *strong* and *fragile*, as proposed by Angell et al. (1995). The viscosity of strong liquids shows an Arrhenius type of dependence, and in these materials viscosity decreases moderately above T_g , compared to fragile liquids which show the WLF dependence with the resultant precipitous drop in viscosity. Most food materials show fragile behavior.

IX. OVERVIEW OF EFFECTS OF WATER ACTIVITY ON SHELF LIFE OF FOODS

The shelf life of foods is limited by biological, chemical, and physical processes, all of which are strongly influenced by water content and water activity. The recognition of the central importance of water resulted in the development of so-called stability maps relating water activity to rates of deterioration of food quality. One such map is presented in Fig. 5.25 (Labuza et al., 1970).

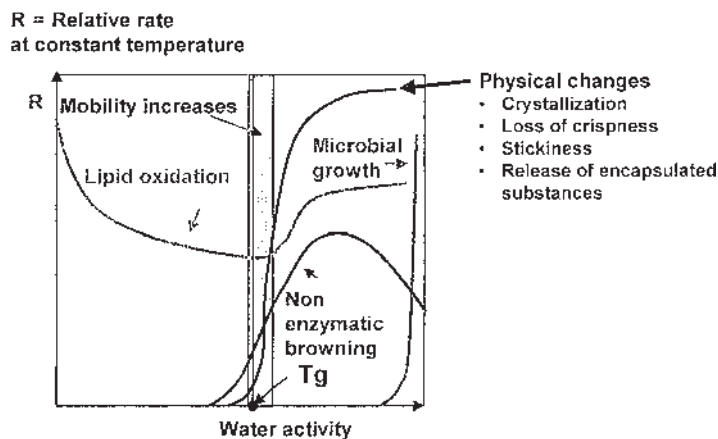


FIGURE 5.25 Relations between rates of food deterioration reactions and water activity “stability map.”

It shows the water activity ranges in which the rates of various deteriorative processes become strongly influenced by water. The map is reflecting the processes at a given storage temperature, usually the room temperature. The figure also shows the location of the water activity at which the glass transition temperature falls below the storage temperature. The influence of water on the shelf life of foods is exerted through several types of effects (Karel et al., 1994).

Physical changes including crystallization of solutes, changes in texture collapse, stickiness and caking, and release and loss of flavors are affected by water primarily through its effect on lowering T_g and the resultant increase in mobility.

Inhibition of microbial growth through lowering of water activity is almost entirely due to osmotic effects.

The role of water in rates of chemical reactions is complex and involves effect due to mobility control, as well as specific effects on reactants, catalysts (including enzymes), and inhibitors.

X. WATER ACTIVITY AND PHYSICAL CHANGES IN FOODS

The major effects of water on the rates of physical changes in foods are related to effects of plasticization by water and the attendant increased mobility of amorphous components of foods. The mobility increases dramatically as the water content is increased to a level, which results in the glass transition temperature being at or below the storage temperature. Figure 5.26 shows typical

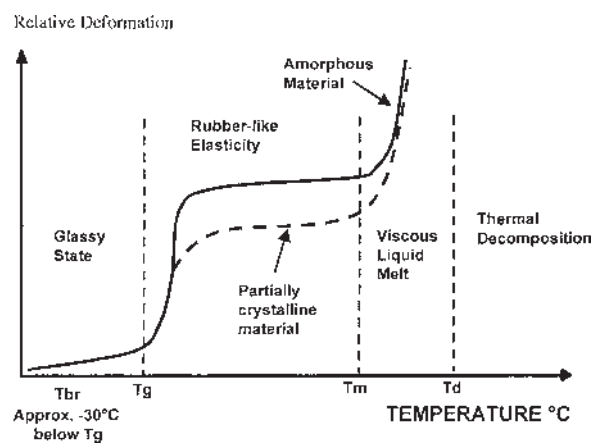


FIGURE 5.26 Mechanical behavior of polymers. Effect of T_g in deformation at constant stress.

changes in the deformation of polymer, at a given applied force as a result of the drop in viscosity shown in Fig. 5.20.

The deformability may be limited if the polymers are cross linked (rubber elasticity) or if there exist crystalline components persisting above T_g Fig. 5.26.

The effects of increased mobility become more pronounced as the quantity $T - T_g$ increases, due to either increasing temperature or increasing water content (which lowers T_g). The most immediate effect of glass transition is an increase in stickiness and caking (Wallack and King, 1988). Stickiness is usually measured by determining the temperature at which the force required for stirring of a powder shows a large increase, the so-called sticky point. The measurement requires control of experimental variables but is capable of producing a reproducible measure of the tendency of particle to adhere. The sticky point occurs in the vicinity of T_g , as shown in Fig. 5.27, and is of great importance in drying, as well in packaging of powders.

An important consequence of the increasing tendency of particle to stick is the development of caking. Caking of powders is an undesirable process which transforms free-flowing powders in lumps and aggregates and eventually into a sticky non-particulate mass. The caking affected by water activity changes applies to hydrophilic solids and usually is due to glass transition. Its occurrence is strongly dependent on the quantity $T - T_g$. In this respect it is similar to stickiness, which usually precedes caking. A recent paper reviewed the phenomena and mechanisms of caking, and the following discussion is based on this paper (Aguilera et al., 1995). Figure 5.28 shows schematically the stages in

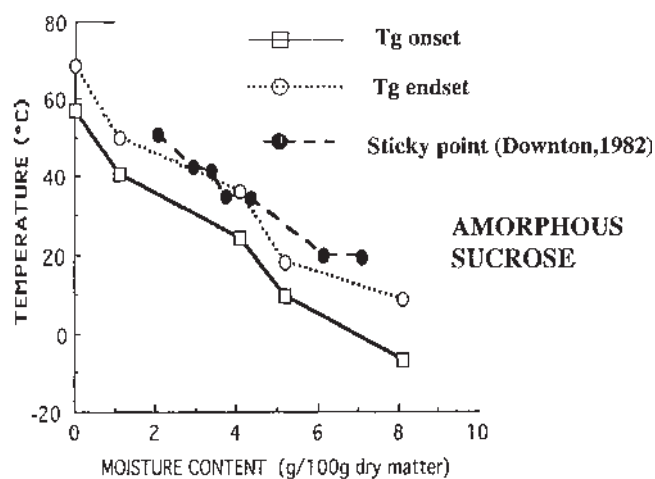


FIGURE 5.27 "Sticky point" and glass transition temperature.






| Stage | $\epsilon(t)/\epsilon(0)$ | $D_{\text{bridge}}/D_{\text{particle}}$ | Morphology |
|---------------|---------------------------|---|---|
| Free flowing | 1 | 0 |  |
| Bridging | $\rightarrow 1$ | $\rightarrow 0$ |  |
| Agglomeration | < 1 | < 0 |  |
| Compaction | $\rightarrow 0$ | $\rightarrow 1$ |  |
| Liquefaction | 0 | 1 |  |

FIGURE 5.28 Stages in caking of powders. $\epsilon(t)$ = porosity at time t ; $\epsilon(0)$ = porosity at zero time; D , diameter.

caking which lead from a free flowing powder to a liquefied material. It should be noted that if the process is carefully controlled, it is possible to arrest it at the agglomeration stage, and such controlled agglomeration is useful in food dehydration. This process will be discussed further in Chapter 13. The measurement of extent and rate of caking is based primarily on empirical tests which are summarized in Figs. 5.29 and 5.30. Tests on caking of fish hydrolyzate powders showed that caking followed first order kinetics, and that

Methods Used to Quantify Caking Phenomena



| Method | Description | |
|--|--|--|
| Caking index | Weight fraction of sample retained by a mesh with an opening size equal to a specified multiple of the maximum particle size of the powder |  |
| Surface Measurements Microscopy Porosity | BET, SEM, Pycnometry |  |

FIGURE 5.29 Measurement of caking of powders—1.

Methods Used to Quantify Caking Phenomena




| Method | Description | |
|-----------------|--|--|
| Flowability | Discharge mass flow rate from a bin or funnel |  |
| Angle of repose | Angle α between powder heap and horizontal plane <math><40^{\circ}\text{C}</math> free flowing powder |  |
| Cohesion | Extrapolated shear stress for a 0 normal stress, determined using a Jenike Flow Factor Tester or annular cells (ring shear tester) |  |

FIGURE 5.30 Measurement of caking of powders—2.

the rate increased with increasing water activity, the corresponding increase in water content and the corresponding increase in $(T - T_g)$. The rate dependence on $(T - T_g)$ was found to follow the WLF equation [Eq. (6)] with constants C_1 and C_2 respectively equal to 11.16 and 10.7. Figure 5.31 shows how caking is related to the three water related quantities: RH of storage, water content, and $T - T_g$. Caking and stickiness are related to another coincident process, occurring as

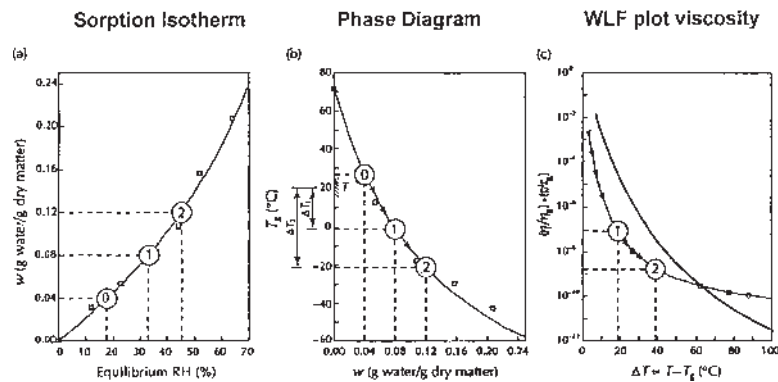


FIGURE 5.31 Critical points for caking of powders. Example: fish protein hydrolyzate. 0, Indicates the stability of the powders against caking; 1, signals the onset of caking; 2, indicates that powder samples cake fast enough to allow easy identification of the defect.

the T_g is exceeded, namely, collapse (Tsourouffis et al., 1976). *Collapse* refers to the loss of original structural of the materials undergoing this process. As the viscosity decreases above T_g the sample can no longer support its own weight, and it deforms under gravitational or applied forces. Of particular importance is the loss of internal porosity since the viscous flow results in pore collapse. Figure 5.32 shows the relation between the glass transition temperature and collapse temperature (temperature at which collapse was observed under defined experimental conditions) for 3 maltodextrins. It is evident that collapse occurs at or above T_g . The consequences of collapse to technology of dehydrated materials will be discussed in the chapters on dehydration and protective packaging. Plasticization of amorphous components of foods changes the texture of foods dramatically. The texture parameter that is most often associated with deteriorative changes due to moisture pickup is *crispness*. Figure 5.33 shows schematically the change in perception of crispness above T_g . Crispness is measured by a variety of mechanical, acoustic, and organoleptic techniques, and while their correlation is often not perfect, they all agree in show dramatic loss of crispness as water sorption results in the lowering of T_g to the test temperature and beyond (Attenburrow and Davies, 1993).

The fourth and often critical physical phenomenon affecting stored water-sensitive food materials is the crystallization of initially amorphous components, and in particular of sugars including sucrose, lactose, and glucose (Hartel, 1993).

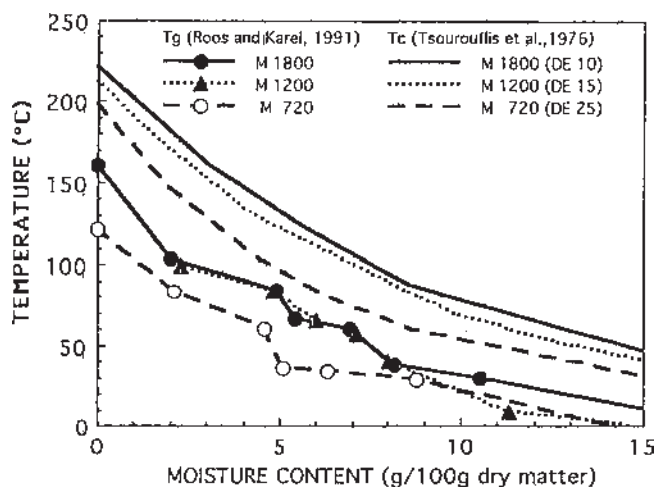


FIGURE 5.32 "Collapse" and glass transition temperature. T_c = collapse temperature.

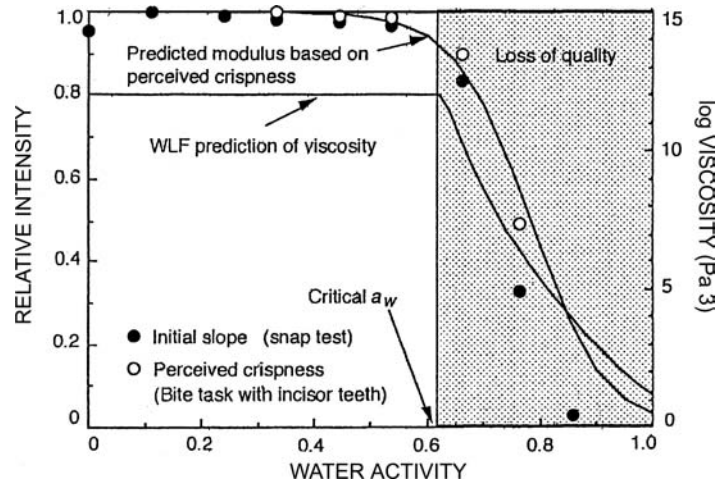


FIGURE 5.33 Loss of crispness and glass transition temperature.

The delayed crystallization is a cause of many defects in stored food products. The length of the induction time before crystallization occurs is primarily a function of the quantity $T - T_g$, or temperature above the glass transition temperature, and T_g of course decreasing with decreasing water content. Figure 5.34 shows schematically the *induction time* to crystallization for

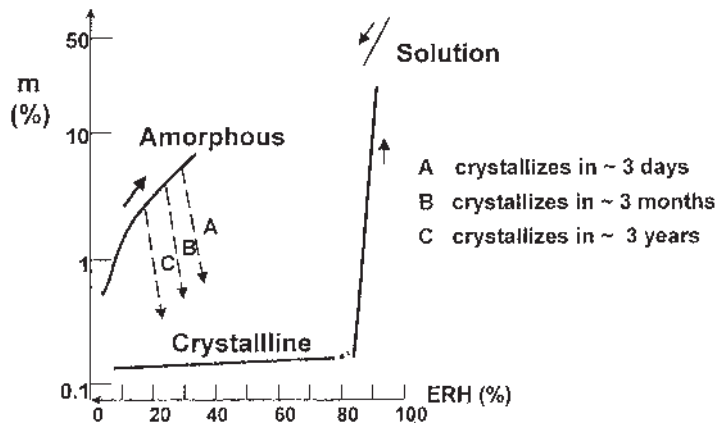


FIGURE 5.34 Induction times for crystallization of amorphous sucrose stored at different water activities at room temperature.

amorphous sucrose stored at room temperature as a function of water activity. Figure 5.35 shows time to crystallization for lactose. This figure also indicates the forms of lactose crystals which may result from the crystallization. For both sugars the effects of plasticization are dramatic. The rates of crystallization are also extremely dependent on $T - T_g$. Figure 5.36 shows the time to complete crystallization. θ was calculated using the Avrami equation which is also shown in Fig. 5.36, along with type of data from which it is calculated. The process was found to follow the WLF equation (Roos and Karel, 1992).

One characteristic of the crystallization of amorphous sugars is of particular importance to food stability. When the sugars crystallizes as anhydrous crystals, they release the water associated with them in the amorphous state. As a result the water content of the still uncrystallized amorphous sugar increases, the T_g of the glass drops, the quantity $T - T_g$ (which controls rate of crystallization) increases, and the crystallization continues to accelerate.

These effects are illustrated in Fig. 5.37, which compares the crystallization of lactose at two conditions that have approximately the same initial $T - T_g$. In one case the water activity is kept constant, and any water released by the crystallizing sugar leaves the sample by evaporating into the surrounding

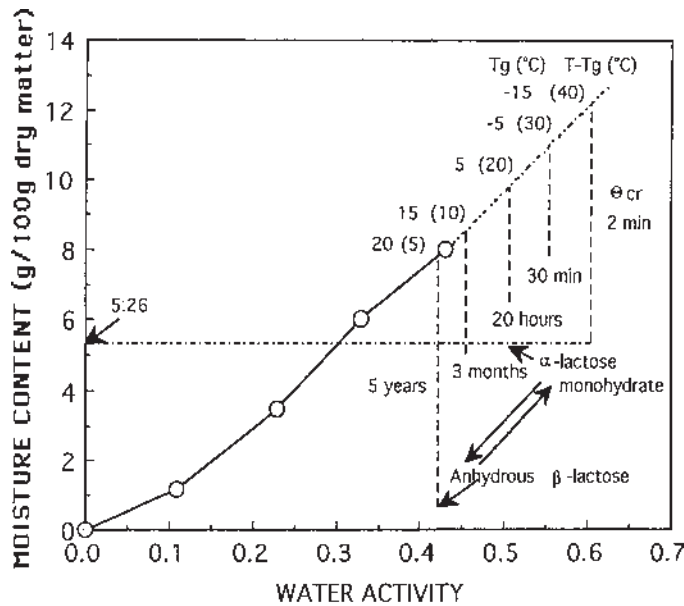


FIGURE 5.35 Induction time for crystallization of lactose stored at room temperature at different water activities.

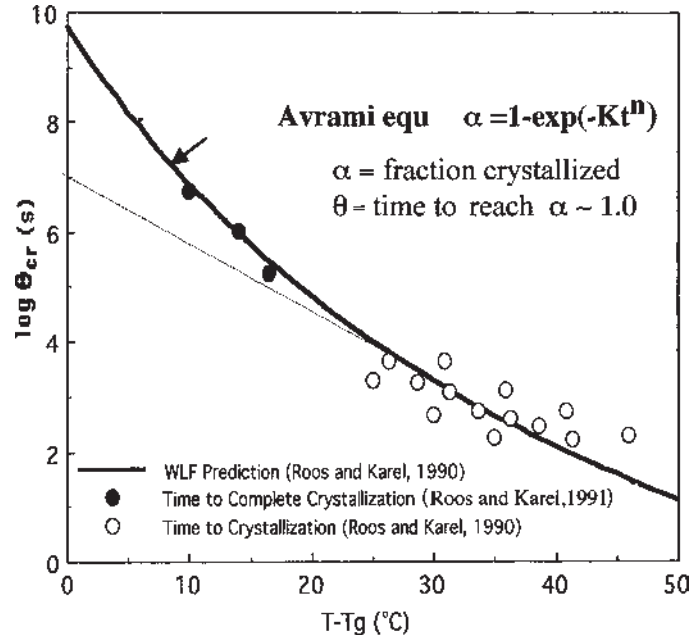


FIGURE 5.36 Time to completion of crystallization of amorphous lactose as a function of temperature above T_g . Time to complete crystallization was calculated using the Avrami equation. (From Roos and Karel, 1991.)

atmosphere. The crystallization proceeds at a constant value of $T - T_g$, because the activity and therefore the water content of the amorphous sugar remains constant. In the second case the crystallization proceeds at constant total water content of sample, as might be the case in a packaged food material. In this case the water content of the amorphous sugar increases continuously as the crystallizing sugar releases water, and the $T - T_g$ increases throughout the process. The figure shows clearly the enormous acceleration of crystallization due to the released water. The examples cited above present results obtained with freeze dried samples of pure sugar solutions. In food the onset, and rate of sugar crystallization is affected by presence of the other food components. There are two reasons for this phenomenon. The first relates to the effect on T_g . The T_g of an amorphous system composed by several components is determined by the weight fractions and T_g values of all components which remain the same phase. When a phase separation occurs, two T_g values may appear, each reflecting the composition of its phase.

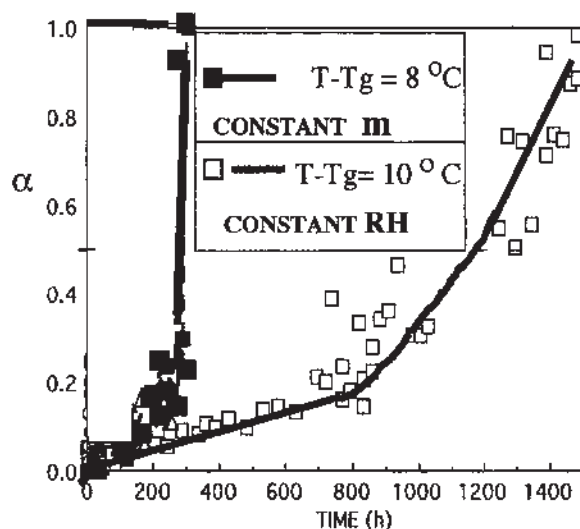


FIGURE 5.37 Crystallization of amorphous lactose at similar values of $T - T_g$ but at two different experimental conditions: \square constant relative humidity; \blacksquare constant moisture content. $m = (\text{weight water}/\text{total weight lactose})$, $\alpha = (\text{crystalline lactose}/\text{total lactose})$.

The second effect relates to the fact that even at a given constant value of $T - T_g$, crystallization in mixtures may be retarded because of specific effects on nucleation and crystallization. Effective crystallization inhibitors include raffinose (which is an effective inhibitor of sucrose crystallization), surfactant (which inhibit the crystallization of a variety of solutes by their effects at interfaces), and polymers (which increase viscosity). The effect of polymeric additives on rates of crystallization of sucrose is shown in Table 5.6.

The physical changes in foods due to changes in water content, and glass transitions have also a very significant effect on mobility of food components. Above T_g , loss of flavors entrapped within the food matrix, or added as encapsulated materials, become greatly accelerated. The increased mobility of the food matrices can also results in changes in component distribution, and in particular in breaking of emulsions, and in migration of fat to the surface, which increases the *free fat* content (usually measured as the fraction of total fat accessible to extraction by nonpolar solvents such as hexane or propane). These mobility changes have also profound effects on diffusion-limited chemical reactions, since they may facilitate diffusion of reactants.

TABLE 5.6 Crystallization of Sucrose in Freeze-Dried Systems at 54% RH at 35°C

| Composition | Induction time | $k_{CR} (h^{-1})^c$ |
|---|----------------|---------------------|
| Sucrose | Hours | 0.11 |
| Sucrose + 4.8% CMC ^a | Hours | 0.06 |
| Sucrose + 9.1% CMC | Hours | 0.04 |
| Sucrose + 23% CMC | Days | 0.005 |
| Sucrose + 43% Avicel ^b + 13% CMC | Weeks | 0.0007 |

^a CMC is carboxymethyl cellulose.

^b Avicel is microcrystalline cellulose.

^c k_{CR} is crystallization rate constant.

Source: From Iglesias and Chirife (1978).

These flavor entrapment by dehydration and its release by hydration will be discussed in Chapter 13. The effects on chemical reactions will be discussed in a subsequent section of the present chapter.

XI. EFFECTS OF WATER ON MICROBIAL GROWTH

As indicated in Fig. 5.25 and noted by numerous reports in the literature, the activity of microorganisms shows a definite limiting water activity below which the probability of microbial growth is considered to be zero (Troller and Christian, 1978). Different microorganisms show different lower limits of water activity allowing growth, but most bacteria do not grow below water activity of 0.85, and no bacterial pathogens are known to grow below that water activity, even when the other environmental parameters (e.g., pH, temperature, nutrient content) are optimal. The growth of xerophilic fungi and of osmophilic yeast does occur at somewhat lower activity, but even their activity becomes insignificant in the range of water activities in the vicinity of 0.7.

The following critical values of water activity are generally accepted as providing adequate margins of safety with respect to microbiologically generated health hazards (Chirife and Buera, 1996).

Growth and toxin production by all types of *Clostridium botulinum*: 0.94
 Anaerobic growth of *Staphylococcus aureus*: 0.91
 Aerobic growth of *Staphylococcus aureus*: 0.85
 Production of toxins by molds: 0.80

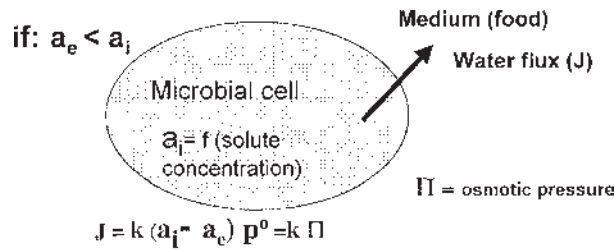
The extensive studies on the subject of microbial safety have been used by the Food and Drug Administration in the formulation of its regulations requiring thermal processing of foods. Under these regulations the thermal processing for

shelf stable foods does not apply to food with an equilibrium water activity of 0.85 or less.

There has been a great deal of literature dealing with the fundamental basis for the existence of fairly sharp limits of microbial activity (Booth, 1998). While some controversy persists with respect to the subject, it is the author's view that the mechanism of prevention of microbial growth in low-moisture foods which is outlined below represents the current consensus view among both food microbiologists and food physicists (Gould and Christian, 1988). Figure 5.38 shows diagrammatically the essence of the mechanisms limiting microbial growth. The membrane surrounding cells is permeable to water, but largely impermeable to most solutes. For this reason equilibration between cell interior and the surrounding medium with respect to the chemical potential of water occurs readily. If a cell in its physiologically normal water activity is placed in a medium with a lower water activity, there exists a water activity difference across the membrane. This difference generates an osmotic pressure Π that is related to the water activity difference as shown in Fig. 5.38. The osmotic pressure provides a driving force for transfer of water from the inside of the cell to the surrounding medium. If this process continues without any counteracting influences cell shrinkage is the result, and the shrinkage may result in irreversible damage to the cell membrane, and to death of the organism. Organisms have metabolic defenses against such an outcome. The most widely occurring type of defensive mechanism is the accumulation of solutes within the cell. There is a wide range of solutes, which may be so accumulated, including in particular salts, amino acids, and polyols, such as glycerol.

The osmotic pressure is related to concentration. The ideal relation for this concentration dependence in the Vant Hoff equation:

$$\Pi = cRT \tag{7}$$



In response to osmotic stress cells accumulate solutes (salts or polyols). This lowers a_i , minimizes flux of water out of cell, and membrane damage due to cell shrinkage. As the concentration of solutes reaches a critical level it results in cessation of growth and reduction of metabolic activity.

FIGURE 5.38 Mechanism of inhibition of microbial growth at low water activities.

where Π is osmotic pressure (KPa), c is molar concentration (mole/m³), R is gas constant [(KPa)(m³)/(K)(mol)], and T is absolute temperature (K).

It should be noted that in the Vant Hoff equation the quantity c , in common with Raoult's law, freezing point depression, and boiling point elevation, refers to kinetic units in solution. Dissociated ionic compounds will therefore have c equal to concentration of ions in solutions.

The increasing intracellular concentration of accumulating solutes decreases the outgoing water flux; and when the intracellular water activity is depressed to the activity level in the surrounding material, water loss ceases, and cell shrinkage is minimized. However, the high internal concentration of solutes has an inhibiting effect on metabolic activities necessary for growth, and the growth ceases when that concentration reaches a critical level corresponding to a critical water activity for growth of the particular organism.

The question remaining unanswered at this point is, what are the mechanisms by which a given solute concentration within the cells results in complete inhibition of growth. A detailed discussion is beyond the scope of this book, and the reader is referred to recent reviews (Chirife and Buera, 1996). The mechanisms seem to include both specific inhibitory effects of low water activity effects on enzymes essential to cell function, and the excessive metabolic cost of the continuing effort to maintain a high solute concentration. It must be noted that while the membrane is very much more permeable water than to solutes, some loss of the accumulating solutes does occur, and the solutes have to be replaced continuously. A very recent paper in *Nature* deals with the mechanisms by which water transport through cell membranes is maintained at a much higher level than that of other small molecules (Murata et al., 2000). It should be noted here also that there is a dissenting view, proposing that the primary growth-inhibiting effect is due to reduced mobility, which in turn is due to the increase of T_g as the water activity decreases. This mechanism, in our opinion, may be of some secondary importance in special circumstances, such as growth of large mold colonies on surfaces, where diffusion of nutrients may become limiting, but the overwhelming weight of evidence suggests that osmotic effects are the dominant effect in the water limitation of microbial growth. Since the osmotic effects are directly related to water activity, any changes in water activity affect the stability of foods with respect to microbial activity. These changes do not necessarily involve overall moisture content changes. Thus, water activity may change due to hysteresis effects.

Another case resulting in water activity changes of a component sensitive to microbial attack may result in a mixture, which is not equilibrated when the storage is initiated, and in which there is water transfer between components, but no net change in the total water content of the mixture. Both cases have important practical consequences, since they may change shelf life.

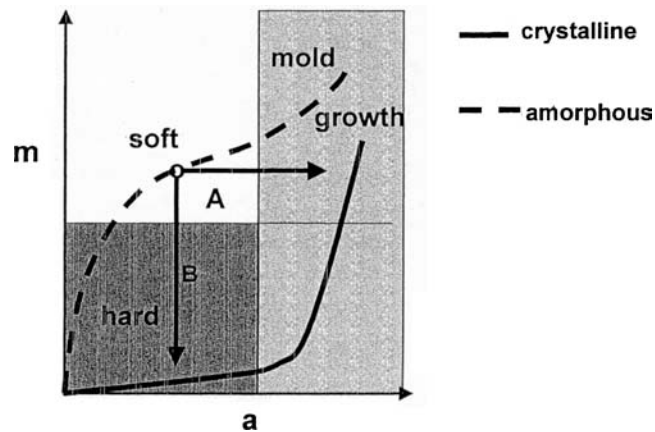


FIGURE 5.39 Effect of crystallization of an amorphous sugar on mold growth and physical state of an amorphous, sugar-containing system. A, crystallization at constant m ; B, crystallization at constant a .

The following two examples may illustrate these situations. Figure 5.39 shows the consequence of crystallization in food product containing a crystallizable sugar. Initially sugar in the product is amorphous, and the product is microbiologically stable and also has a moisture content which is sufficiently high to assure product softness. If crystallization occurs: two extreme possibilities exist for its consequences. If an unpackaged product is stored in a constant humidity environment, line B is followed and the product loses moisture and becomes hard but remains stable with respect to microbial deterioration. If the product is in a hermetically sealed package there is no moisture change, but because the crystals have a low *hygrocapacity* (low moisture content at a given water activity), the water activity increases into the range which permits mold growth. In the present example it is assumed that the softness of the texture of product is unaffected, because the water released by the sugar as it crystallizes plasticizes other texture-determining components, but of course this is not always the case, and crystallization may lead to texture defects as well. A well-known example of such defects is crystallization of lactose in ice cream, which leads to *grittiness* or *sandiness*. A situation in which components are initially not at equilibrium is illustrated in Fig. 5.40 (Larumbe et al., 1991). A composite candy product consists of caramel jam and chocolate. The initial water activity is 0.85, and the chocolate is 0.46. At an activity of 0.85 the jam develops mold growth within 10 days of storage. However during storage there is a tendency for slow equilibration, and the jam loses moisture to the chocolate. Chocolate has

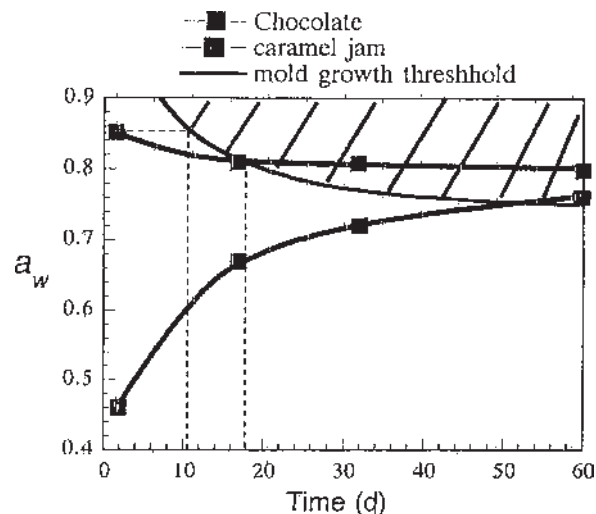


FIGURE 5.40 Mold growth in a composite candy product. (From Larumbe et al., 1991.)

a very low hygrocapacity, but enough water is transferred from the jam to extend its mold-free shelf life from 10 to 18 days by lowering its water activity below 0.8.

XII. WATER AND CHEMICAL REACTIONS IN FOODS

In the preceding discussions was argued that physical changes in foods are affected by water mainly through its plasticizing action and the resulting depression of the glass transition temperature. The effects of water on growth of microorganisms was attributed primarily to osmotic effects and therefore to changes in water activity.

The effects of water on chemical reactions in foods, whether catalyzed by enzymes or other catalysts, autocatalytic, or uncatalyzed, are difficult to attribute to a single mechanisms. The mechanisms are complex.

Enzymatic reactions are often initiated only above a critical water activity range characteristic for a given enzyme–substrate combination, as shown schematically in Fig. 5.41. Furthermore once enzymatic reactions are initiated, the initial rates seem to be dependent on water activity, as well as the extent of conversion during the reaction, as shown in Fig. 5.42. The apparent cessation of enzyme activity after a partial conversion of the substrate, however, is not due to enzyme inactivation since a hydration to a higher water

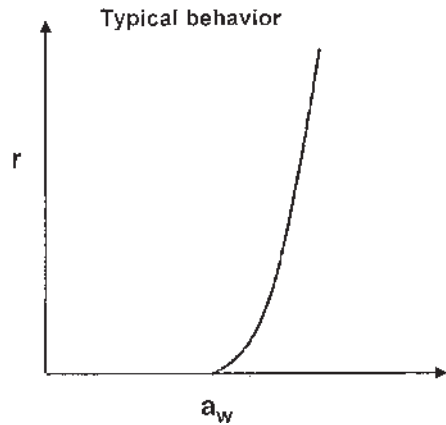


FIGURE 5.41 Dependence of enzyme activity on water activity at constant temperature. r = initial rate.

activity results in resumption of enzyme activity, as shown in Fig. 5.43. A number of studies have been carried to establish the nature and limits of the requirements for some enzyme hydration. We studied sucrose hydrolysis by invertase in a dehydrated system and concluded that the observed reaction

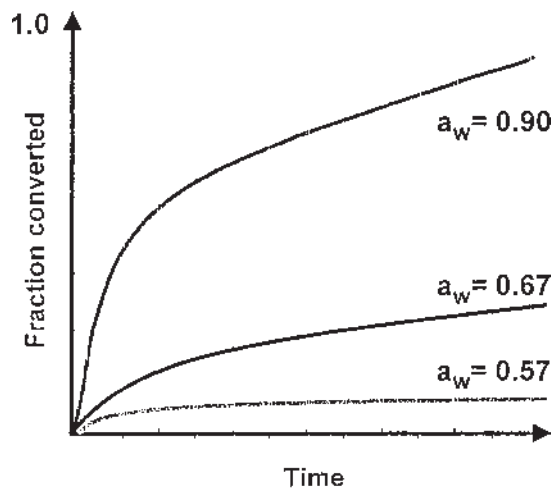


FIGURE 5.42 Effect of water activity on substrate conversion, typical behavior. (From Silver and Karel, 1981.)

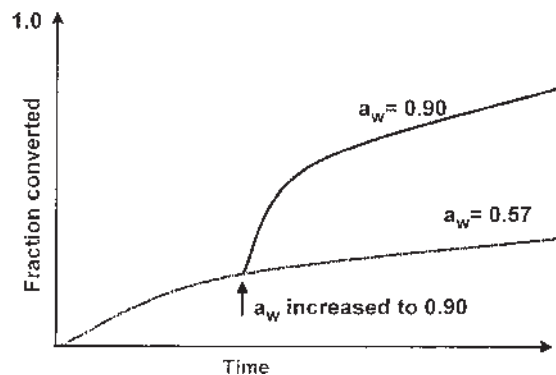


FIGURE 5.43 Effect of water activity on substrate conversion when an initially low water activity is increased during incubation. (From Silver and Karel, 1981.)

kinetics were not consistent with a hypothesis of a diffusional limitation on diffusion of the substrate and/or products in the matrix. The most likely limitation on reaction rates at low water contents seem to lie in conformation of the enzyme (Silver and Karel, 1981).

The understanding of enzyme reactions at limiting water activities was further enhanced by studies in nonaqueous solvents (Klibanov, 1997). In these systems viscosity is low and there is no limitation of substrate diffusion in the medium, nevertheless there exists a defined limiting water activity that corresponds to different water contents depending on solubility of water in the solvent. The more soluble water is in the solvent, the higher the required minimum water concentration. This situation is consistent with an assumption that it is the hydration of the enzyme itself that is the critical factor, since that hydration depends on the water activity and the sorption isotherm of the specific protein. Similar conclusions were reached in studies on reactions with gaseous substrates and interaction in supercritical fluids (Barzana et al., 1987; Hammond et al., 1985). Reasons for reduced enzyme activity at low water contents were recently reviewed (Klibanov, 1997). Klibanov concludes that the major factor is the conformational mobility of the protein. Other important effects include destabilization of transitional states by the absence of water and effect on pH.

Among nonenzymatic reactions in stored foods two are preeminently important: nonenzymatic browning and lipid oxidation.

Nonenzymatic browning is actually a series of reactions initiated primarily by aldehyde–amino condensation. Foods containing reducing sugars as well as amino groups are particularly susceptible. A simplified scheme

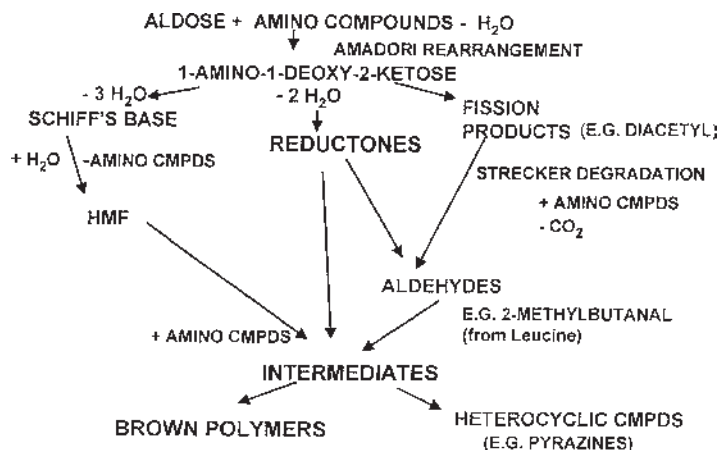


FIGURE 5.44 Browning reactions-simplified scheme.

showing some of the important reactions in the nonenzymatic browning reaction complex is shown in Fig. 5.44. The progress of the overall reaction measured by the rate of formation of brown pigments, by formation of intermediates such as hydroxy methyl furfural, or by the depletion of the initially reacting aldehyde (in most case a mono- oligio-saccharide, such as glucose or lactose) is extremely sensitive to water activity and corresponding water content, as shown in Fig. 5.25.

The generally accepted explanation for the occurrence of a rate maximum in the intermediate water activity range is as follows: Many of the reaction in the NEB scheme are bimolecular, including the initial aldehyde–amino condensation and subsequent aldol and aldimine condensations.

In the high water activity range the reactants are in solution and further dilution by water reduces the reaction rate by the well-known *law of mass action*, i.e., the reaction rate is proportional to reactant concentration, and the concentration is decreasing with increasing water content.

The effects observed in the low water activity may be explained by one of two assumptions:

1. It may be assumed that the reaction occurs only in solution. When the water content falls below the saturation level for a given reactant, the concentration remains constant, but the amount of solution per unit weight of food decreases and the reaction rate calculated on the weight basis of the food decreases. This assumption leads to the conclusion that reaction ceases when there is insufficient water for solutions to exist. The logical expectation would then be that reaction cease at

the “solubilization” water content for a given reacting solute (the so-called NSW shown in Table 5.2).

2. An alternate approach is to assume that reactions can proceed in the “solid” state existing in the supercooled or supersaturated matrix but are progressively slowed down by diffusional limitations. One would expect then that the dominant feature would be the increase in viscosity at low water contents and that the reactions rates follow the WLF equation. The regions in which the proposed models apply are shown schematically in Fig. 5.45.

Literature provides some support for each assumption, and as we shall see in the arguments concluding this chapter, the effects of diffusional limitations on reaction rates depend strongly on the particular reaction step being observed.

Before discussing the reasons for this complexity it may be useful to review the other major set of food deteriorative reaction, those due to oxidation of lipids. This set of reactions is typical of free radical reaction chain reactions, a basic reaction scheme shown in Fig. 5.46. The substrate being oxidized is denoted as RH and is usually an unsaturated lipid, such as a fatty acid or triglyceride. Free radicals may be initiated directly from the substrate by energy input (e.g., light or ionizing radiations), but in foods the initiation is mainly due to decomposition of hydroperoxides (ROOH), which are the main product of the oxidation (propagation steps in Fig. 5.46). The reaction is therefore autocatalytic and is extremely sensitive to initial hydroperoxide content $PV(o)$ usually measured in milliequivalents of oxygen per kg of substrate). The hydroperoxide scission is greatly accelerated by metals, heme proteins, and the enzyme lipoxidase. The reaction is terminated by reactions between free radicals and very effectively

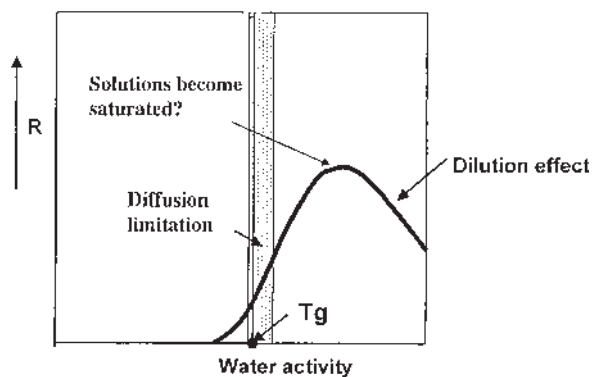
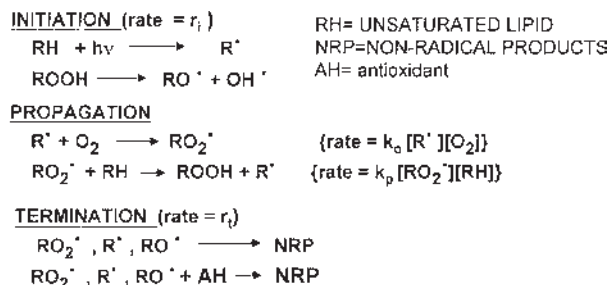


FIGURE 5.45 Effect of water activity on rates of nonenzymatic browning. R = relative rate at constant temperature.



- SCISSION OF HYDROPEROXIDES AND SUBSEQUENT REACTIONS PRODUCE MANY FLAVORS AND OFF-FLAVORS
- TERMINATION LEADS TO PRODUCTION OF POLYMERS
- RADICALS AND OXIDATION PRODUCTS REACT WITH PROTEINS

FIGURE 5.46 Basic scheme of autoxidation of lipids.

by antioxidants (AH) or compounds reacting with free radicals and thus inhibiting the progress of the reaction. The overall rate of the reaction $r(o)$ depends on the rates of the individual steps. Using simplifying assumptions [for a somewhat more detailed discussion the reader is referred to Karel (1992)] $r(o)$ may be related to the rate of initiation (r_i) and to the concentrations of substrate RH, oxygen (O_2), and antioxidant (AH), as summarized in Fig. 5.47. The dominating role of ROOH and AH is evident from results of experiments on methyl linoleate shown in Fig. 5.48. Oxidation results in rapid increase in ROOH within 10 days in a sample which had no antioxidant and was substantially from peroxides at the time the experiment was started (C). The addition of 0.1% of an antioxidant delays the rapid phase of the reaction for well over 100 days. This delay (induction time) is terminated when the antioxidant is finally depleted by reacting with free radicals. When peroxides are preformed by irradiating the samples with gamma rays before exposing them to oxidation in air, the reaction proceeds rapidly and is not prevented by the antioxidant addition.

Water has very significant effects on the autoxidation reactions. It can act as an antioxidant by interfering with decomposition of hydroperoxides, it may reduce the effectiveness of metal catalysts by hydrating them, and it may promote the nonenzymatic browning reactions that are known to result in some compounds with antioxidant activity (Karel, 1980). Water can also promote oxidation by facilitating mobility in an amorphous matrix within which lipids are located and allowing the lipid access to the surface where the reaction with atmospheric oxygen occurs (Shimada et al., 1981). Water may also solubilize

OVERALL RATE OF OXIDATION = $r(o)$

$$r(o) = d(\text{ROOH})/dt$$

$r(o)$ is proportional to (rate of initiation)^{1/2}

When initiation is due to hydroperoxides:

AT ATMOSPHERIC OXYGEN PRESSURE

$$r(o) = K (\text{ROOH})(\text{RH})$$

AT LOW OXYGEN PRESSURES

$$r(o) = K' (\text{ROOH})(\text{O}_2)$$

IN PRESENCE OF ANTIOXIDANT (AH)

$$r(o) = K'' (\text{ROOH})(\text{RH}) / (\text{AH})$$

ANTIOXIDANT IS DEPLETED AT A RATE EQUAL TO RATE OF INITIATION OF FREE RADICALS

$$-d(\text{AH})/dt = K^* (\text{ROOH})$$

K, K', K'', K^* are constants

FIGURE 5.47 Simplified relations for rate of autoxidation under specified conditions.

catalysts and allow them to come in contact with lipids, often at water–oil interfaces.

The role of mobility in controlling reactions limiting shelf life of foods has been noted by a number of investigators, and it has been occasionally claimed that

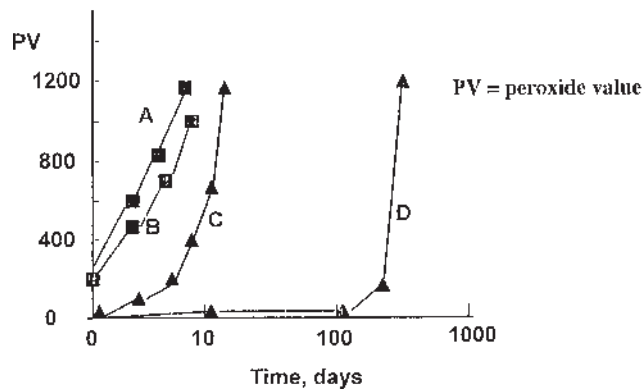


FIGURE 5.48 Oxidation of methyl linoleate in air at 24°C. A, preformed peroxide (irradiation 4.65 Mrad); B, antioxidant and preformed peroxide; C, control; D, with antioxidant (0.01% propyl gallate).

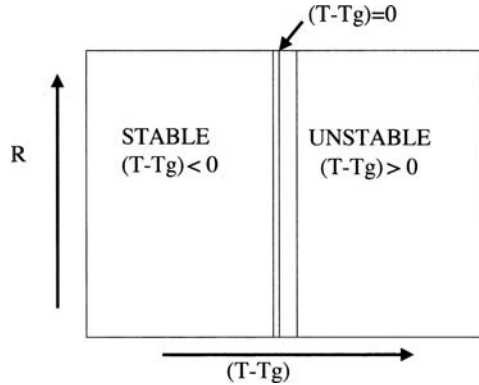


FIGURE 5.49 Stability “map” based on glass transition temperature as a critical stability factor. Is there a general rule that all food deterioration reactions are minimized below T_g ? R = relative rate of deterioration.

a useful map can be constructed based on glass transition temperature as the determinant of food stability, as shown in Fig. 5.49. However, experimental results fail to produce consistent support for such a map. Many food deterioration processes seem to cease below T_g , but many others do not.

It is the present author’s firmly held opinion, that a general rule establishing T_g or some other mobility limiting parameter as a unique guide to food stability is not feasible (Karel, 1993). The reasoning behind this opinion is presented below.

Consider the mobility effect as a diffusion limitation in a simple bimolecular reaction as shown in Fig. 5.50. Basic considerations lead to

In a bimolecular reaction:
 $dC/dt = k [A][B]$
 k is reaction rate constant ($L s^{-1} mole^{-1}$)
 If there is limitation on diffusion of reactants
 $dC/dt = k' [A][B]$
 k' is the apparent k in ($L s^{-1} mole^{-1}$)
 $k' = k / [1 + (k/\alpha D)]$
 D =diffusivity (cm^2/s), α = a constant
 ideally $\alpha = 4 \pi r f$
 r = "collision radius", f = a conversion factor

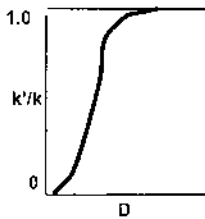


FIGURE 5.50 Effects of diffusion on observed rates of bimolecular reactions.

the following equation shown in Fig. 5.50, in which we also define the symbols (Atkins, 1990).

$$k' = \frac{k}{1 + \frac{k}{\alpha D}} \quad (8)$$

It should be obvious that the observed reaction rate, as expressed by k' depend very strongly on two parameters, the reaction rate constant k (measured under conditions in which diffusion is not limiting) and the diffusivity D . If we consider values of D which may exist in various media in which food-relevant reactions occur, as is done in Fig. 5.51, we note that values of D may range from 10^{-5} in low viscosity liquids down to less than 10^{-13} in glasses. Thus D may vary by 8 orders of magnitude or more. The variations in values of k for different reactions occurring in foods are equally large, as shown in Fig. 5.52. The constant for autoxidation initiation due to ROOH decomposition (k_i) is 6 to 8 orders of magnitude lower than the hydrogen abstraction constant (k_p) and 12 orders of magnitude lower than the constant (k_0) in the same reaction. Nonenzymatic reactions constants (k_B) have been reported to be in a range intermediate between these extremes.

If we assume an arbitrary value of α in Eq. (8), we can show the variation of the quantity k/k' , which reflects the reaction rate in a system limited by diffusion divided by the reaction rate in a system in which diffusion is not limiting, with the magnitude of D . Figure 5.53 shows such a plot. In this case we used the ideal value of α , as shown in Fig. 5.50, as the arbitrary

| | | |
|----------------|------------------|--------------------------|
| Small solutes | Liquids | 10^{-6} to 10^{-5} |
| Polymers | Liquids | 10^{-7} to 10^{-5} |
| Polymers | Rubbery polymers | 10^{-8} to 10^{-6} |
| Small solutes | Rubbery polymers | 10^{-8} to 10^{-5} |
| Gases | Glassy polymers | 10^{-12} to 10^{-6} |
| Small solutes | Glasses at Tg | 10^{-13} to 10^{-10} |
| Polymers | Glasses | $< 10^{-13}$ |
| All diffusants | Crystals | ~ 0 |

FIGURE 5.51 Typical range of diffusivity values D (cm^2/s).

| | |
|--|-------------------------------|
| Bimolecular ROOH decomposition | 10^{-6} |
| $2 \text{ ROOH} \longrightarrow \text{ROO}\cdot + \text{RO}\cdot + \text{H}_2\text{O} \quad (k_i)$ | |
| Non Enzymatic Browning Steps | $10^{-4} \text{ to } 10^{-2}$ |
| Hydrogen abstraction from olefins | $1 - 100$ |
| $\text{ROO}\cdot + \text{RH} \longrightarrow \text{ROOH} + \text{R}\cdot \quad (k_p)$ | |
| O₂ addition to olefin radicals | 10^6 |
| $\text{R}\cdot + \text{O}_2 \longrightarrow \text{ROO}\cdot \quad (k_o)$ | |

FIGURE 5.52 Magnitudes of bimolecular rate constants. All values in (L mole⁻¹s⁻¹).

values for calculation. It should be immediately apparent that within the range of diffusivities relevant to food media, some reactions will be limited by diffusion even in low viscosity liquids, other reactions will not show diffusional limitation even in glass below T_g . Thus the observed variation of results in the literature is found to be expected on theoretical grounds and

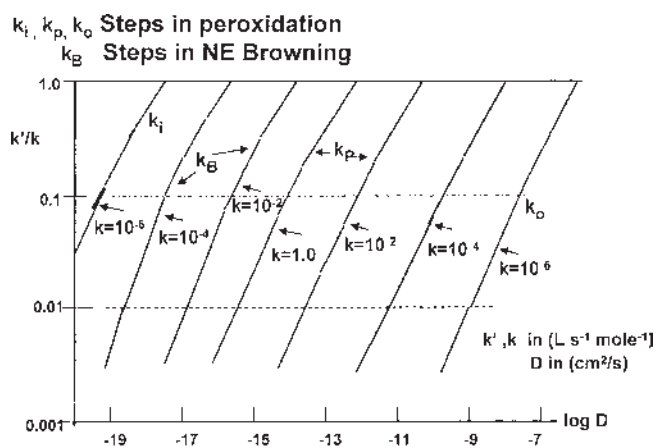


FIGURE 5.53 The ratio of observed rate constant (k') to the bimolecular rate constant (k) as a function of diffusivity of reactants, with k as a parameter.

cautions us to consider individual reaction in a less simplified manner than postulated in a stability map presented in Fig. 5.49.

SYMBOLS

| | |
|--------------------|--|
| a, a_w | Water activity |
| a_m | Water activity at moisture content m |
| BET | Brunauer Emmet Teller equation |
| c | Molar concentration |
| $C, C', C_1, C_2,$ | Constants |
| $a_0, k, \kappa,$ | |
| C'_g | Maximal freeze concentration |
| c_p | Specific heat |
| ERH | Equilibrium RH |
| GAB | Guggenheim, Anderson, DeBoer equation |
| H | Enthalpy |
| k' | Apparent reaction rate constant |
| k, k_i, k_p, k_B | Reaction rate constants |
| k_{CR} | Crystallization rate constants |
| M, MW | Molecular weight |
| m | Moisture content |
| m_1 | Monolayer value |
| NFW | Nonfreezing water |
| NSW | Nonsolvent water |
| p | Partial pressure |
| p° | Vapor pressure |
| R | Gas constant |
| T | Temperature |
| T_g | Glass transition temperature |
| T'_g | T_g at maximal freeze concentration |
| T_M | Melting point |
| v | Molar volume |
| w | Weight fraction |
| WLF | Williams, Lendel Ferry equation |
| X | Mole fraction |
| ΔH_A | Isosteric heat of sorption |
| ΔH_T | Total heat of vaporization ($\Delta H_A + \Delta H_v$) |
| ΔH_v | Latent heat of vaporization |
| Π | Osmotic pressure |
| α | Constant |
| ϕ | Constant |

| | |
|---------------|---------------------------------------|
| γ | Surface free energy, surface tension |
| η | Viscosity |
| μ | Chemical potential |
| θ_{CR} | Time to completion of crystallization |
| τ | Sticking time |

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6

Heat Processing

I. INTRODUCTION

Preservation of food has occupied and continues to occupy a large portion of man's time and effort. Early man preserved his food supply by applying methods of preservation available to him in his environment. Sun drying, salting, and fermentation were used to provide food in periods when fresh were not available. As civilization developed, demand for greater quantities of better quality processed food also increased. Hence there has developed a large food-preservation industry which attempts to supply food that is satisfying, nutritious, and economical. Thermally processed foods constitute a large part of this industry.

II. APPLICATION OF HEAT ENERGY TO FOODS

It is appropriate to introduce this subject on the basis of objectives of the heat process. General principles governing heat transfer and response of foods to heat energy can be applied to all heat processes, but each type of thermal process has specific objectives. Severity of the thermal process is dependent on these objectives.

A. Cooking

Cooking is a heating process with the primary object to produce a more palatable food. The word *cooking* is a broad term embodying at least six forms of heating, including baking, broiling, roasting, boiling, frying, and stewing. The method of applying heat energy and the duration differs somewhat for each of these processes. Baking, broiling, and roasting usually require dry heat at relatively high temperatures (greater than 100°C), boiling and stewing are done by placing the product in boiling water, and frying involves cooking oil and temperatures much greater than 100°C.

Cooking can be thought of as a preservation technique since cooked foods generally can be stored for longer periods than uncooked foods provided recontamination of the food with spoilage organisms is minimized. Refrigerated storage following cooking is a common household method of preservation. Two important preservative changes occur in food as a result of cooking: destruction or reduction of microorganisms and inactivation of undesirable enzymes.

Other desirable changes that may occur during cooking include (1) destruction of potentially hazardous toxins present naturally or through microorganisms; (2) alteration of color, flavor, and texture; and (3) improved digestibility of food components. Undesirable changes also may occur, such as degradation of nutritive components and sensory attributes. Principles that can be applied to describe the effect of cooking on the reduction of microorganisms and enzymes also can be applied to other changes occurring during cooking. Application of these principles is dealt within Sec. III.F.

B. Blanching

Blanching is a heat treatment commonly applied to tissue systems prior to freezing, drying, or canning. The objectives of blanching depend on the process that follows it. Blanching prior to freezing or dehydration is done primarily to inactivate enzymes. Unblanched frozen or dried foods exhibit relatively rapid changes in such properties as color, flavor, and nutritive value as a result of enzyme activity.

Two of the more heat-resistant and widely distributed enzymes in plant tissues are peroxidase and catalase. Activity of these enzymes, therefore, can be used to evaluate the effectiveness of a blanching treatment. If both are inactivated then it can be assumed that other significant enzymes also are inactivated. The heating time necessary to destroy catalase or peroxidase depends on the type of fruit or vegetable, the method of heating, the size of the fruit or vegetable, and the temperature of the heating medium. For commercial blanching, typical times at 100°C are given in Table 6.1. Heating media other than water (e.g., steam, hot air, microwave) and at temperatures other than 100°C can be used. Although

TABLE 6.1 Blanching Times for Vegetables Prior to Freezing

| Vegetable in water at 100°C | Blanching time (min) |
|-----------------------------|----------------------|
| Asparagus | |
| < 5/16 in. per butt | 2 |
| 5/16–9/16 in. per butt | 3 |
| > 10/16 in. per butt | 4 |
| Beans, green and wax | |
| Small | 1–12 |
| Medium | 2–3 |
| Large | 3–4 |
| Beets | |
| Small, whole | 3–5 |
| Diced | 3 |
| Broccoli | 2–3 |
| Corn | 2–3 |
| Peas | 1–12 |
| Spinach | 12 |

Source: Lund (1975).

blanching of vegetables is most often done in hot water or steam, blanching of fruits is often done in calcium brines to firm the fruit through the formation of calcium pectates. Colloidal thickeners, such as pectin, carboxymethyl cellulose, and alginates, also can be used to aid fruit firmness following blanching.

For frozen fruits which are not to be further heated after thawing, blanching is not used because it results in undesirable changes in texture and flavor. Instead, other preservative techniques are used to combat undesirable enzymatic changes (mainly oxidative browning and oxidation of ascorbic acid). This is accomplished by chemical inactivation of enzymes, avoidance of contact with oxygen (for example, by packing in sugar syrups), and addition of antioxidants (for example, ascorbic acid).

Blanching prior to conventional canning fulfills several important objectives: remove tissue gases, increase the temperature of the tissue, cleanse the tissue, wilt the tissue to facilitate packing, and activate or inactivate enzymes. Since the product generally receives a thermal process severe enough to inactivate enzymes, enzyme inactivation is not necessarily a primary objective of blanching. Removal of tissue gases and preheating the product prior to filling, however, are important objectives of precanning operations since they have a great influence on the final level of oxygen in the container and therefore directly influence storage life. Accomplishment of these two objectives results in high can

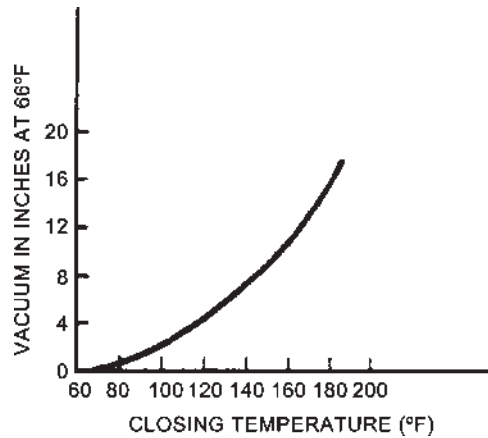


FIGURE 6.1 Relation of can vacuum to closing temperature.

vacuum, which necessarily implies low gas concentration in the product. Figure 6.1 shows the relationship between can vacuum and closing temperature.

In at least one instance blanching prior to canning is used to activate an enzyme. With some green beans, the epidermis is loosened upon heating, and this results in a quality defect known as *sloughing*. A moderate heat treatment (less than 80°C) followed by a holding period prior to thermal processing can prevent sloughing through heat activation of an enzyme, pectin methylesterase, which demethylates the pectin molecule allowing cross linking with calcium ions. This cross-linking bonds the outer layer of tissue to the underlying structure, thus preventing sloughing.

C. Pasteurization

Pasteurization is a heat treatment that kills part but not all of the vegetative microorganisms present in the food, and consequently it is used for foods that are to be further handled and stored under conditions which minimize microbial growth. In many cases, the primary objective of pasteurization is to kill pathogenic microorganisms (e.g., pasteurization of milk). Some vegetative spoilage organisms can survive this heat treatment, and thus more severe preservation methods are needed if microbial spoilage is to be prevented. In other cases (e.g., beer), pasteurization serves primarily to kill vegetative spoilage organisms.

Other preservation methods used in conjunction with pasteurization include (1) refrigeration, (2) chemical additives which result in an undesirable environment for microbial growth (e.g., sugar in sweetened condensed milk, food

acids in pickles and fruit juices), (3) packaging (e.g., maintenance of anaerobic conditions in bottled beer), and (4) fermentation with desirable organisms.

The time-temperature treatment used in pasteurization depends on (1) the heat resistance of the particular vegetative or pathogenic microorganisms the process is designed to destroy and (2) the sensitivity of product quality to heat. The high-temperature and short-time (HTST) method involves a comparatively high temperature for a short time (e.g., 72° C for 1 s for milk), whereas the low-temperature and long-time procedure involves relatively low temperatures for longer times (e.g., 63°C for 30 min for milk). Optimization of the pasteurization process depends on the relative destruction rates of organisms as compared to quality factors, but generally the HTST process results in maximum product quality.

For market milk, pasteurization conditions are based on thermal destruction of *Coxiella burnetti*, the rickettsia organism responsible for Q fever. The thermal resistance parameters for this organisms are given in Table 6.5. For high-acid fruits, such as cherries, the pasteurization process is based on successful destruction of yeast or molds. For fermented beverages, such as wine or beer, destruction of wild yeasts is the pasteurization criterion.

D. Sterilization

A sterile product is one in which no viable microorganisms are present—a viable organisms being one that is able to reproduce when exposed to conditions optimum for its growth. Temperatures slightly above the maximum for bacterial growth result in the death of vegetative bacterial cells, whereas bacterial spores can survive much higher temperatures. Since bacterial spores are far more heat resistant than are vegetative cells, they are of primary concern in most sterilization processes.

Sterilization is not a good term to apply to thermal processing of foods since the criterion of success is the inability of microorganisms and their spores to grow under conditions normally encountered in storage. This means that there could be some dormant nonpathogenic microorganisms in the food (any pathogenic microorganisms are dead) but that environmental conditions are such that the organisms do not reproduce. Foods which have been thermally processed with this as the criterion are referred to as *commercially sterile*, *bacterially inactive*, or *partially sterile*.

The thermal conditions needed to produce commercial sterility depend on many factors, including (1) nature of the food (e.g., pH); (2) storage conditions of the food following the thermal process; (3) heat resistance of the microorganisms or spore; (4) heat transfer characteristics of the food, its container, and the heating medium; and (5) initial load of microorganisms.

The food being heated affects not only the type of organism on which the process should be based but also the resistance of the organism to heat energy. Food that is commercially sterile is generally present in a hermetically (gas-tight) sealed container to prevent recontamination. Since low oxygen levels are purposely achieved in most of these containers, microorganisms that require oxygen (obligate aerobes) are unable to grow sufficiently to pose spoilage or health problems. Also spores of most obligate aerobes are less heat resistant than are spores of organisms that are capable of growing under anaerobic conditions (facultative or obligate anaerobes). However, in canned, cured, meat products where oxygen is not completely removed and where a mild heat treatment is used in conjunction with other preservative methods (curing agents and/or refrigeration), such aerobes as *Bacillus subtilis* and *Bacillus mycoides* have been found to cause spoilage.

For processes based on inactivation of facultative or obligate anaerobes, pH of the food is a critical factor. There are some extremely heat-resistant spores that might survive a commercial process, but due to the low pH of the food they do not constitute a health or spoilage hazard. For thermal process design, foods are divided into three pH groups: (1) high-acids foods with pH values less than 3.7, (2) acid foods with pH values between 3.7 and 4.5, and (3) low-acid foods with pH values greater than 4.5. Tables 6.2 and 6.3 contain examples of foods in the acid and low-acid groups along with their pH values. Since spore-forming bacteria do not grow at pH values less than 3.7, heat processes for high-acid foods are generally based on inactivation of yeasts or molds. The pH value 4.5, which represents the dividing line between acid and low-acid foods, was carefully chosen to be slightly lower than the pH at which strains of *Clostridium botulinum* can grow and produce toxin. *Clostridium botulinum* is an obligate anaerobe which is widely distributed in nature and is assumed to be present on all products intended for canning. For low-acid canned foods the anaerobic conditions that prevail are ideal for growth of and toxin production by *C. botulinum*. This organism is also the most heat-resistant, anerobic, spore-forming pathogen that can grow in low-acid canned foods, and consequently its destruction is the criterion for successful heat processing of this type of product. There are several important strains of *C. botulinum* which produce toxin, the most heat-resistant spores being types A and B. The toxin is extremely potent (one millionth of a gram will kill man) but can be destroyed by exposing it to moist heat for 10 min at 100°C.

There exists a nontoxic obligate anaerobic sporeformer that is significantly more resistant to heat than *C. botulinum*, and it is used to determine safe thermal processes for low-acid foods. This mesophilic organism, identified only as putrefactive anaerobe (PA) 3679, resembles *Clostridium sporogenes*. Fortunately, contamination of food with the more heat-resistant strains of PA 3679 is minimal. PA 3679 instead of *C. botulinum* is used to determine process adequacy for low-acid foods because it is nontoxic, is easy to assay, and has suitable heat resistance.

TABLE 6.2 Canned Foods with pH Values Less than 4.5 (Acid Foods)

| Canned product | pH value | | |
|---------------------------|----------|---------|---------|
| | Average | Minimum | Maximum |
| Apples | 3.4 | 3.2 | 3.7 |
| Applesauce | 3.6 | 3.2 | 4.2 |
| Apricots | 3.9 | 3.4 | 4.4 |
| Blackberries | 3.4 | 3.3 | 3.5 |
| Cherries, black | 4.0 | 3.8 | 4.2 |
| Cherries, red sour | 3.5 | 3.3 | 3.8 |
| Cherries, Royal Ann | 3.8 | 3.5 | 4.0 |
| Cranberry sauce | 2.6 | 2.4 | 2.8 |
| Grape juice | 3.2 | 2.9 | 3.7 |
| Grapefruit juice | 3.2 | 2.8 | 3.4 |
| Lemon juice | 2.4 | 2.3 | 2.8 |
| Loganberries | 2.9 | 2.7 | 3.3 |
| Orange juice | 3.7 | 3.5 | 4.0 |
| Peaches | 3.8 | 3.6 | 4.0 |
| Pears, Bartlett | 4.1 | 3.6 | 4.4 |
| Pickles, fresh cucumber | 3.9 | 3.5 | 4.3 |
| Pickles, sour dill | 3.1 | 2.6 | 3.5 |
| Pickles, sweet | 2.7 | 2.5 | 3.0 |
| Pineapple juice | 3.5 | 3.4 | 3.5 |
| Plums, Green Gage | 3.8 | 3.6 | 4.0 |
| Plums, Victoria | 3.0 | 2.8 | 3.1 |
| Prunes, fresh prune plums | 3.7 | 2.5 | 4.2 |
| Raspberries, black | 3.7 | 3.2 | 4.1 |
| Raspberries, red | 3.1 | 2.8 | 3.5 |
| Sauerkraut | 3.5 | 3.4 | 3.7 |
| Strawberries | 3.4 | 3.0 | 3.9 |
| Tomatoes | 4.3 | 4.1 | 4.6 |
| Tomato juice | 4.3 | 4.0 | 4.4 |
| Tomato puree | 4.4 | 4.2 | 4.6 |

Source: Pflug and Esselen (1967).

In low-acid foods, processing could be based on inactivation of spores more heat resistant than those of *C. botulinum* since such spores do exist. Of greatest importance are facultative anaerobes such as *Bacillus stearothermophilus*. Spores of this organism are extremely heat resistant (up to 20 times more resistant than *C. botulinum* spores). Growth of these spores result in “flat sour” spoilage because

TABLE 6.3 Canned Foods with pH Values Greater than 4.5 (Low-Acid Foods)

| Canned product | pH value | | |
|--------------------------|----------|---------|---------|
| | Average | Minimum | Maximum |
| Asparagus, green | 5.5 | 5.4 | 5.6 |
| Asparagus, white | 5.5 | 5.4 | 5.7 |
| Beans, baked | 5.9 | 5.6 | 5.9 |
| Beans, green | 5.4 | 5.2 | 5.7 |
| Beans, lima | 6.2 | 6.0 | 6.3 |
| Beans and pork | 5.6 | 5.0 | 6.0 |
| Beans, wax | 5.3 | 5.2 | 5.5 |
| Beets | 5.4 | 5.0 | 5.8 |
| Carrots | 5.2 | 5.0 | 5.4 |
| Corn, whole grain, brine | 6.3 | 6.1 | 6.8 |
| Corn, cream style | 6.1 | 5.9 | 6.3 |
| Figs | 5.0 | 5.0 | 5.0 |
| Mushrooms | 5.8 | 5.8 | 5.9 |
| Olives, ripe | 6.9 | 5.9 | 8.0 |
| Peas, Alaska | 6.2 | 6.0 | 6.3 |
| Peas, sweet wrinkled | 6.2 | 5.9 | 6.5 |
| Potatoes, sweet | 5.2 | 5.1 | 5.4 |
| Potatoes, white | 5.5 | 5.4 | 5.6 |
| Pumpkin | 5.1 | 4.8 | 5.2 |
| Spinach | 5.4 | 5.1 | 5.9 |

Source: Pflug and Esselen (1967).

acid is produced but little or no gas. *Bacillus stearothermophilus* is sometimes referred to as FS (flat sour) 1518. Optimum growth temperatures for these flat sour thermophiles vary from about 49 to 55°C (120–131°F). Fortunately, most do not grow at temperatures below about 38°C (100°F). In the commercial processing of canned foods these types of microorganisms can be ignored provided the product is quickly cooled and stored below 110°F. This causes the organisms to remain in a dormant state.

For acid foods, thermal processes are usually based on facultative anaerobes, such as *Bacillus coagulans* (*B. thermoacidurans*), *B. mascerans*, and *B. polymyxa*. There are several obligate anaerobes that are important in food spoilage, but they are less heat resistant than the *Bacillus* organisms. For tomatoes and tomato products, destruction of *B. coagulans* is the basis of the thermal process. Summarized in Table 6.4 are sporeforming spoilage organisms that are important at various storage conditions and food pH values.

TABLE 6.4 Spore-Forming Bacteria Important in Spoilage of Canned Food

| Approximate temperature range for vigorous growth (°C) | Acidity of food | |
|--|--|---|
| | Acid | Low-acid |
| Thermophilic (> 40) | 3.7 < pH < 4.5 <i>B. coagulans</i> | pH > 4.5 <i>C. thermosaccharolyticum</i> <i>C. nigrificans</i> <i>B. stearothermophilus</i> |
| Mesophilic (40–10) | <i>C. butyricum</i> <i>C. Pasteurianum</i> <i>B. mascerans</i> <i>B. polymyxa</i> | <i>C. botulinum, A and B</i> <i>C. sporogenes</i> <i>B. licheniformis</i> <i>B. subtilis</i> |
| Psychrotrophic (35– <5) | | <i>C. botulinum E</i> |

Source: Ingram (1969).

III. INTERACTION OF HEAT ENERGY AND FOOD COMPONENTS

A. Introduction

In order to assess whether objectives of a thermal process have been accomplished, the food product must be tested. The test may be for surviving microorganisms, for active nutrients, or for such quality factors as color, texture, or flavor. If the outcome of the test indicates that the objective has been met, the process can be adopted. This was the procedure used to develop thermal processes before mathematical approaches and prediction of events were available, i.e., before reaction rates and their dependence on temperature were incorporated into procedures for establishing thermal processes. Use of these techniques has not totally replaced the experimental techniques since validity of the calculated process must be verified by actual testing. When the test procedure involves microorganisms, it is referred to as an inoculated pack.

Mathematical methods allow a process to be calculated based on known behavior of the system. In this instance, the system is the food and its components, and the response is the effect of heat on the components (including microorganisms). Two types of information are needed: (1) reaction rate constants for the particular component under conditions that prevail in practice and (2) dependence of the rate constants on temperature.

B. Reaction Kinetics

The basis of reaction kinetics used in thermal process design was introduced in the chapter on chemical kinetics. For continuity in this chapter, the principles will be briefly reviewed here.

As pointed out earlier, a majority of reactions occurring in foods obey well-established kinetics. The thermal destruction of microorganisms, most nutrients, quality factors (texture, color, and flavor), and enzymes generally obey first-order reaction kinetics. That is, the destruction rate of each of these components is dependent on the concentration of the component. This relationship is frequently referred to as *logarithmic order of inactivation or destruction* since regardless of the initial concentration, a constant fraction of the remaining substrate reacts per unit time. In other words, if at a given temperature the concentration reduces by 0.9 in 1 min, then 0.9 of the remaining concentration reacts in the next minute, 0.9 the third minute, and so on.

Since microorganisms are so important and are the basis of thermal process calculations, microbial inactivation is used here to illustrate first-order kinetics. Expressing the first-order response mathematically gives

$$\frac{-dc}{dt} = kc \quad (1)$$

where $-dc/dt$ is the rate at which concentration decreases, c is the concentration of viable microorganisms, and k is the first-order reaction rate constant.

Integrating Eq. (1) between limits, c_1 at $t_1=0$, and c at time t results in

$$-\int_{c_1}^c \frac{dc}{c} = k \int_{t_1}^t dt$$

$$-\ln c + \ln c_1 = k(t - t_1)$$

or

$$\log c = \log c_1 - \frac{kt}{2.303} \quad (2)$$

The graphical expression of Eq. (2) is shown in Figure 6.2. The initial concentration is $c_1 = 10^5$ survivors per unit volume. The number of survivors for any heating time can be obtained directly from the curve. The slope of the line is $-k/2.303$.

From our previous discussion of kinetics for thermal processing, the decimal reduction time (D -value) is used to describe time dependence of concentration. The D -value is the time required for the survivor curve to transverse one log cycle and corresponds to a 90% reduction in the number

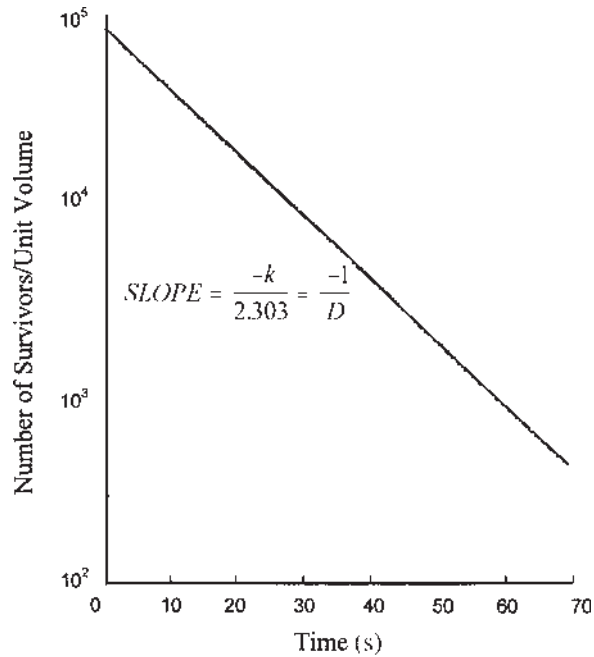


FIGURE 6.2 First-order destruction of microorganisms.

of survivors. The D value is related to the k value by

$$D = \frac{2.303}{k} \quad (3)$$

C. Temperature Dependence on Kinetics

In the chapter on chemical kinetics, three models for temperature dependence were presented: (1) Arrhenius model, (2) thermal death time model (TDT), and (3) Q_{10} model. The Arrhenius model and TDT model have both been used to develop mathematical models for thermal process calculations. The principles will be briefly reviewed here.

The dependence of reaction rate constants on temperature as described by the Arrhenius equation is

$$k = s \exp \frac{-E_a}{RT} \quad (4)$$

where

k is the reaction rate constant (min^{-1}).
 s is a constant, the frequency factor (min^{-1}).
 E_a is the activation energy (cal/mol).
 R is the gas constant (1.987 cal/K mol).
 T is the absolute temperature (K).

The frequency factors can be evaluated by letting the reaction rate constant be k_1 at temperature T_1 . Then,

$$s = k_1 \exp \frac{-E_a}{RT_1} \quad (5)$$

Substitution of Eq. (5) into Eq. (4) and taking the logarithm yields

$$\log \frac{k}{k_1} = \frac{-E_a}{2.303R} \left(\frac{1}{T} - \frac{1}{T_1} \right) = \frac{-E_a}{2.303R} \left[\frac{T_1 - T}{T_1 T} \right] \quad (6)$$

The thermal death time (TDT) method was introduced by Bigelow (see Ball and Olson, 1957), who observed that when the thermal death time (minimum time to accomplish a total destruction) was plotted vs temperature ($^{\circ}\text{F}$), a straight line resulted. Figure 6.3 is a typical thermal death time curve.

The following equation describes a TDT curve:

$$\log \left(\frac{TDT_1}{TDT_2} \right) = \frac{-(T_1 - T_2)}{z} = \frac{T_2 - T_1}{z} \quad (7)$$

where

TDT_1 is the thermal death time at temperature T_1 (min).
 TDT_2 is the thermal death time at temperature T_2 (min).
 T_1 is temperature 1 ($^{\circ}\text{F}$).
 T_2 is temperature 2 ($^{\circ}\text{F}$).
 z is the F temperature change required to change the TDT by a factor of 10.

The slope of a TDT curve, $-1/z$, is used to characterize the dependence of the reaction rate constant on temperature, and it is therefore related to E_a . The significance of z with respect to relative effects of temperature on reaction rates is readily illustrated. A small z value (say 10°F) indicates that the destruction time decreases by a factor of 10 for a 10°F temperature increase, whereas a large z value (say 50°F) indicates that the temperature must increase 50°F to reduce the destruction time by a factor of 10. Therefore, reactions that have small z values are highly temperature dependent, whereas reactions with large z values are less influenced by temperature.

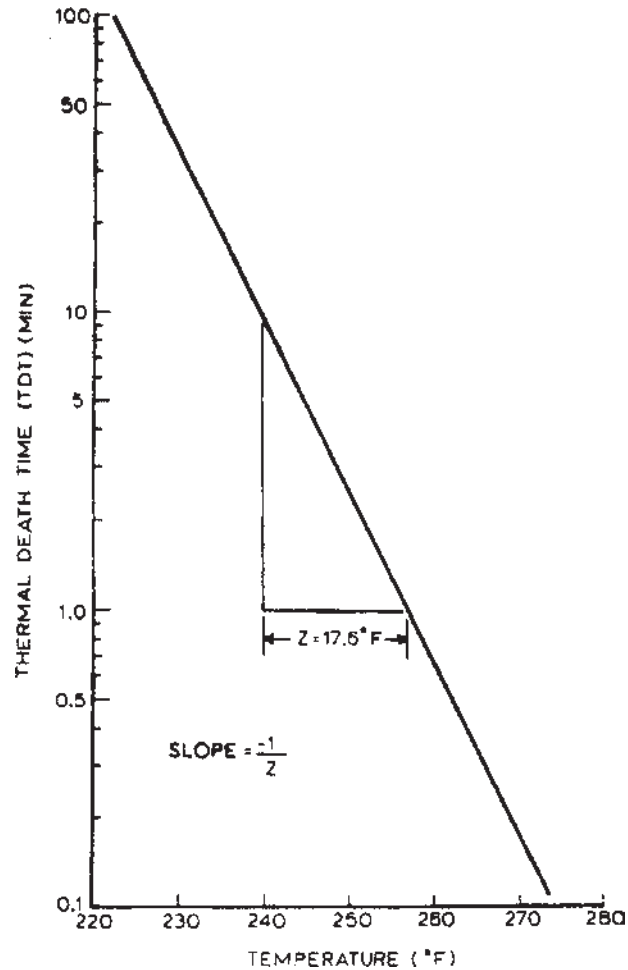


FIGURE 6.3 Thermal death time (TDT) curve of *Clostridium botulinum* in phosphate buffer. (From Esty and Meyer, 1922.)

For microbial inactivation the thermal death time is given the symbol F . Since the F value is dependent on temperature and is specific for one organism, it is usually identified with a superscript denoting the z value of the organism and a subscript denoting the temperature ($^{\circ}\text{F}$). Thus F_{250}^{18} denotes the thermal death time for a microorganism at 250°F that is characterized by $z = 18F$. Substituting

the F notation in Eq. (7) and using 250°F as a reference temperature yields.

$$\log \frac{F_T^z}{F_{250}^z} = \frac{250 - T}{z} \quad (8)$$

An equation similar to Eq. (8) also can be developed for the decimal reduction value of a food component. If this is done, the procedure is referred to as the thermal resistance method and the resulting curve is called a *thermal resistance curve*. This curve describes the effect temperature has on the time to reduce the concentration of the component 90%. The thermal resistance equation is

$$\log \frac{D}{D_1} = \frac{(T_1 - T)}{z} \quad (9)$$

Since k and D are related by Eq. (3), substitution into Eq. (9) results in

$$\log \frac{k_1}{k} = (T_1 - T)/z \quad (10)$$

or

$$\log \frac{k}{k_1} = \frac{1}{z}(T - T_1) \quad (11)$$

Equation (11) states that the logarithm of the reaction rate constant is directly proportional to temperature. This appears to be in direct contradiction to Eq. (6), which states that the logarithm of the reaction rate constant is inversely proportional to temperature. This apparent contradiction has concerned investigators for many years. The basis of thermal processes was traditionally the TDT method, but it could not be reconciled with reaction kinetic theory (Arrhenius method). However, if it is recognized that over small temperature ranges $T \propto \frac{1}{T}$, then the systems are reconcilable.

The relationship between E_a and z can be obtained by equating Eqs. (6) and (11) and changing °F in Eq. (11) to K. Then

$$\frac{-E_a}{2.303R} \left(\frac{T_1 - T}{T_1 T} \right) = \left(\frac{T - T_1}{z} \right) \frac{9}{5} = \frac{-(T_1 - T)9}{z5} \quad (12)$$

Rearrangement yields

$$E_a = \frac{2.303RTT_1}{z} \left(\frac{9}{5} \right) \quad (13)$$

where

T_1 is the reference temperature (K).

T is the temperature (K).

$1/z$ is the slope of the TDT curve °F.
 $9/5$ is the conversion °F to K.
 R is the gas constant (1.987 cal/mol K).
 E_a is the activation energy (cal/mol).

It is noteworthy that Eq. (13) is dependent on a reference temperature even though both z and E_a are independent of temperature. This dependence on reference temperature results from the fact that the relationship between reciprocal absolute temperature (K^{-1}) and temperature (°F) is defined for a small temperature range about a reference temperature. The relationship between E_a and z for reference temperature of 210 and 250°F is shown in Figure 6.4. The value of T was chosen z °F less than T_1 .

D. Thermal Destruction of Microorganisms

As mentioned, when microorganisms are subjected to moist heat at temperatures slightly above the maximum growth temperature, reduction of viable cells or

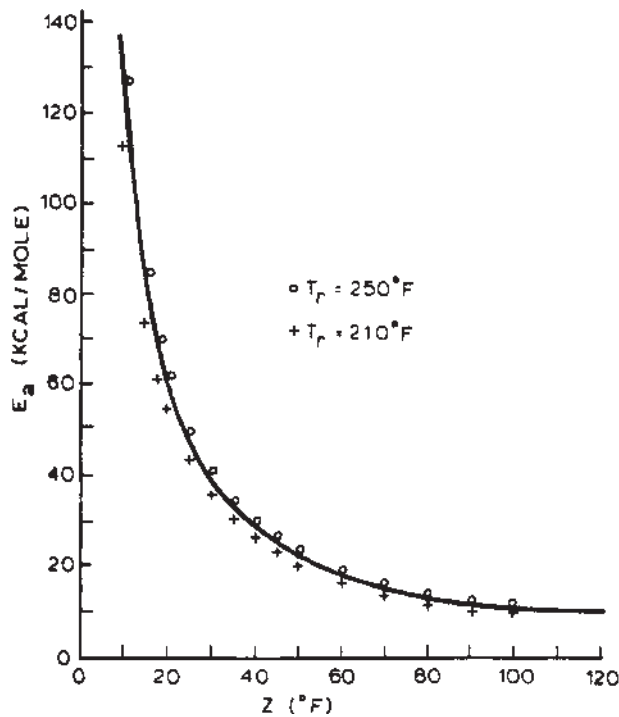


FIGURE 6.4 Relationship between activation energy (E_a) and z value.

spores generally follows first-order kinetics. There are several factors which can cause deviation from the logarithmic order of death but deviations usually involve factors other than a change in the order of destruction. For a discussion of these factors, see Stumbo and Longley (1966).

Many explanations have been suggested to account for the logarithmic order of death of bacteria. One of the most popular is that offered by Rahn (1945) who has suggested that loss of reproductive ability is due to the denaturation of one gene or a protein essential to reproduction. This is consistent with first-order kinetics observed when microorganisms are inactivated by heat, chemicals, or radiation. Although there is evidence that other models for inactivation of microorganisms also accurately describe time dependence for thermal inactivation, first-order kinetics continues to be used since it has passed the test of time. Furthermore, since thermal inactivation of all microorganisms can be described by the same kinetics this simplifies comparison of the heat resistance of different species at a given temperature and, more importantly, to different temperatures.

There are two important concepts to gain from the logarithmic relationship for inactivation of bacteria: (1) the smaller the initial concentration of bacteria, the less the heating time needed to achieve a given final concentration; (2) the survivor curve never reaches zero population. The first concept is extremely important since it implies that a standard heat treatment given a product may be insufficient depending on initial population. It is therefore necessary at each stage of food preparation prior to heat treatment to minimize contamination. The attitude that a standard thermal process can take care of any microbial population is erroneous but difficult to eradicate.

The second concept, that the microbial population may approach but never attain zero, can be easily illustrated. If the initial concentration of a suspension is 10^4 spores/ml, then for each D minutes the suspension is heated the population is reduced 90% as shown below.

| Duration of heating (min) | Number of spores present during heating |
|------------------------------|--|
| 0 | 10^4 |
| D | 10^3 |
| $2D$ | 10^2 |
| $3D$ | 10^1 |
| $4D$ | 10^0 |
| $5D$ | 10^{-1} |
| $6D$ | 10^{-2} |

The meaning of the negative powers becomes readily apparent when interpreted in terms of probability of survival. Suppose, for example, that

100 experiments are run under the same conditions. Then 1/10 survival means that 10 out of 100 samples heated for $5D$ min have one surviving spore per sample. Similarly 1/100 survival obtained after $6D$ min means that one sample out of 100 contains a surviving spore. The concept of probability of survival is extremely important when one considers the number of cans of thermally processed products that reach the consumer yearly.

1. Factor Affecting Thermal Resistance

It has been pointed out in Sec. II.D that spores are more heat resistant than vegetative cells and that spores of different species exhibit a wide range of heat resistance. For thermal process calculations in nonacid foods, the heat process is based on the resistance of spores. Many factors affect the thermal resistance of microorganisms, and failure to consider all of these factors has contributed to conflicting results. The three general types of factors affecting thermal resistance of microorganisms are (1) inherent resistance, (2) environment influences active during growth and formation of cells or spores, and (3) environmental influences active during the time of heating cells or spores.

Inherent resistance is illustrated by the fact that different strains of the same species prepared under the same conditions exhibit widely different degrees of resistance. Those spores or cells with the greatest resistance are believed to contain proteins with the greatest stability.

Conditions present during sporulation or growth which affect heat resistance are (1) temperature, (2) ionic environment, (3) organic compounds other than lipids, (4) lipids, and (5) age or phase of growth of the culture (Stumbo and Longley, 1966).

1. Temperature. Effect of growth temperature on resistance of microorganisms has been studied extensively. Generally spores produced at higher temperature are more heat resistant than those produced at lower temperatures.
2. Ionic environment. Although the ionic environment affects spore resistance, there is no general trend. Ions shown to influence spore resistance are calcium, magnesium, iron, phosphates, manganese, sodium, and chloride. Since salts can influence resistance, the exact composition of the growth medium should be specified.
3. Organic compounds other than lipids. The presence of various organic compounds has been shown to influence the resistance of microorganisms to heat. Again, no general inference can be drawn except to reemphasize that specification of conditions for producing the spores or cell suspension is a prerequisite for obtaining reliable, interpretable data.

4. Lipids. Sugiyama (1951) reported that *C. botulinum* spores exhibited increased heat resistance when low concentrations of certain saturated or unsaturated fatty acids were present during sporulation.
5. Age or phase of growth of the culture. For spores, there is little evidence that the age of the spores influences heat resistance. For vegetative cells, it has been generally observed that growth phase affects thermal resistance, but no rule of thumb can be applied. Some investigators have found that young cells are more susceptible to heat destruction than older, more mature cells; others have found that resistance increases during the early logarithmic phase; and still others have reported that resistance increases during the initial stationary phase, decreases when reproduction begins, and arrives at a minimum during the logarithmic growth phase (Stumbo 1973). Thus, for vegetative cells, there is sufficient evidence to suggest that the phase of growth should be specified when thermal resistance is reported.

The third group of factors are the environmental influences active during the heat treatment; (1) pH and buffer components, (2) ionic environments, (3) water activity, and (4) composition of the medium.

1. pH and buffer components. Generally spores are less heat resistant at pH extremes than near neutrality. Optimal resistance may be exhibited at slightly alkaline or acidic pH depending on the species, but most species of significance are more resistant in slightly acidic conditions. As pointed out in Sec. II.D, pH of the food product dictates the microorganism to be used for the basis of the thermal process. Buffer constituents have been shown to influence heat resistance of microorganisms, but generalizations are not possible.
2. Ionic environment. Presence of ionic species has been shown to influence spore resistance, but reports are conflicting and generalities are difficult to make. In phosphate buffer, low concentrations of magnesium or calcium reduced spore resistance, as did the presence of chelating agents, such as EDTA (ethylene diamine tetraacetic acid) or glycylglycine. Early reports claimed that sodium chloride increased spore resistance, but the results could not be duplicated. At levels present in foods it is doubtful that sodium chloride has any effect on resistance.
3. Water activity. Spores are much more resistant to dry heat than to moist heat. This difference is related to the mechanisms of spore destruction in the two environments: denaturation of protein in moist heat and oxidation in dry heat. Since oxidation requires greater energy input than denaturation, equivalent time-temperature treatments for dry and moist heat result in greater destruction with moist heat. For example,

dry spores of *C. botulinum* can be inactivated in 120 min at 120°C dry gas heat, but inactivation is achieved in only 4–10 min at 121°C in moist heat.

4. Composition of the medium. The carbohydrate, protein, and lipid contents of the substrate; the presence of colloidal systems, such as emulsions or foams; and the presence of other organic or inorganic compounds can influence the apparent thermal resistance of microorganisms. The response of the microorganism to heat while present in a specified medium depends on the microorganism, and generalities are once again subject to exceptions. However, at the risk of oversimplification, some trends are apparent. High concentrations of soluble carbohydrates generally result in increased thermal resistance. Although the mechanism of the protecting action is obscure, some have suggested that the increased resistance is due to passive dehydration of the protoplasm. This apparently is not the only protective mechanism since protection is not proportional to molarity of the carbohydrate. Proteins likewise have protective effects, as do lipids. In dry fat, organisms may show a pronounced increase in resistance presumably due to the localized absence of moisture. With increased salt concentration and in the presence of germicidal or antibiotic substances, thermal resistance generally decreases.

Although all of the factors previously mentioned affect the thermal resistance of microorganisms directly, there is still one other critical factor: the outgrowth medium used after thermal processing. Usually the microorganisms are incubated in the heating medium to determine whether there are survivors, and this automatically establishes the culture environment. However, agents which inhibit germination may be present as a result of heating, and this may produce misleading information about thermal resistance. Thus the supposed resistance may be due to inhibition of germination after heating rather than the direct action of heat energy. To overcome this problem, the culture is sometimes transferred to a new medium (subculture) following completion of heating. If a subculture is used, its nature should be reported in detail.

In summary, the thermal resistance of microorganisms is dependent on many factors, each of which must be considered and reported. To increase the reliability and usefulness of thermal destruction data, the National Food Processors Association has published procedures for preparation of spore and cell suspensions (Olson and Stevens, 1939).

2. Methods of Measuring Resistance

In the time that food microbiologists have been measuring thermal resistance of microorganisms several techniques have been developed for obtaining data.

Generally the techniques consist of putting the inoculated menstroom into containers and then subjecting the containers to a thermal treatment. Since the object is to describe the response of the microorganism to a particular time-temperature treatment, primary emphasis has been devoted to the design of heating vessels where thermal lags in heating and cooling are minimized. The glass tube method (7 mm i.d. Pyrex), the capillary tube method (0.8 mm i.d.), and the can method (208 × 006) (63 mm diameter × 9.53 mm height) are the most popular systems. Pflug and Schmidt (1968) and Stumbo (1973) have discussed the advantages and disadvantages of the various methods for obtaining thermal resistance data.

Interpretation and reliability of thermal-resistance data are dependent on the method of obtaining the data. Although the first impression may be that determination of thermal resistance is a relatively easy task, this is not true. Considerable effort is required to generate a standard spore or cell suspension, to perform the series of heat treatments (which requires replication at several temperatures), and to analyze the data.

As stated in Sec. II.D, the thermal process applied to a food is based on the most heat resistant microorganism that could present a health hazard or cause spoilage if it should grow following the thermal process. Summarized in Table 6.5 are the approximate resistance of bacterial spores of importance in foods.

Although the D value can be used for comparative purposes, a parameter defining the thermal process should describe the total reduction in population that must be accomplished. Since thermal destruction is logarithmic, total destruction theoretically cannot be accomplished. However, the probability of survival can be reduced to some small nonzero level. The question is what should that level be? For nonacid foods the thermal process was based on the reduction of *C. botulinum* and on the classic work of Esty and Meyer (1922). Esty and Meyer experimented with the largest concentration of spores of *C. botulinum* they could effectively manipulate in buffer, and it was assumed that this was equivalent to 10^{12} spores per milliliter. The indicated thermal death time at (121°C) for reduction to $10^0 (= 1)$ survivors in phosphate buffer was 2.78 min. Later Townsend et al. (1938) corrected these data for thermal lag and reported a heating time of 2.45 min at 121°C to reduce the population by a factor of 10^{12} . Use of a heating time at 121°C to reduce the population by a given factor is a very convenient way of comparing heat treatments which a product may receive. While the D value gives the time for the reduction of 90% of the population, the F value gives the time to reduce the population by a multiple of the D value. The F value is the thermal death time as defined in Eq. (8). For *C. botulinum* the F value represents the heating time necessary to reduce the population by a factor of 10^{12} (12 D values) at 121°C. When $z = 10C$ (*C. botulinum*) and the temperature is 121°C, the symbol F_0 is used. Since the F_0 value describes the time to reduce the population by a factor of 10^{12} and the D value describes the time to reduce

the population by a factor of 10^1 , then

$$F_o = D \log \frac{a}{b} \quad (14)$$

where a is initial number of microorganisms and b is final number of microorganisms. With *C. botulinum*, $F_o = 12D$.

A thermal process equivalent to the F_o of *C. botulinum* is referred to as the *bot cook* and the destruction of 10^{12} spores as the *12D concept*. To restate the *12D* concept, if 1000 *C. botulinum* spores (estimated maximum) were in each container of low-acid food then the incidence of survival of *C. botulinum* following a *12D* process would be less than one in 10^9 containers. At first this may seem to be gross overprocessing and that the probability of survival can be increased. However, when it is realized that United States' production alone amounts to billions of cans of low-acid foods, the *12D* concept is justified.

Sometimes the situation exists wherein products which receive a thermal process sufficient to inactivate spore-forming pathogens exhibit high spoilage rates as a result of growth of mesophilic spore-forming bacteria. In this case, such microorganisms as those listed in Table 6.4 are used as the basis of the process. They exhibit D_{250} values on the order of 1 min. For a *12D* process, this would result in an F_o of 12 min. A thermal process based on this F_o value would result in a product of low quality due to the many heat-induced physical and chemical changes. Consequently, the process is based on keeping the frequency of spoilage at a level economically tolerable to the processor. Most processors would like to keep spoilage rates at less than one container per thousand. To assure that this is not exceeded, a *5D* value can be used for the process. This results in

$$F_o = 1.0(5) = 5.0 \text{ min}$$

When the *5D* process based on a mesophilic spore-forming bacterium is used, it is necessary to verify that the F value is at least equivalent in lethality to a *12D* process based on the most heat-resistant spore-forming pathogenic microorganism presumed present in the food.

When canned foods are stored at high temperatures where thermophillic anaerobes can cause spoilage, the thermal process must be extremely severe. From Table 6.5 the D_{250} value for *C. thermosaccharolyticum* is on the order of 3–4 min. and thus for a *5D*₂₅₀ process.

$$F_o = 4(5) = 20 \text{ min}$$

Under these circumstances it is imperative to use preventive measures for minimizing microbial load on the product since a process of this severity must be very damaging to product quality.

The multiple of D used in thermal processing has been termed the *order of the process* factor. A factor of 12 is used for commercial processing of low-acid

TABLE 6.5 Thermal Resistance Characteristics of Spore-Forming Microorganisms Used as a Basis of Thermal Processing

| Organism | <i>z</i> value (°F) | <i>D</i> ₁₂₁ value (min) |
|---------------------------------------|---------------------|-------------------------------------|
| <i>B. stearothermophilus</i> | 12.6 | 4.0 |
| <i>B. subtilis</i> | 13.3–23.4 | 0.48–0.76 |
| <i>B. cereus</i> | 17.5 | 0.0065 |
| <i>B. megaterium</i> | 15.8 | 0.04 |
| <i>C. perfringens</i> | 18.0 | B |
| <i>C. sporogenes</i> | 23.4 | 0.15 |
| <i>C. sporogenes</i> (PA 3679) | 19.1 | 0.48–1.4 |
| <i>C. botulinum</i> | 17.8 | 0.21 |
| <i>Coxiella burnetti</i> ^b | 8 | B |
| <i>C. thermosaccharolyticum</i> | 16–22 | 3.0–4.0 |

Source: Lund (1975).

foods, whereas a factor of 5 or less is used when mesophilic spore-forming bacteria or thermophilic spore-forming bacteria are the most heat-resistant organisms of concern.

E. Thermal Destruction of Enzymes

Before considering methods of calculating thermal processes for foods, the effect of time-temperature treatments on enzymes and other food components should be discussed. With enzymes, the objective of the thermal process generally is inactivation, whereas with nutrients and other quality attributes, such as flavor, color, or texture, the objective is maximum retention. In order to compare the total effect of equivalent heat processes it is necessary to know the response of each component of the food to thermal energy.

The thermal stabilities of enzymes are, like those of microorganisms, dependent on many factors. In fact the same factors that affect microbial inactivation can be expected to affect enzyme inactivation since the most popular theory dealing with microbial inactivation holds that denaturation of a critical gene or protein causes loss of reproductive ability. A complete review of enzyme inactivation by heat is not necessary here; however, knowledge of the relative dependence of enzyme inactivation on temperature is essential. Whitaker (1972) has discussed the effect of heat on enzymes in great detail.

The dependence of enzyme inactivation on temperature can be expressed in the same ways that have been used for microorganisms, i.e., with *D* and *z* values. For most enzymes the *D* and *z* values are the same order of magnitude as those for microorganisms. However, there are some heat-resistant isozymes causing off

flavor and off color which exhibit unusually great thermal resistance. For these heat-resistant isozymes the z value may be as much as two to four times greater than those for the heat-labile isozymes. For example, Adams and Yawger (1961) have reported that peroxidase in peas has a z value of 30°C (55°F) ($E_a = 20$ kJ/mol). A denaturation reaction characterized by such a low activation energy indicates that the active site of the protein is dependent on few bonds, perhaps a disulfide bond [e.g., the activation energy for H_2S formation from corn is on the order of 30 kJ/mol (Whitaker, 1996), or four to five H bonds ($E_a = 5$ kJ/mol each)].

In thermal process calculations based on enzyme inactivation, the most heat-resistant enzyme which can alter product quality during storage is selected as the basis of the process, just as the most heat-resistant pathogenic or spoilage organism is used for microbial inactivation. To reiterate the point made in the discussion of blanching, generally peroxidase or catalase is selected as the basis of the process.

F. Thermal Destruction of Nutrients and Quality Factors

It is evident from a TDT curve of microorganisms that there are an infinite number of time-temperature combinations that can produce commercial sterility. Part of the responsibility of the food processor is not only to produce a commercially sterile product but also to provide a product that is wholesome and retains nutritional and quality attributes to a maximum degree. To accomplish this objective, the processor must be aware of the relative changes in nutrients and quality factors as a function of the time-temperature treatment.

Many of the same factors that accelerate or inhibit microbial destruction by heat also affect nutrient destruction. If one of the requirements of a thermal process is retention of a particular nutrient, it is necessary to establish the kinetics of its degradation in the system and the dependence of the rate constant on temperature.

Presented in Table 6.6 is a summary of the reaction rate-temperature relationship for microorganisms, enzymes, nutrients, and a few quality attributes. Thiamine is the most thoroughly investigated nutrient in food systems, and activation energies and relative reaction rates in foods are fairly abundant. As is to be expected, the activation energies characterizing the degradation of nutrient and quality factors are similar to those for chemical reactions.

A striking pattern emerging from Table 6.6 is that the z values for nutrient and quality-factor destruction are larger than for microorganisms or heat-labile enzymes. That is, a given increase in temperature causes a larger increase in the rate of destruction of microorganisms than in the rate of destruction of nutrients or quality factors. This situation is exploited to good advantage in high-temperature and short-time processing (e.g. 270°C for a few seconds). At 270°C the rate of destruction of microorganisms would be at least tenfold ($z = 10\text{C}$) greater, and

TABLE 6.6 Kinetic Parameters for the Thermal Degradation of Food Components

| Component | Medium | pH ^a | Temperature range (°F) | z (°F) | E _a (kcal/mol) | D _{121^b} | Other |
|---------------------|----------------------------|-----------------|------------------------|--------|---------------------------|------------------------------|-------------|
| Thiamine | Whole peas | Nat. | 220–270 | 47 | 21.2 | 164 min | |
| Thiamine | Carrot puree | 5.9 | 228–300 | 45 | 27 | 158 min | |
| | Green bean puree | 6.6 | 228–300 | 45 | 27 | 145 min | |
| | Spinach puree | 6.5 | 228–300 | 45 | 27 | 134 min | |
| | Beef heart puree | 6.1 | 228–300 | 45 | 27 | 115 min | |
| | Beef liver puree | 6.1 | 228–300 | 45 | 27 | 124 min | |
| | Lamb puree | 6.2 | 228–300 | 45 | 27 | 120 min | |
| | Pork puree | 6.2 | 228–300 | 45 | 27 | 157 min | |
| Thiamine | Phosphate buffer | 6.0 | 250–280 | 45 | 29.4 | 156.8 min | |
| | Pea puree | Nat. | 250–280 | 48 | 27.5 | 246.9 min | |
| | Beef puree | Nat. | 250–280 | 48 | 27.5 | 254.2 min | |
| | Peas-in-brine puree | Nat. | 250–280 | 49 | 27.0 | 226.7 min | |
| Thiamine | — | — | — | 56 | 20.0 | — | |
| Riboflavin | — | — | — | 50 | 23.0 | — | |
| B ₁ -HCl | Liquid multivita-min prep. | 3.2 | 39–158 | 44.5 | 26 | 1.35 days | |
| d-Pantothenic acid | Liquid multivita-min prep. | 3.2 | 39–158 | 56 | 21 | 4.46 days | |
| C | Liquid multivita-min prep. | 3.2 | 39–158 | 50 | 23.1 | 1.12 days | |
| B ₁₂ | Liquid multivita-min prep. | 3.2 | 39–158 | 50 | 23.1 | 1.94 days | |
| Folic acid | Vitamin prep. | 3.2 | 39–158 | 66 | 16.8 | 1.95 days | (continued) |

TABLE 6.6 Continued

| Component | Medium | pH ^a | Temperature range (°F) | z (°F) | E _a (kcal/mol) | D ₁₂₁ ^b | Other |
|--------------------------|-------------------|-----------------|------------------------|--------|---------------------------|-------------------------------|------------------------------------|
| A | | | | | | | |
| Inosinic acid | Vitamin prep. | 3.2 | 39–158 | 72 | 14.6 | 12.4 days | |
| IMP | Buffer soln. | 3 | 140–208 | 34 | 34.0 | — | |
| IMP | Buffer soln. | 4 | 140–208 | 38.5 | 30.4 | — | |
| IMP | Buffer soln. | 5 | 140–208 | 30.4 | 28.1 | — | |
| Chlorophyll ^a | Spinach | 6.5 | 260–300 | 92 | 15.5 | 13.0 min | |
| Chlorophyll ^b | Spinach | 5.5 | 260–300 | 143 | 7.5 | 14.7 min | |
| Chlorophyll | Pea puree | Nat. | 240–280 | 66 | 16.1 | 14.0 min | Blanched |
| Chlorophyll | Pea puree | Nat. | 240–280 | 81 | 12.6 | 13.9 min | Unblanched |
| Chlorophyll | Pea puree | 6.5 | 175–280 | 52 | 22 | 113 min | |
| Chlorophyll | Pea puree | 6.5 | 175–280 | 59 | 18 | 116 min | |
| Chlorophyll ^a | Spinach puree | — | 32–122 | 143 | 7.5 | — | |
| Chlorophyll ^b | Buffer soln. | — | 32–122 | 125 | 9.0 | — | |
| Chlorophyll | Buffer soln. | Nat. | 190–212 | 84 | 12.0 | 10.1 min | |
| Color ^(-a/b) | Peas | Nat. | 175–300 | 71 | 15.0 | 25.0 min | |
| | Asparagus | Nat. | 175–300 | 75 | 14.0 | 17.0 min | |
| | Green beans | Nat. | 175–300 | 70 | 15.0 | 21.0 min | |
| Quality by taste panel | Whole kernel corn | Nat. | 175–300 | 57 | 19.5 | 6.0 min | Time for taste panel to judge |
| | Whole peas | Nat. | 175–300 | 51 | 22.5 | 2.3 min | 4.0/9.0 compared to frozen control |
| | Whole green beans | Nat. | 175–300 | 52 | 22.0 | 4.0 min | |
| Chlorophyll ^a | Spinach | Nat. | 212–266 | 81 | 12.5 | 34.1 min | |
| Chlorophyll ^b | Spinach | Nat. | 212–266 | 106 | 10.0 | 48.3 min | |

| | | | | | | | |
|----------------------------------|-----------------------|---------|---------|------|------|-----------|----------------------------|
| Maillard Rxn. | Apple juice | Nat. | 100-266 | 45 | 27.0 | 4.52 hr | |
| Nonenzymatic browning | Apple juice | Nat. | 100-266 | 55 | 20.7 | 4.75 hr | |
| B ₁ | Pork | Nat. | ?-250 | 57.6 | 19.5 | 6.03 hr | |
| Anthocyanin | Grape juice | Nat. | 68-250 | 41.7 | 28.0 | 17.8 min | |
| | Boysenberry | Nat. | 68-250 | 55.7 | 20.0 | 102.5 min | |
| | Strawberry juice | Nat. | 68-250 | 59.8 | 19.0 | 110.3 min | |
| Cyanidin-3-rutinoside | Citrate buffer | 4.5 | 170-225 | 49 | 23.7 | 28.5 min | |
| | Plum juice | 4.5 | 170-225 | 50 | 23.1 | 41.6 min | |
| Peonidin-3-rutinoside | Citrate buffer | 4.5 | 170-225 | 44.5 | 26.2 | 21.6 min | |
| | Plum juice | 4.5 | 170-225 | 46 | 22.1 | 27.7 min | |
| Carotenoids | Paprika | Nat. | 125-150 | 34 | 34.0 | 0.038 min | |
| Betain | Buffer | 5.0 | 122-212 | 81 | 12.5 | 19.5 min | |
| | Beet juice | 5.0 | 122-212 | 106 | 10.0 | 46.6 min | |
| Browning | Goat's milk | 6.5-6.6 | 200-250 | 45 | 27.0 | 1.08 min | Homogenized |
| | Goat's milk | 6.5-6.6 | 200-250 | 45 | 27.0 | 0.91 min | Unhomogenized |
| Methyl methionine | Sodium citrate buffer | 6.0 | 178-212 | 33.5 | 34.8 | 8.4 min | |
| Sulfonium | Sweet corn | 6.9 | 178-212 | 37 | 31.6 | 4.5 min | |
| Bromide | Tomato | 4.4 | 178-212 | 45 | 27.2 | 23.2 min | |
| Lysine | Soybean meal | — | 212-260 | 38 | 30.0 | 13.1 hr | |
| Texture and overall cook quality | Peas | Nat. | 170-200 | 58 | 19.5 | 1.4 min | Time to acceptable product |
| | Peas | Nat. | 210-240 | 58 | 19.5 | 2.5 min | |
| | Beets | Nat. | 180-210 | 34 | 34.0 | 2.0 min | |
| | Whole kernel corn | Nat. | 212-250 | 66 | 16.0 | 2.4 min | |

(continued)

TABLE 6.6 Continued

| Component | Medium | pH ^a | Temperature range (°F) | z (°F) | E _a (kcal/mol) | D ₁₂₁ ^b | Other |
|--|--------------|-----------------|------------------------|--------|---------------------------|-------------------------------|---|
| Trypsin inhibitor Peroxidase <i>C. botulinum</i> | Broccoli | Nat. | 212–250 | 80 | 13.0 | 4.4 min | |
| | Squash | Nat. | 182–240 | 46 | 25.0 | 1.5 min | |
| | Carrots | Nat. | 176–240 | 30 | 38.0 | 1.4 min | |
| | Green beans | Nat. | 182–240 | 28 | 41.0 | 1.0 min | |
| | Potato | Nat. | 161–240 | 42 | 27.5 | 1.2 min | |
| | Soybean milk | Nat. | 200–250 | 60 | 18.5 | 13.3 min | |
| | Whole peas | Nat. | 230–280 | 67 | 16.0 | 3.0 min | |
| | Growth | 6.2 | 125–135 | 44 | 26.4 | | Temperature dependent activation energy |
| Toxin-type E | Media | 6.2 | 135–140 | 22 | 57.4 | 3.0 min at 60°C | |
| Staphylococcus enterotoxin B | Media | 6.2 | 140–145 | 6 | 153.5 | | |
| | Milk | 6.4–6.6 | 210–260 | 44 | 25.9 | 9.4 min | |
| <i>C. botulinum</i> spores (types A and B) | Variety | > 4.5 | 220–? | 12–19 | 64–82 | 0.1–0.2 min | |
| | Variety | > 4.5 | 230–? | 12–22 | 53–82 | 4.0–5.0 min | |

^a Nat. indicates the natural pH of the system.

^b D value at 121°C.

Source: Lund (1975).

the rate of destruction of nutrients and quality factors would be only two to threefold greater than at a standard temperature of 121°C.

D values for thermal destruction of various nutrients and quality factors are more dependent on environmental conditions than are z values. Therefore, such conditions as pH and composition of medium must be specified when D values are reported. From Table 6.6 it can be seen that D values for nutrients and quality factors are generally 100–1000 times greater than those for microorganisms. For example, for *C. botulinum* the D_{121} value is 0.1–0.2 min, whereas for thiamine the D_{121} value is on the order of 150 min. The fact that microorganisms have much smaller D values than do quality factors and nutrients permits foods to be sterilized by heat without total destruction of quality and wholesomeness factors. If the D values for nutrients and quality factors were essentially equal to those for microorganisms and a $12D$ process were used, then a product containing N mg nutrient at the start of the process would contain $N \times 10^{-12}$ mg at the end of the process and would be nutritionally worthless. The z and D_{121} values of nutrients and quality factors also can be used to optimize thermal processes for nutrient or quality-factor retention, as is shown in Sec. VI.A.

IV. HEAT PENETRATION INTO FOODS

A. Introduction

The basic principles of heat transfer in food processing were presented in Chapter 3 on heat transfer. The specific application to thermal process design will be briefly represented here.

In order to calculate the effectiveness of a thermal process two items of information are needed: (1) the thermal resistance characteristics of the microorganism used as the basis of the process (z and F value) and (2) the temperature history of the product. Thermal processing of food is accomplished in one of two ways. Either the food is heated to accomplish commercial sterility and then placed in a sterile container and sealed, or the food is placed in a container, sealed, and then heated. The first method is referred to as aseptic processing, whereas the second corresponds to conventional canning.

If a sealed container of product at low temperature is placed in a vessel and the vessel is filled with steam at high temperature, the steam condenses on the container and the latent heat of condensation is transferred through the wall of the container and into the product. The process involves unsteady-state heat transfer since there is no point in the container where the temperature is constant. In this situation, the temperature at any point in the container is a function of (1) the surface heat-transfer coefficient, (2) the physical properties of the product and container, (3) the difference between the steam temperature and the initial temperature of the product, and (4) the size of the container. For thermal

processing in condensing steam it is reasonable to assume that the surface heat transfer coefficient is very large compared to the thermal conductivity of the product and, therefore, the only resistance to heat transfer is the product.

The rate of heat penetration into the container is dependent on the mechanism of heat transfer within the product. Some food products are relatively nonviscous or contain small particles in brine. These products exhibit relatively rapid heat penetration because natural convection currents occur in the container. The natural convection currents can be aided by rotating or agitating the can, thus increasing the heating rate. This approach is used in continuous retorts (Sec. VI.B).

Extremely viscous or solid food products heat primarily by conduction. For these products, the charts developed for unsteady-state heat transfer can be used to predict the temperature-time heating curve (see Chapter 3 on heat transfer). Examples include cream style corn, pumpkin, most thick pureed vegetables, potato salad, baked beans, and most intact food tissues.

Finally, there are products in which the mode of heat transfer changes from convection to conduction during heating. Since convection heating is much faster than conduction heating, these products exhibit a change in the rate of heating, and a plot of temperature vs heating time shows an abrupt change in temperature rise. This is referred to as a *broken heating curve*. Foods containing significant quantities of starch that gels upon heating exhibit this behavior. Examples of products exhibiting broken heating curves are cream-style corn (when the starch has not been gelatinized prior to initiating the thermal process), soups, and noodle products.

B. Determination of Time–Temperature Profile for Thermal Process Calculations

Since commercial sterility must be assured throughout the container, process evaluation is based on the slowest heating point in the container. It is then assumed that if the slowest heating point receives a heat process sufficient to accomplish commercial sterility then all other points have received an equal or greater thermal process and are also commercially sterile. For conduction heating foods the center is the slowest heating point in the container since it is the farthest point from the heat source. For convection heating products, however, the center is not the slowest heating point. The slowest heating point (cold point) for convection heating products in cans is located on the vertical axis near the bottom of the container. These differences are illustrated in Fig. 6.5. For those products in which the mode of heat transfer changes, causing broken heating curves during heating, it is difficult to predict the point at which heating occurs most slowly, and therefore, this point must be determined experimentally. If a thermal process is being designed for a new product, it is advisable to determine the cold point in the container. This is done by placing a series of thermocouples along the vertical

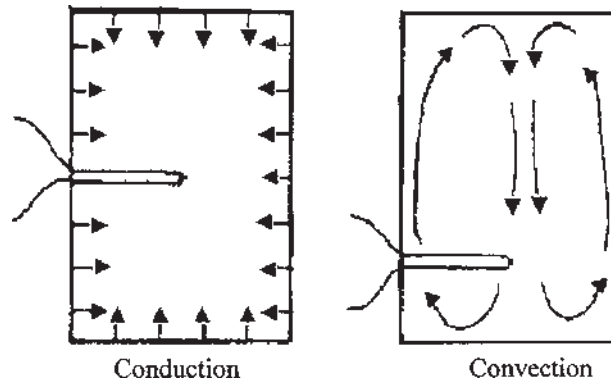


FIGURE 6.5 Heat penetration into food in cans.

axis at appropriate intervals (depending on the size of the container) and conducting a heat penetration test.

To determine the temperature changes at the slowest heating point, a temperature-sensing device is inserted into the container at this point. A heating process is then started and the temperature is recorded as a function of time. The most popular means of measuring temperature in heat penetration tests involves a thermocouple. Radiotelemetry has been used primarily for monitoring temperature in continuous, agitated retorts where thermocouples are not appropriate. The radiotelemetry system, which is based on the change in resistance of a thermistor with temperature, requires no electrical hookup to the recording or readout device.

C. Evaluation of Heat Penetration Data

In the chapter on heat transfer, two cases were presented for modeling heat transfer to food products in cans: (1) perfect mixing case and (2) pure conduction case. The equations representing these two cases are, respectively,

Perfect mixing case:

$$\frac{T_R - T}{T_R - T_i} = \exp \frac{-UA t}{mC_p} \quad (15)$$

Pure conduction case:

$$\frac{T_R - T}{T_R - T_i} = 2.0396 \exp \left[\left(-\frac{(2.4048)^2}{R^2} - \frac{\pi^2}{4l^2} \right) \alpha t \right] \quad (16)$$

Both of these equations can be represented by the generalized equation:

$$\frac{T_R - T}{T_R - T_i} = j \exp \frac{-2.303t}{f_h} \quad (17)$$

where $j = \frac{(T_R - T_{pjh})}{(T_R - T_i)}$, T_R = heating medium temperature, and T_i = initial product temperature, and T_{pjh} = pseudoinitial temperature at the start of heating.

In Eq. (17) j is the heating lag factor and, from Eqs. (15) and (16), theoretically varies between 1.0 and 2.04. In Eq. (17) f_h is the time constant base 10 for the heating curve and can be calculated from

$$\frac{2.303}{f_h} = \frac{UA}{mC_p} \quad (\text{perfect mixing case}) \quad (18)$$

and

$$\frac{-2.303}{f_h} = - \left(\frac{(2.4048)^2}{R^2} + \frac{\pi^2}{4l^2} \right) \alpha \quad (\text{pure conduction case}) \quad (19)$$

In practice, heat penetration data are most easily evaluated and utilized by plotting heat penetration curves. For calculating the lethality of a thermal process by the general method (Sec. V.B), heat penetration data need not be plotted unless one desires to know the temperature at a time when a measurement has not been taken. Once the data are plotted, the desired information can be easily obtained by interpolation. For the mathematical method of calculating lethality of thermal processes, some parameters that characterize the rate of heating are needed, and therefore heat penetration data must be plotted.

Heat penetration data plotted according to Eq. (17) are shown in Figure 6.6. From this figure the various parameters needed to model the heating curve can be easily obtained. I_h is the initial temperature difference between the heating medium and the initial temperature at the cold point (lowest temperature) in the food product. j_h is the ratio of the y intercept of the linear portion of the heat penetration plot ($T_R - T_{pjh}$) to the initial temperature difference ($T_R - T_i$). f_h is the time in minutes for the temperature difference to go through one logarithm cycle and is related to the slope as slope = $-1/f_h$ base 10. Heat penetration curves which are linear throughout the heating process are referred to as simple heating curves; whereas heating curves exhibiting an abrupt change in heat transfer rate are referred to as broken heating curves.

A simple way of plotting heat penetration data also can be developed from examination of Figure 6.6. It is evident that $T_R - T = 1$ on the left-hand axis corresponds to $T = T_R - 1$ on the right-hand axis. By means of this relationship, product temperature can be plotted directly on semilog paper and the mechanical

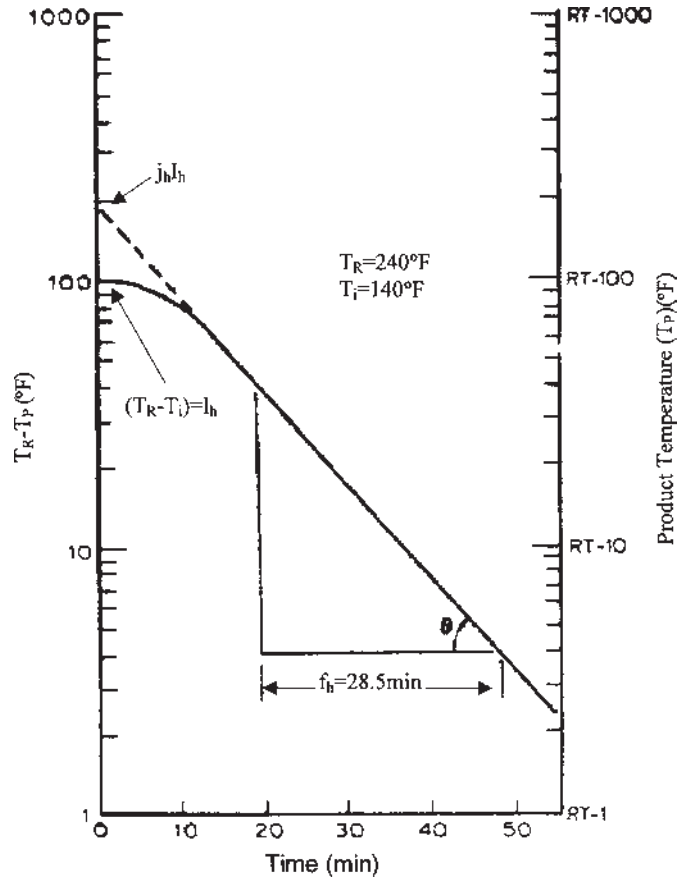


FIGURE 6.6 Heat penetration curve.

step of subtracting T from T_R need not be done. This is accomplished by inverting the semilog paper 180° and labeling the top line with a numeral equivalent to $T_R - 1$. The next log cycle is labeled with a numeral equivalent to $T_R - 10$, and the third with a numeral equivalent to $T_R - 100$. This method of plotting heat penetration data is shown in Figure 6.7.

There are several important characteristics of a heat penetration curve. First, in the development of a mathematical method for calculating sterility of a thermal process it is necessary to express the temperature of the slowest heating point as a function of time. This is easily done on a linear heating curve by giving the slope and a characteristic intercept. Second, it should be

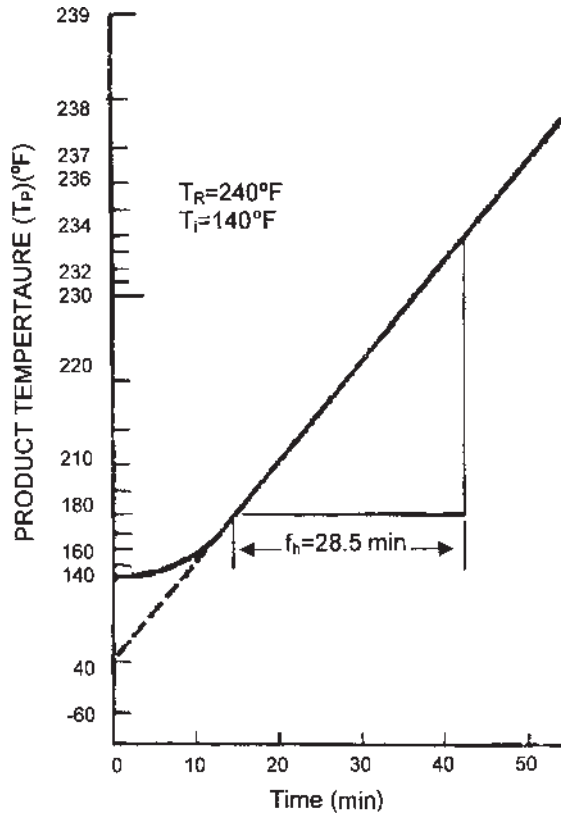


FIGURE 6.7 Plotting heat penetration data.

recognized that theoretically the product cold point never reaches retort temperature. The cold point may get very close to T_R but $T_R - T$ can never be zero. This concept is important in the Formula method of calculating thermal processes.

For thermal process calculations, at the end of heating time there will be some finite temperature difference between the heating medium temperature and the temperature at the cold point. In practice, the heating time is identified as B and the finite final temperature difference is called g . Substituting these into Eq. (17) results in

$$\frac{g}{I_h} = j10^{-B/f_h} = je^{-2.303B/f_h} \quad (20)$$

Rearranging Eq. (20) yields

$$B = f_h \log \frac{jI_h}{g} \quad (21)$$

Equation (21) is referred to as “The Formula” in the Formula method of calculating thermal processes for food products.

Equation (21) can be used to calculate heating times if the value of g is known. In the Formula method for process calculations, means for determining the g value have been developed.

As pointed out earlier, heat penetration into a product is dependent on many factors. There are methods available for adjusting f_h and j_h for changes in these variables; however, discussion of these methods is beyond the scope of this chapter. Suffice it to say that a change in process conditions, container size, or fill weight generally should be accompanied by a new series of heat penetration tests.

Another important factor to consider in heat penetration tests is that the test should be conducted under conditions that duplicate those that are encountered in a commercial retort. If a batch-type retort is used then the slowest heating point must be determined in that container which receives the least thermal energy. The packing characteristics of the retort can influence the accessibility of steam to can surfaces.

Finally, in thermal process calculations temperatures at the cold point also must be known for the cooling phase. In many processes wherein the product heats by conduction the cooling portion of the process can contribute significantly to the overall lethality of the process. The cooling curve can be characterized in a manner analogous to that used for heating (parameters j_c and f_c). In plotting cooling data the ordinate is labeled $\log (T_p - T_c)$ (T_c = cooling water temperature) or $\log T_p$ if the scale is labeled $T_c + 100$ on the line corresponding to $T_p - T_c = 100$ and is thereafter numbered in the same manner as for the heating curve.

V. METHODS OF DETERMINING LETHALITY OF THERMAL PROCESSES

A. Introduction

Three procedures have been developed for evaluating lethality of thermal processes: (1) Improved General method, (2) Formula method, and (3) Nomogram method (Stumbo, 1973).

The General method was the first scientific approach to calculating the adequacy of thermal processes. Basically, the method involves graphical integration of the total lethal effect for the time-temperature combinations which the cold point experiences in a thermal process. The underlying principles form the basis of both the Formula and Nomogram methods. The General method has

undergone modification resulting in the Improved General method, which is accurate and does not rely on assumptions about the nature of the heat penetration curve. However, its broad applicability and accuracy are counterbalanced by the fact that it is laborious.

The Formula method is more rapid and as accurate as the Improved General method. Its use with products exhibiting simple heating curves (linear on semilogarithmic plots) is very straightforward and requires a minimum of calculations. Stumbo (1973) presents methods of applying the Formula method to products exhibiting broken heating curves.

The Nomogram method is the quickest and least complicated method available for thermal process calculations. The parameters from heat penetration and thermal death time curves must be known before the Nomogram method can be used. Ball and Olson (1957) cautioned that this method should be used only by those thoroughly familiar with the assumptions inherent in establishing the nomogram. Determination of whether the particular process meets the assumptions must be done before the method is applied.

B. Improved General Method

In the Improved General method, use is made of the fact that different combinations of time-temperature conditions can achieve the same lethal effect on microorganisms. Since the method was developed using °F, the presentation here will also use °F.

Recall Eq. (8), which is the equation for a TDT curve:

$$\log \frac{F_T^z}{F_{250}^z} = \frac{250 - T}{z}$$

$$\frac{F_T^z}{F_{250}^z} = 10^{(250-T)/z} = \frac{TDT_T}{1} \quad (22)$$

For convenience in thermal process calculations, the right-hand term in Eq. 22 ($TDT_T/1$) is used. This term, calculated from $10^{(250-T)/z}$, is equal to the thermal death time at temperature T (TDT_T) equivalent to 1 min at 250°F ($F = 1$). This approach, while absolutely sound, arbitrarily establishes an F value of 1.0 as the starting basis for thermal process calculations. This is done to simplify calculations, and conversion to the actual F value for the process is easily accomplished as the last step in the calculation. Using Eq. (22), for example, if the product temperature is 232°F and $z = 18$ F, then

$$10^{(250-T)/z} = 10^{(250-232)/18} = 10^1 = 10 = \frac{TDT_T}{1}$$

This means that 10 min at 232°F is equivalent in lethality to 1 min at 250°F. For purposes of determining the total lethal effect during a heat process, it is convenient to express the lethality in terms of minutes at some reference temperature. Obviously, 250°F is a convenient reference temperature for low-acid food processing since the TDT curve is defined with 250°F as the reference temperature. In order to express the lethal effect at temperature T in terms of the lethal effect at 250°F, it is convenient to use the reciprocal of the term on the right-hand side of Eq. (22):

$$\frac{1}{TDT_T} = \frac{1}{10^{(250-T)/z}} = 10^{(T-250)/z} \quad (23)$$

In terms of the example just cited,

$$\frac{1}{TDT_T} = \frac{1}{10^{(250-T)/z}} = \frac{1}{10^{(250-232)/18}} = \frac{1}{10} = 0.1$$

This means that 1 min at 232°F is equivalent to 0.1 min at 250°F. In other words, if the value for the process is 1.0 min, then $(1/TDT_T) = 0.1$ is the fraction of unit sterility (unit sterility is a thermal process resulting in inactivation of microorganisms characterized by $F = 1.0$ min) accomplished in 1 min at temperature T . The term $1/TDT_T$ is called *lethal rate* and is used in graphical integration procedure to determine thermal process time. Since lethal rate is a function only of product temperature and z , it is possible to prepare a series of tables of lethal rates. Table 6.7 gives lethal rates for a z value of 18°F. The z value for the microorganism upon which the process is based is used in the lethal rate calculations.

The procedure used in applying the Improved General Method requires heat penetration data and the conversion of product temperature to lethal rates. To obtain the temperature profile, the temperature-sensing device is located at the cold point and the can is sealed and placed in the retort. Steam is brought in at the desired retort temperature. The time required to bring the retort up to operating temperature must be noted. The temperature at the cold point is recorded initially and at frequent intervals thereafter. The interval is dependent on the rate at which the product heats. When the can has been processed until the cold point temperature is within 1° or 2° of retort temperature, the steam is shut off, air pressure is maintained if required, and water is added for cooling. During cooling, temperature also should be recorded. The same cooling procedure should be followed in the test as is to be used in the actual process. The data obtained consist of a series of cold point temperatures at various times. From the product temperatures lethal rate values can be calculated by Eq. (23) or obtained from tables such as Table 6.7.

The lethal rate values are now plotted on arithmetic graph paper vs. process time. A typical curve known as a lethal rate curve is shown in Figure 6.8. The area

TABLE 6.7 Lethal Rates^a (Minutes at 250°F per Minute at T) for a z Value of 18

| T , Temp. (°F) | Minutes at 250°F/min at T | T , Temp. (°F) | Minutes at 250°F/min at T | T , Temp. (°F) | Minutes at 250°F/min at T |
|---------------------|-----------------------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|
| 214 | 0.010 | 232 | 0.100 | 250 | 1.000 |
| 215 | 0.011 | 233 | 0.114 | 251 | 1.136 |
| 216 | 0.013 | 234 | 0.129 | 252 | 1.292 |
| 217 | 0.015 | 235 | 0.147 | 253 | 1.468 |
| 218 | 0.017 | 236 | 0.167 | 254 | 1.668 |
| 219 | 0.019 | 237 | 0.190 | 255 | 1.896 |
| 220 | 0.022 | 238 | 0.215 | 256 | 2.154 |
| 221 | 0.024 | 239 | 0.245 | 257 | 2.448 |
| 222 | 0.028 | 240 | 0.278 | 258 | 2.783 |
| 223 | 0.032 | 241 | 0.316 | 259 | 3.162 |
| 224 | 0.036 | 242 | 0.359 | 260 | 3.594 |
| 225 | 0.041 | 243 | 0.408 | 261 | 4.084 |
| 226 | 0.046 | 244 | 0.464 | 262 | 4.642 |
| 227 | 0.053 | 245 | 0.527 | 263 | 5.275 |
| 228 | 0.060 | 246 | 0.600 | 264 | 5.995 |
| 229 | 0.068 | 247 | 0.681 | 265 | 6.813 |
| 230 | 0.077 | 248 | 0.774 | 266 | 7.743 |
| 231 | 0.088 | 249 | 0.880 | 267 | 8.800 |
| | | | | 268 | 10.000 |

^aLethal rate = $1/10^{(250-T)/z}$.

under the curve corresponding to a value of one is called a *unit sterility area* and represents a process equivalent to 1 min at 250°F ($F_{250}^z = 1$ min). Since most processes based on microbial inactivation have values greater than 1 min, the total thermal process must result in an area F times the unit sterility area. The graphical integration procedure enables us to readily find the area and calculate process time. The area under the curve can be estimated either with a planimeter, by counting squares, or by numerical integration.

Since it is improbable that the steam would be shut off and cooling would be started to yield exactly a process equivalent to commercial sterility, it is usually necessary to interpolate to other steam-off times. For convection heating products this is done by drawing in a cooling curve parallel to the determined cooling curve. Since the lethality accomplished in cooling is counted in the process, a simple procedure for determining steam-off time is to draw two or three cooling curves parallel to the measured cooling curve. Then by counting the total area under each heating/cooling process and by knowing steam shut-off

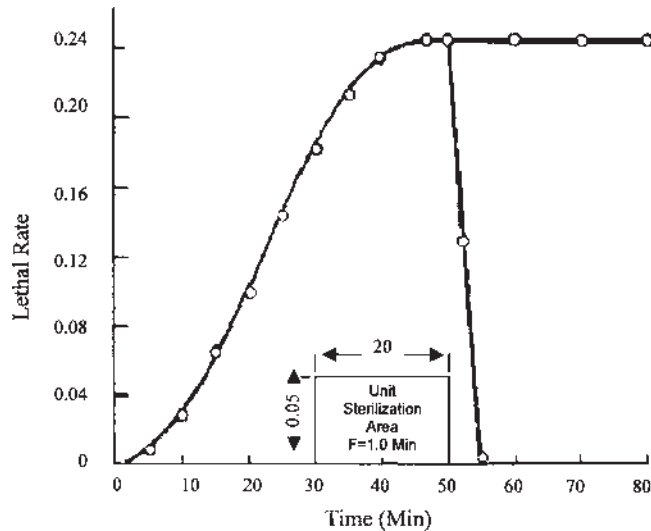


FIGURE 6.8 Lethal rate curve.

time, a plot can be made of total area versus steam shut-off time. The appropriate steam shut-off time can be easily determined from this figure.

For conduction heating products, this procedure for determining steam shut-off time should not be used. In these products, significant thermal lag usually occurs at the start of cooling, and if the center of the product is not near retort temperature at the time of steam off, the center temperature continues to rise. This additional temperature rise can contribute significantly to lethality since the lethal rates are large at high temperatures (lethal rate = 1.0 at 250°F). Since the additional temperature rise is not easily predicted it is necessary to run cooling curves at several different steam shut-off times for conduction heating products.

Thermal processes are always reported based on steam shut-off time. Since cooling lethality is counted in the total lethality of the process it is necessary to state conditions for cooling and to use cooling procedures in the test that actually are to be used in practice.

C. Formula Method

Equation (21) is the basis of the formula method.

$$B = f_h \log \frac{j_h I_h}{g} \quad (24)$$

It states that process time (B) can be calculated if the following are known: (1) slope of the heating line (f_h), (2) retort temperature minus initial product temperature ($T_R - T_{ih}$), (3) the factor identifying the thermal lag [$j_h = (T_R - T_{pih})(T_R - T_{ih})$], and (4) retort temperature minus cold point temperature at the end of the heating process (g). The first three parameters are either known from conditions of the process or can be obtained from a heat penetration curve. The fourth factor, g , is not as easily obtained.

In developing the Formula method, Ball (1923) recognized that the g value obtained for a product and process was a function of several factors: (1) slope of the heating curve (f_h), (2) time of the process (expressed as the TDT of the microorganism at retort temperature), (3) z value, and (4) driving force for cooling (retort temperature minus cooling water temperature).

Ball related the g value to the dimensionless ratio f_h/F_{RT}^z for various z values and various driving forces for cooling. Since most processes are given in terms of the F_{RT}^z value, it was necessary to calculate the F_{RT}^z by knowing the TDT at 250°F. This was done as follows. Ball chose to call U the TDT at the retort temperature. The relationship between U and F_{RT}^z can be easily comprehended from Figure 6.9. There are two TDT curves in Figure 6.9: one is the real TDT curve for the microorganism being considered and the other is a reference or phantom TDT curve. The reference TDT curve has the same slope as the real TDT curve but passes through 1 min at 250°F. In other words, the reference TDT curve represents the thermal resistance of the microorganism if $F_{RT}^z = 1.0$ min. F_{RT}^z on the reference TDT curve is called F_i . When the TDT at retort temperature is called the U value, then the equation for the real TDT curve is

$$\log U = \log F_{250}^z - \frac{1}{z}(T_R - 250) \quad (25)$$

The equation for the phantom TDT curve is

$$\log F_i = \log 1 - \frac{1}{z}(T_R - 250)$$

or

$$\log F_i = -\frac{T_R - 250}{z} \quad (26)$$

Combining Eqs. (25) and (26) yields

$$\log U = \log F_{250}^z + \log F_i \quad \text{or} \quad U = F_i F_{250}^z \quad (27)$$

Tables giving F_i as a function of z and retort temperature are available in Stumbo (1973). Thus, U can be readily calculated if F_{250}^z is known.

The fourth factor on which the g value depends is the thermal driving force for cooling. Since the temperature difference between retort temperature

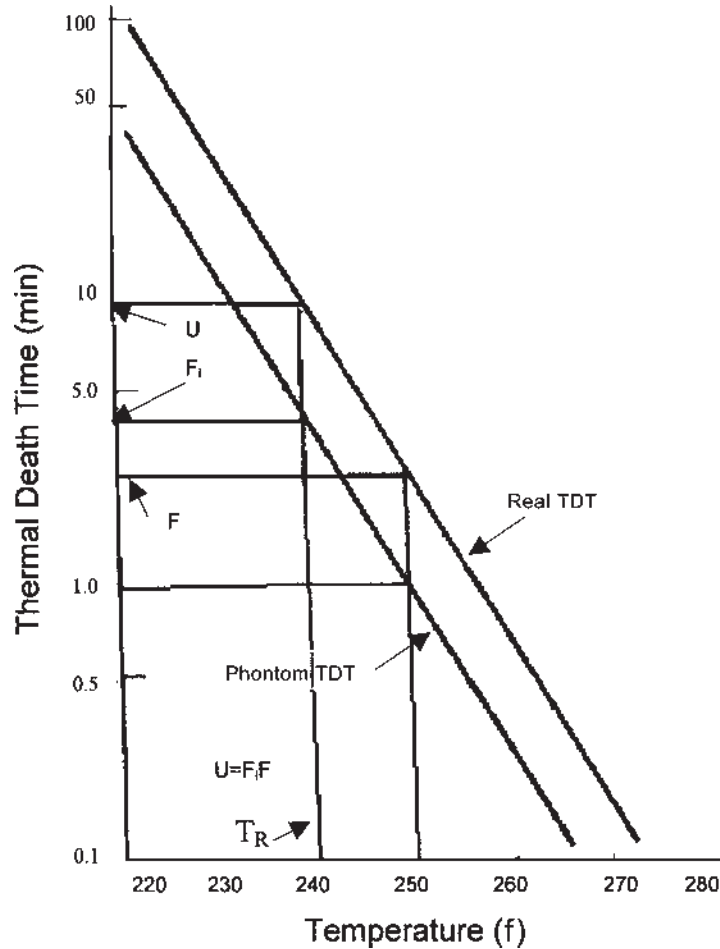


FIGURE 6.9 TDT curve for defining formula method parameters.

and cooling water temperature is $T_R - T_C$, the driving force can be expressed in terms of I_c and g . If I_c is defined (analogously to I_h) as the center temperature at the start of cooling (T_{CC}) minus the cooling water temperature (T_C), then $I_c + g = T_R - T_C$. Stumbo and Longely (1966) made a series of calculations to determine the influence of variations in $I_c + g$ on calculated lethality values of processes. It was found that on the average, a difference of 10°F in $I_c + g$ caused about a 1% difference in the calculated F_{250}^z value. Thus, tables published in Stumbo 1973) are for one value of $I_c + g$. Stumbo chose $I_c + g = 180^\circ\text{F}$ as

the basis of his tables since that would be fairly representative of values actually experienced. If the center temperature reached 240 to 250°F at the end of heating and the cooling water temperature was 60 to 70°F, then $170^\circ\text{F} < I_C + g < 190^\circ\text{F}$. If a correction is desired, the actual F_{250}^z value can be obtained by subtracting 1% from the theoretical F_{250}^z for every 10° the $I_C + g$ value is above 180°F and by adding 1% for every 10° the $I_C + g$ value is below 180°F .

Stumbo and Longley (1966) suggested the incorporation of another parameter in establishing the $f_h/U:g$ charts, and this parameter relates to the cooling lag factor (j_c). Lag in temperature response of the product center can have a significant effect on overall process lethality since it occurs at temperatures where the lethal rate is very large. Consequently Stumbo and Longley presented their f_h/U table with j_c as an additional parameter. The j_c value is defined as

$$j_c = \frac{T_c - T_{pic}}{T_c - T_{ic}} \quad (28)$$

and is determined from the heat penetration curve. Table 6.8 gives the $f_h/U:g$ correlations for various j_c values at $z = 18^\circ\text{F}$. Extensive tables are given in Stumbo (1973).

For a better grasp of the Formula method an example will be given. A particular product is to be processed under the following conditions:

$$T_{ih} = 140^\circ\text{F} \quad T_R = 240^\circ\text{F} \quad z = 18^\circ\text{F} \quad F_{250}^z = 7.0 \text{ min}$$

From a heat penetration test the following data were obtained:

$$f_h = f_c = 25 \text{ min} \quad j_h = 2.00 \quad j_c = 1.40$$

Calculate the process time.

Since process time is desired, Eq. (21) must be solved.

$$B = f_h \log \left(\frac{j_h I_h}{g} \right)$$

Where $I_h = (T_R - T_{ih}) = 240 - 140 = 100^\circ\text{F}$.

To find g , calculate $U = F_{250}^z F_i$. From F_i tables in Stumbo (1973, p. 210) at retort temperature of 240°F and $z = 18^\circ\text{F}$, $F_i = 3.594$. Therefore $U = 7(3.594) = 25.1 \text{ min}$.

From Table 6.8 for $f_h/U = 1.0$ and $j_c = 1.40$, $g = 0.608^\circ\text{F}$, and $B = 25 \log [(2.00)(100/0.608)] = 25 \log 328.9 = 25(2.52)$. Thus, $B = 62.9 \text{ min}$.

This is the process time required to achieve a lethality equivalent to $F_{250}^z = 7.0 \text{ min}$. If the process time had been given, it would have been possible to solve for the F value by working the problem in reverse.

The calculated process time is applicable to all processes wherein the product at the start of the process is immediately put in contact with steam at

TABLE 6.8 f_h/U : g relationships when $z = 18F$

| f_h/U | Values of g for j of cooling curve | | | | | | | | | |
|---------|--|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|--|
| | 0.40 | 0.60 | 0.80 | 1.00 | 1.20 | 1.40 | 1.60 | 1.80 | 2.00 | |
| 0.20 | 4.09×10^{-5} | 4.42×10^{-5} | 4.76×10^{-5} | 5.09×10^{-5} | 5.43×10^{-5} | 5.76×10^{-5} | 6.10×10^{-5} | 6.44×10^{-5} | 6.77×10^{-5} | |
| 0.30 | 2.01×10^{-3} | 2.14×10^{-3} | 2.27×10^{-3} | 2.40×10^{-3} | 2.53×10^{-3} | 2.66×10^{-3} | 2.79×10^{-3} | 2.93×10^{-3} | 3.06×10^{-3} | |
| 0.40 | 1.33×10^{-2} | 1.43×10^{-2} | 1.52×10^{-2} | 1.62×10^{-2} | 1.71×10^{-2} | 1.80×10^{-2} | 1.90×10^{-2} | 1.99×10^{-2} | 2.09×10^{-2} | |
| 0.50 | 4.11×10^{-2} | 4.42×10^{-2} | 4.74×10^{-2} | 5.06×10^{-2} | 5.38×10^{-2} | 5.70×10^{-2} | 6.02×10^{-2} | 6.34×10^{-2} | 6.65×10^{-2} | |
| 0.60 | 8.70×10^{-2} | 9.43×10^{-2} | 1.02×10^{-1} | 1.09×10^{-1} | 1.16×10^{-1} | 1.23×10^{-1} | 1.31×10^{-1} | 1.38×10^{-1} | 1.45×10^{-1} | |
| 0.70 | 0.150 | 0.163 | 0.176 | 0.189 | 0.202 | 0.215 | 0.228 | 0.241 | 0.255 | |
| 0.80 | 0.226 | 0.246 | 0.267 | 0.287 | 0.308 | 0.328 | 0.349 | 0.369 | 0.390 | |
| 0.90 | 0.313 | 0.342 | 0.371 | 0.400 | 0.429 | 0.458 | 0.487 | 0.516 | 0.545 | |
| 1.00 | 0.408 | 0.447 | 0.485 | 0.523 | 0.561 | 0.600 | 0.638 | 0.676 | 0.715 | |
| 2.00 | 1.53 | 1.66 | 1.80 | 1.93 | 2.07 | 2.21 | 2.34 | 2.48 | 2.61 | |
| 3.00 | 2.63 | 2.84 | 3.05 | 3.26 | 3.47 | 3.68 | 3.89 | 4.10 | 4.31 | |
| 4.00 | 3.61 | 3.87 | 4.14 | 4.41 | 4.68 | 4.94 | 5.21 | 5.48 | 5.75 | |
| 5.00 | 4.44 | 4.76 | 5.08 | 5.40 | 5.71 | 6.03 | 6.35 | 6.67 | 6.99 | |
| 6.00 | 5.15 | 5.52 | 5.88 | 6.25 | 6.61 | 6.98 | 7.34 | 7.71 | 8.07 | |
| 7.00 | 5.77 | 6.18 | 6.59 | 7.00 | 7.41 | 7.82 | 8.23 | 8.64 | 9.05 | |
| 8.00 | 6.29 | 6.75 | 7.20 | 7.66 | 8.11 | 8.56 | 9.02 | 9.47 | 9.93 | |
| 9.00 | 6.76 | 7.26 | 7.75 | 8.25 | 8.74 | 9.24 | 9.74 | 10.23 | 10.73 | |
| 10.00 | 7.17 | 7.71 | 8.24 | 8.78 | 9.32 | 9.86 | 10.39 | 10.93 | 11.47 | |
| 15.00 | 8.73 | 9.44 | 10.16 | 10.88 | 11.59 | 12.31 | 13.02 | 13.74 | 14.45 | |

(continued)

TABLE 6.8 Continued

| f_h/U | Values of g for j of cooling curve | | | | | | | | | |
|---------|--|-------|-------|-------|-------|-------|-------|-------|-------|--|
| | 0.40 | 0.60 | 0.80 | 1.00 | 1.20 | 1.40 | 1.60 | 1.80 | 2.00 | |
| 20.00 | 9.83 | 10.69 | 11.55 | 12.40 | 13.26 | 14.11 | 14.97 | 15.82 | 16.68 | |
| 25.00 | 10.7 | 11.7 | 12.7 | 13.6 | 14.6 | 15.6 | 16.5 | 17.5 | 18.4 | |
| 30.00 | 11.5 | 12.5 | 13.6 | 14.6 | 15.7 | 16.8 | 17.8 | 18.9 | 19.9 | |
| 35.00 | 12.1 | 13.3 | 14.4 | 15.5 | 16.7 | 17.8 | 18.9 | 20.0 | 21.2 | |
| 40.00 | 12.8 | 13.9 | 15.1 | 16.3 | 17.5 | 18.7 | 19.9 | 21.1 | 22.3 | |
| 45.00 | 13.3 | 14.6 | 15.8 | 17.0 | 18.3 | 19.5 | 20.8 | 22.0 | 23.2 | |
| 50.00 | 13.8 | 15.1 | 16.4 | 17.7 | 19.0 | 20.3 | 21.6 | 22.8 | 24.1 | |
| 60.00 | 14.8 | 16.1 | 17.5 | 18.9 | 20.2 | 21.6 | 22.9 | 24.3 | 25.7 | |
| 70.00 | 15.6 | 17.0 | 18.4 | 19.9 | 21.3 | 22.7 | 24.1 | 25.6 | 27.0 | |
| 80.00 | 16.3 | 17.8 | 19.3 | 20.8 | 22.2 | 23.7 | 25.2 | 26.7 | 28.1 | |
| 90.00 | 17.0 | 18.5 | 20.1 | 21.6 | 23.1 | 24.6 | 26.1 | 27.6 | 29.1 | |
| 100.00 | 17.6 | 19.2 | 20.8 | 22.3 | 23.9 | 25.4 | 27.0 | 28.5 | 30.1 | |
| 150.00 | 20.1 | 21.8 | 23.5 | 25.2 | 26.8 | 28.5 | 30.2 | 31.9 | 33.6 | |
| 200.00 | 21.7 | 23.5 | 25.3 | 27.1 | 28.9 | 30.7 | 32.5 | 34.3 | 36.2 | |
| 250.00 | 22.9 | 24.8 | 26.7 | 28.6 | 30.5 | 32.4 | 34.3 | 36.2 | 38.1 | |
| 300.00 | 23.8 | 25.8 | 27.8 | 29.8 | 31.8 | 33.7 | 35.7 | 37.7 | 39.7 | |
| 350.00 | 24.5 | 26.6 | 28.6 | 30.7 | 32.8 | 34.9 | 37.0 | 39.0 | 41.1 | |
| 400.00 | 25.1 | 27.2 | 29.4 | 31.5 | 33.7 | 35.9 | 38.0 | 40.3 | 42.3 | |
| 450.00 | 25.6 | 27.8 | 30.0 | 32.3 | 34.5 | 36.7 | 38.9 | 41.2 | 43.4 | |
| 500.00 | 26.0 | 28.3 | 30.6 | 32.9 | 35.2 | 37.5 | 39.8 | 42.1 | 44.4 | |
| 600.00 | 26.8 | 29.2 | 31.6 | 34.0 | 36.4 | 38.8 | 41.2 | 43.6 | 46.0 | |
| 700.00 | 27.5 | 30.0 | 32.5 | 35.0 | 37.5 | 39.9 | 42.4 | 44.9 | 47.4 | |
| 800.00 | 28.1 | 30.7 | 33.3 | 35.8 | 38.8 | 40.9 | 43.5 | 46.0 | 48.6 | |
| 900.00 | 28.7 | 31.3 | 34.0 | 36.6 | 39.9 | 41.8 | 44.4 | 47.0 | 49.7 | |

Source: Stumbo (1973).

the retort temperature. This is the case when continuous retorts are used. However, in batch retorts there may be a time lag in getting the retort to process temperature. In these circumstances the calculated process time is not the same as the operator's time. In this instance, the retort operator usually times the process from the time the retort reaches retort temperature. To correct for the lag, Ball (1923) determined that approximately 40% of the lag time contributes to the heating process and thus $0.4 P$ (where $P =$ lag time) actually contributes to process time. Therefore, the process time (P_i) in a batch retort should be

$$P_i = B - 0.4P \quad (29)$$

The Formula method utilizing Eq. (21) is applicable only to food products having linear heating curves on a semilogarithmic plot (simple heating curve). A method for calculating process times for products having broken heating curves is given in Stumbo (1973) and is based on the same principles.

Equation (21) also gives the process time based on the assumption that every point receives an integrated lethal effect at least as great as that received by the cold point. This assumption is certainly true in products which heat by convection. For conduction heating products, however, this assumption is not necessarily true. Consider, for example, product with a temperature profile such as that shown in Figure 6.10. The center temperature may be considerably lower than retort temperature at the end of heating time. At the start of cooling the outer portion starts to cool, but the center still sees a thermal driving force for influx of heat. Thus, an actual temperature inversion may be experienced in the cross section of the container. Each point in the cross section receives a different

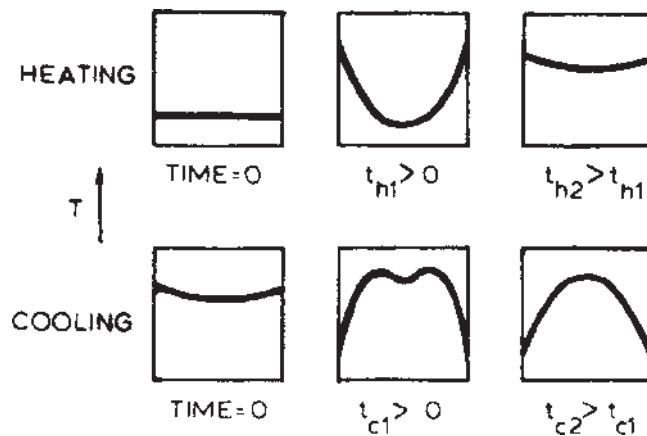


FIGURE 6.10 Temperature profiles in conduction heating foods.

thermal process. Teixeira et al. (1969) showed that the location of the “least lethal point” in a conduction heating product is a function of container geometry and processing condition. However, in thermal process calculations, the center temperature still can be regarded as the cold point since the probability of survival of microorganisms does not vary appreciably within a small zone surrounding the center point. Nevertheless, inoculated pack experiments should be used to validate use of the calculated process.

When it is desirable to know average lethality for the entire container of a conduction heating food (e.g., determining average retention of nutrient or quality factors or probability of microbial survival), then the temperature profile must be considered. The calculations are complex and require computer facilities.

The preceding discussion has centered on calculation of thermal processes based on microorganisms. The same procedures can be applied for calculating process times for destruction of enzymes and nutrients, provided the appropriate data are known. For nutrient destruction calculations, the process time is generally known, and it is desired to calculate the percent nutrient remaining. The Formula method can be used by substituting D_{250}^z for F_{250}^z . The value obtained is the maximum retention since the process is based on the point receiving the least thermal process. For other methods which have been developed for estimating average nutrient retention see Stumbo (1973) and Hayakawa (1969).

In discussing the dependence on temperature of the reaction rate constant for thermal destruction, it was pointed out that the Arrhenius equation was applicable. However, both the Improved General method and the Formula method are based on the empirical TDT curve, and although a system based on the Arrhenius equation has been developed, the TDT-based method is still most widely employed.

D. Aseptic Processing

In aseptic processing, the product is subjected to a thermal process to inactivate vegetative cells or spores prior to being placed in a sterile container. Consequently, the thermal process is applied to the product in either continuous flow conditions (a pumpable fluid or fluid containing particles) or in batch operations. If the thermal process is applied in batch operation, the procedures for assessing the proper processing conditions of time and temperature are determined using calculation methods described in the previous conditions. That is, the thermal history is determined in a manner similar to that for determining the thermal history of food in a can and applying lethality calculations. If, however, the food is processed in continuous flow conditions, then a different procedure for assessing the proper thermal process to achieve commercial sterility is applied.

The mathematics of the lethality calculation is straightforward. Combining Eq. (1), (3) and (9) yields

$$D_R \log \frac{C_i}{C_f} = \int_0^t \frac{1}{10^{(T_R - T)/z}} dt \quad (30)$$

where D_R is the decimal reduction time at temperature T_R , $\log (c_i/c_f)$ is the number of log cycles the concentration of viable cells or spores must go through, and z is the temperature change necessary to change the decimal reduction value (D value) by a factor of 10. $D_R \log (c_i/c_f)$ is the thermal death time, and the actual value achieved by the process (time-temperature exposure of the product) must be equal to or greater than the legally specified thermal death time, called the F value.

The only requirement to fulfill the design equation is that the z value be independent of temperature. For conventional thermal processes which are carried out over relatively narrow temperature ranges (100–130°C), the assumption for constant z value is valid. However, many aseptic processes are carried out over much broader temperature ranges (e.g., 100–150°C). As shown in Eq. (13), if E_a is constant, then z must be temperature dependent, and the assumption of constant z value is no longer valid. For this reason, there are more safety factors built into the design of aseptic thermal processes than conventional canning thermal processes.

To calculate the lethality of an aseptic process, the time-temperature profile must be determined experimentally or described mathematically with a high degree of accuracy. The problem arises in aseptic processes that are applied to products subjected to fluid flow. Under flow conditions the products will exhibit a residence time distribution because of the velocity distribution in the hold tube. The velocity distribution results in a distribution of temperature-time treatments because of the distribution of residence time. Since the legal requirements for a thermally processed, low acid food is that the food must be “commercially sterile” (i.e., no outgrowth of microorganisms or their spores that results in infection or intoxication under the conditions found in the container stored at ambient temperature), the residence time distribution is required so that the fastest moving element (shortest residence time) can be used to calculate the minimum lethality delivered to the product.

Residence time distribution in continuous flow aseptic processes has received considerable attention. Singh (1993) discussed the importance of residence time distribution in aseptic processes, and Lund and Singh (1993) discuss research results on measuring the fluid-particle interfacial heat transfer coefficient. Although both of these concepts (i.e., residence time distribution and fluid to particle interfacial heat transfer coefficient) are very important, they are

beyond the scope of the discussion presented here. The reader is referred to the cited references for further information.

For purposes of defining the lethality of an aseptic process in our discussion, we will only consider the lethality that occurs in the hold tube of the system. Clearly some lethality is contributed in the heating section of the system as well as in the cooling section. Generally this additional lethality is considered a safety factor.

The hold tube is a tube of circular cross section into which flows the product at a desired set point temperature. The tube is of such diameter and length that the desired residence time is achieved to deliver the required lethality. The hold tube is usually covered with a shroud so that there is minimal heat loss through the tube wall and ultimately to the surroundings. This minimizes the temperature drop of the product as it flows through the hold tube. It is illegal to surround the hold tube with a heating medium (hot air, hot water, steam, or electrical heating devices). The exit temperature from the hold tube is used as the temperature for purposes of calculating lethality delivered to the product.

The velocity distribution in a fluid flowing in a tube of circular cross section is dependent on the nature of the fluid (i.e., Newtonian or non-Newtonian) and the Reynolds number ($Re = \rho Dv/\mu$), the ratio of kinetic forces to viscous forces. For Newtonian fluids [viscosity is independent of shear stress (dv/dt)], if $Re > 4000$, flow is usually turbulent and the mean velocity v is 82% of the maximum velocity v_{\max} (i.e. $v/v_{\max} = 0.82$). If $Re < 2100$, flow is generally laminar (unless there are turbulence promoters in the flow channel) and the velocity profile is parabolic with maximum velocity at the center and zero velocity (nonslip assumption) at the tube wall. It can be shown that $v/v_{\max} = 0.5$ under these conditions. Using v_{\max} under these conditions and knowing the length of the hold tube, the minimum residence time can be calculated from

$$v_{\max} = \frac{L}{t_{\min}} \quad t_{\min} = \frac{L}{v_{\max}} \quad (31)$$

where v_{\max} = maximum velocity (m/s), L = hold tube length (m) and t_{\min} = minimum residence time (s). The lethality accomplished in the hold tube is the product of the lethal rate at the hold tube temperature (exit temperature of the hold tube) and the minimum residence time (in minutes).

$$F = \text{lethality} = (\text{lethal rate})(t_{\min}) = 10^{(T_{\text{HO}} - 121.1)/z} t_{\min} \quad (32)$$

where F = lethality (min), T_{HO} = temperature at the exit of the hold tube ($^{\circ}\text{C}$), and z = temperature change to increase the decimal reduction value by a factor of 10 ($^{\circ}\text{C}$).

From the previous discussion, if the fluid is Newtonian and flow is laminar, then $v_{\max} = 2v$, and the determination of the maximum velocity is easily accomplished. However, most food fluids are non-Newtonian, and v_{\max} will be less

than twice the mean velocity. Consequently assuming laminar flow and Newtonian behavior as the basis for determining v_{\max} will result in an overestimation of the maximum velocity and therefore underestimation of the residence time. Although this is acceptable from a product safety standpoint, the underestimation of residence time is undesirable from a product quality standpoint.

The true nature of viscous behavior of food products can be taken into account when determining v_{\max} (i.e., t_{\min}) by considering the relationship between viscosity and shear stress. The defining relationship between shear rate and shear stress is,

$$\tau = \tau_o + k \left(\frac{dv}{dr} \right)^n \quad (33)$$

where τ = shear stress, τ_o = yield shear stress, k = apparent viscosity, dv/dr = shear rate, and n = flow behavior index. If $\tau_o = 0$ and $n = 1$, then this equation reduces to describe a Newtonian fluid. If $n \neq 1.0$, the fluid is referred to as a power-law fluid. For most food fluids under flow conditions, $\tau_o = 0$ and $n < 1.0$. These fluids are called shear thinning since viscosity decreases as shear rate increases. They are also referred to as pseudoplastics. For $n > 1.0$, apparent viscosity increases with shear rate, and these fluids are called dilatant. There are very few dilatant food fluids. Care must be exercised in determining viscous behavior, however, because fluids in which starch is gelatinizing or in which large particles are disintegrating may appear to be shear thickening.

For non-Newtonian fluids in laminar flow, it can be shown that the velocity profile is dependent on n according to the following equation:

$$\frac{\bar{v}}{v_{\max}} = \frac{1 - n}{1 + 3n} \quad (34)$$

where n = flow behavior index.

For $n = 1.0$, this equation reduces to the case for a Newtonian fluid ($\bar{v}/v_{\max} = 0.5$). For $n < 1.0$ (i.e., pseudoplastic fluids), $\bar{v}/v_{\max} > 0.5$. The relationship between Re and \bar{v}/v_{\max} is given in Figure 6.11 (Palmer and Jones, 1976). It can be seen that for Newtonian ($n = 1.0$) and pseudoplastic fluids ($n < 1.0$), $\bar{v}/v_{\max} = 0.5$ is a limiting case that yields the maximum velocity compared to the mean velocity and therefore the minimum residence time.

Since viscosity is dependent on shear stress for a non-Newtonian pseudoplastic fluid, the Reynolds number must be modified. The generalized

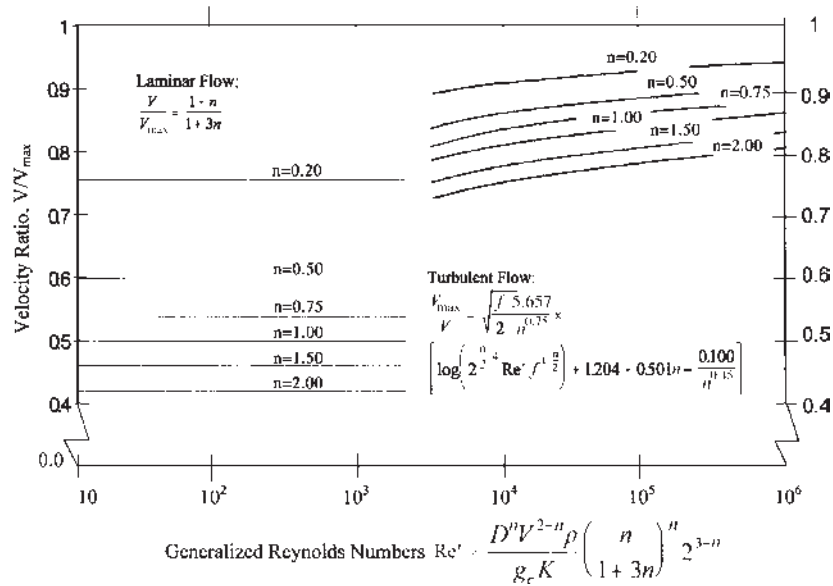


FIGURE 6.11 Velocity ratio-generalized Reynolds number correlation for power-law fluids.

Reynolds number taking into account the flow behavior index is

$$Re' = \frac{D^n v^{2-n} \rho}{k} \left[\frac{n}{1+3n} \right]^n 2^{3-n} \quad (35)$$

This equation is used to calculate the Re' for use in Figure 6.11.

In summary, the principles for calculating the lethality delivered to a product subjected to aseptic processing are

1. Lethality only occurs in the holding tube.
2. The minimum residence time is a function of fluid behavior (Newtonian or non-Newtonian) and type of flow (laminar or turbulent).
3. The length of the hold tube is determined by design to achieve the required lethality for the product.

The foregoing discussion applies to fluids and fluids with particles if the particles can be assumed to be at the same temperature as the fluid. If the particle leaves the heat section of the system before achieving thermal equilibrium with the surrounding fluid, then the center point of the particle will continue to heat and experience temperature rise. Since the system must be designed to deliver

a minimum lethality to both fluid and particles, the temperature history of the particle as well as particle residence time must be taken into consideration.

Although a detailed discussion of aseptic processing of particulate food is beyond the scope of this text, there are several excellent books on the subject (Willhoft, 1993; David et al., 1996; Sastry, 2002). A few brief comments will be made here. Since most food liquids subjected to aseptic processing are viscous and non-Newtonian, the convective heat transfer coefficient from the liquid to the surface of the particle is quite small (e.g., 50–100 $\text{w/m}^2\text{K}$). Consequently generally the liquid receives a much greater thermal treatment than does the particle. This can present quality problems in the aseptically processed product. Some systems such as the Jupiter system heat the particles separately with both direct and indirect steam and then add the commercially sterile liquid after cooling the particles. The commercially sterile fluid with particles is then pumped to the aseptic filler for final dispatch into packaging containers.

One further comment should be pointed out about aseptic process calculations. There are aseptic processing systems that use direct contact of the product with steam for heating. Two systems have been designed: (1) steam injection [adding high pressure steam to the product under flow or nonflow (batch) conditions] and (2) steam infusion adding the cold product (usually in the form of small droplets or a liquid film) to a hot steam atmosphere]. In both systems heating is caused by condensation of the steam resulting in dilution of the product. Generally, steam injection and steam infusion heating systems are followed by flash cooling the product. In flash coolers, the product is sprayed or applied as a film to a tank wall in a vacuum to get rapid flashing (evaporation) of water resulting in very rapid cooling. This system can also strip the product of considerable volatile odors and flavors that may have developed during steam injection or infusion. Generally the vacuum in the flash tank is adjusted so that the amount of water evaporated is exactly equal to the amount of water added as condensed steam resulting in no dilution of the product.

VI. PROCESS APPLICATION

The objective of extending the storage life of foods through thermal processing is to make available a varied diet that provides adequate nutrients. Thus the thermal process ultimately used should meet two criteria: (1) it must accomplish the process objectives from a microbial or enzymatic standpoint, and (2) it should yield a maximum retention of nutrients. Although a detailed analysis of the optimization of thermal processes for nutrient retention is beyond the scope of this discussion, some general observations on optimization of blanching, pasteurization, and commercial sterilization processes can be made. For this purpose, the relative heat resistance of nutrients, enzymes, and microorganisms

given in Table 6.6 are used along with a consideration of the objectives of the thermal process.

A. Optimization of Thermal Processes for Nutrient Retention

In blanching, where enzyme inactivation is desired, it is difficult to predict an optimum thermal process since the z values for thermally resistant enzymes, nutrients, and quality factors are approximately the same. Thus, blanching at higher temperature for a shorter time may not have an advantage over blanching at lower temperatures and longer times. However, in the blanching operation thermal degradation of nutrients and quality factors may not be the primary mechanism of loss. For example, blanching in hot water can result in a considerable loss of nutrients due to leaching. Similarly, losses due to oxidation can result during blanching in hot air. Considering leaching and oxidative losses, HTST would result in greater nutrient retention since contact time, not temperature, is the more important factor.

For pasteurization and commercial sterilization, optimization of the thermal process is important since microbial inactivation has a significantly different temperature dependence than destruction of nutrients. For foods or food fluids which are pasteurized, high-temperature and short-time processes result in maximum nutrient retention. This occurs because a given increase in process temperature accelerates microbial destruction more than nutrient degradation.

For commercial sterilization, optimization of a thermal process is not so straightforward. The mode of heating within the product becomes an important factor. For those products that heat by convection, the high-temperature and short-time process results in optimum nutrient retention. Again, a comparison of z values indicates that the rate of destruction of nutrients is less temperature dependent than is the rate of destruction of microbial spores. Therefore, the high-temperature and short-time process favors nutrient retention. However, as the temperature is raised and the process time is shortened, a point is eventually reached where the process destroys microbial spores but does not destroy heat-resistant (HR) enzymes. This occurs because of a difference in reaction rate constants for the destruction of HR enzymes as compared to spores. At low temperature, the destruction rate for HR enzymes is greater than it is for spores, but as the temperature is raised the destruction rate for spores increases faster than that for HR enzymes. Therefore, some high temperature X exists at which the destruction rates for the HR enzymes and spores are equal. Above temperature X the destruction rate of spores is greater than that for HR enzymes, and a thermal process based on the destruction of spores does not totally inactivate HR enzymes. Therefore, spoilage of the product due to enzyme activity may occur. In these instances, the process must be based on inactivation of HR

enzymes rather than on inactivation of spores. The temperature at which the destruction rate for HR enzymes equals that for spores is generally in the range of 130–143°C. For products that are processed above these temperatures, it is difficult to accurately calculate conditions that result in inactivation of HR enzymes and spores while causing minimum damage to nutrients and other quality attributes.

For all products which heat by convection, one important assumption is made concerning the thermal process, i.e., pieces in the brine receive the same lethal treatment as the brine. This assumption is valid when the food particulates are sterile in the center and they have large surface heat transfer coefficients. However, food particulates do exist that are not sterile in the center (e.g., foods that contain meat balls, stuffed noodles) and which have surface heat transfer coefficients that are small (thus, surface temperatures are significantly lower than the brine temperature). In these instances, it cannot be assumed that the lethal treatment in the particulate equals or exceeds that in the brine. Under these conditions and when most of the nutrients are located in particulates, the problem of designing the thermal process for optimization is basically the same as that for conduction heating foods.

In conduction heating foods, as pointed out earlier, each point in the cross section of the container receives a different thermal process than every other point, and the thermal process is based on the slowest heating point. At the conclusion of heating and the start of cooling, a complexity arises since the slowest heating point (center) can continue to increase in temperature for a significant period. In this situation, the overall lethality for the process is the integrated effect of the heat treatment at every point in the container. Methods developed for calculating lethality of a thermal process in conduction heating foods have been applied to optimize thermal processes for nutrient retention. All of these methods are time consuming and apply only to conduction heating foods. For our purposes, the concept of optimization can be illustrated by the work of Teixeira et al. (1969). These authors presented a relationship between various time-temperature treatments providing equal microbial lethality and retention of nutrients with different z values (Fig. 6.12) it can be seen that retention of a nutrient with a small z value is favored by a low-temperature and long-time process, whereas retention of a nutrient with a large z value is favored by a high-temperature and short-time process. The curve for $z = 25^\circ\text{C}$, $D = 188$ min, represents thiamine destruction in green bean puree. Note that the optimum process in green bean puree is 90 min at 120°C , very close to that used commercially. More significantly, note that as the temperature of the process is raised, thiamine retention decreases rapidly.

It should be pointed out that these methods for conduction heating foods cannot be applied to those retorting and heating conditions where the product

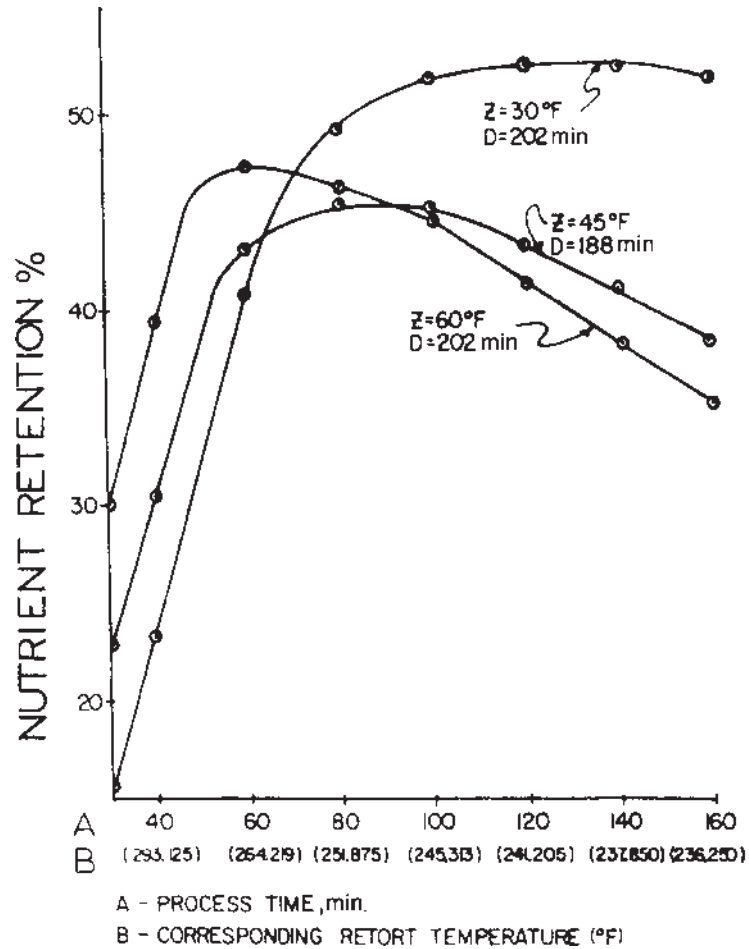


FIGURE 6.12 Multinutrient optimization. Percent nutrient versus process time with corresponding retort temperature.

is intimately mixed, such as in the Orbitort and in scraped-surface heat exchangers. Under these circumstances, the product usually receives sufficient mixing so that every point in the food receives nearly the same lethal heat treatment. Consequently, a high-temperature and short-time process favors nutrient retention.

Table 6.9 summarizes the methods of optimizing blanching, pasteurization, and commercial sterilization processes for nutrient retention.

TABLE 6.9 Optimization of Thermal Processes for Nutrient Retention

| Process | Method of optimization |
|--------------------------|--|
| Blanching | Base on considerations other than thermal losses (e.g., leaching losses, oxidative degradation, damage to product). |
| Pasteurization | HTST if heat-resistant enzymes are not present. |
| Commercial sterilization | Convection heating foods and aseptic processing: HTST until heat-resistant enzymes become important. Conduction heating foods: not HTST, necessarily; difficult to predict. |

B. Process Equipment

1. Blanching

Most blanching operations are accomplished by putting the product in contact with either hot water or steam for an appropriate time. The time is dependent on the objectives of the process; that is, whether enzymes are to be inactivated or activated and whether partial cooking is desired.

Lee (1958) presented an excellent evaluation of hot water and steam blanching from a nutrient viewpoint. In general steam blanching results in greater retention of water-soluble nutrients since less leaching occurs.

Steam blanching can be carried out as a batch process; however, in most modern canneries, continuous systems are used. In steam blanching, generally the material is layered on a belt which moves the product through a steam tunnel. The product is heated by steam jets from below and above. With leafy vegetables, such as spinach, care must be taken not to overload the belt since upon heating these products tend to wilt and mat. Heat transfer through this mat is very slow and underblanching could occur.

The thermal screw also has been used to steam blanch products. Here the product is conveyed in a trough by a closely fitting helical screw. Steam injected at regular intervals is used to heat the product. Similar designs use hot water as the transfer medium, and this reduces abrasion and damage to such sensitive products as mushrooms. A unique steam blanching system was developed for reducing the effluent and heating inequities that can occur in deep-bed steam blanching. The system is individual quick blanch IQB and consists of two steps: (1) a heating step wherein the product mass-average temperature is raised and (2) an adiabatic holding step wherein thermal gradients within the product are allowed to equilibrate. Effluent reduction can be further accomplished by predrying

the product by 6% (w/w) prior to steam heating. This allows the steam condensate to remain on the piece and not to run off and leach solids from the product.

Water blanching also can be conducted on a batch basis by simply dipping a batch of product in hot water (usually 90–99°C) for the required time. Continuous hot water blanchers can be screw types, drum types, or pipe types. The drum type consists of a perforated drum fitted internally with a helical screw. The residence time is regulated by the rpm of the screw and agitation is provided by action of the screw. The water can be heated by direct injection of steam into the blancher, or the water can circulate outside the blancher and be steam heated. Water blanchers of this type generally have large waste streams since fresh water must be continually added to dilute the solids content of the blanch water. Concentrations in excess of 2–3% solids in the blanching water can contribute to off flavors in the final product.

The pipe blancher can be used with solid food particles that can be pumped in water. Water and product are combined using 8–10 l water per kilogram of product and pumped through 10–15 cm diameter pipe at a rate of approximately 1 m/s. At this velocity most vegetables remain fluidized, and yet agitation is not so vigorous as to damage the product. At the discharge end, the product is separated from the water at a dewatering reel and the water is recycled. Some makeup water is required so the solids content of the water does not get too high.

Hot gas blanching using combustion gas as the heat transfer medium has been successfully applied to spinach and other vegetables. The main advantage of the method is that there is practically no effluent since there is no steam condensation. In fact the product generally loses considerable water in the process and the hot gas stream must be humidified. Since partial dehydration can be accomplished in hot gas blanching, the method is particularly well suited for products that are subsequently to be dried. The method is not well suited for products such as corn since the high temperatures employed can cause surface browning.

Microwaves or microwaves in combination with hot water or steam give satisfactory blanching, but equipment cost is high.

2. Pasteurization

Since pasteurization is normally accomplished at temperatures less than 100°C, solid food products can be pasteurized in the same type of equipment as that used for blanching. For acid food products or meat products a water bath is the simplest pasteurization equipment. Crates of the packaged food product are placed in steel tanks for heating with hot water. At the end of the process cold water is added for cooling. A continuous water bath pasteurizer is used in

the pickle industry and in fruit processes. The equipment consists of a long tank through which the product moves on a belt.

Continuous water spray equipment is used for pasteurizing bottled beer and fruit juices. In this unit, the product is conveyed on a belt through several temperature zones where water is sprayed onto the containers. The zones are first preheat, second preheat, pasteurization, precool, and final cool. Water economy is accomplished by using the water from the first preheat section to precool and then using this water again for preheating.

When glass containers are processed, care must be taken to avoid thermal shock. This can be done best by keeping the driving force for heat transfer around 40°C. For cooling, the driving force should be around 27°C.

Steam pasteurizers are also used but are more amenable to metal containers than glass because of the danger of thermal shock. Tunnels can be designed with various temperature zones by controlling the steam-air mixture in each zone. Cooling is accomplished by water sprays or by immersing the containers in water.

When metal and glass containers are cooled, it is desirable to remove them from the cooling zone at temperatures near 38°C. At these temperatures the surface water evaporates, avoiding corrosion problems during storage.

For fruit, fruit juices, and tomatoes, the continuous, agitating, atmospheric cooker is widely used. Operation of the unit is similar to the continuous, agitating, pressure cooker wherein the cans are screw conveyed through the unit. The unit operates at atmospheric pressure with either steam, hot water, or a combination of steam and hot water as the heating medium. Processing rates of up to 250–300 cans per minute can be achieved.

Pasteurization of unpackaged liquids is most commonly accomplished in indirect heat exchangers. In these units the product is passed along one side of a wall while the heating medium (steam or hot water) is passed along the other. A plate-type indirect heat exchanger is most commonly used for pasteurizing liquids. In this type of heat exchanger the product is separated from the heating medium by a thin metal plate. The plate is usually indented to promote turbulent flow, thereby resulting in large heat transfer coefficients. Film heat transfer coefficients on the order of 5,500 to 1,100 $\text{Wm}^{-2}\text{K}^{-1}$ are not uncommon with relatively non-viscous fluids, such as milk. Plate heat exchangers are used extensively for pasteurization of milk and beer. Added economy in heating is achieved by a process called *regenerative heating*. In this process, the hot pasteurized fluid is used to partially heat the cold incoming product.

Direct injection of steam has been used to pasteurize milk. However, its use is limited because culinary steam is required and localized overheating can occur at the point of injection. Localized overheating can result in undesirable precipitation of such inverse solubility salts as $\text{Ca}_3(\text{PO}_4)_2$ or denaturation of protein.

3. Commercial Sterilization

There are two basic methods used to obtain commercial sterility in foods: (1) heating the food after it has been placed in the container and (2) heating and cooling the food and then packaging it aseptically. The first process is the conventional canning method and is, in principle, the same method that was used by Appert, the Frenchman who invented canning (conventional canning thus is sometimes referred to as *Appertizing*). The second method is generally referred to as aseptic canning. For a more detailed treatment of canning, the reader is referred to the three volume book set on canning by Downing (1996).

a. Conventional Thermal Processing. The conventional canning operation consists of (1) preparing the food (cleaning, cutting, grading, blanching, etc.), (2) filling the container, (3) sealing the container, and (4) subjecting the container to a heat-cool process sufficient for commercial sterility. There are several methods of accomplishing the thermal process, and all are governed by principles of heat transfer and sterilization that have been discussed above. Since it is desirable to increase production rates while causing minimal damage to product quality, most developments have dealt with improved rates of heating.

The still retort is the oldest type of equipment used for thermal processing. It is currently used in large canning plants for processing large containers of conduction heating foods and for glass packed products and in small canning plants for all types of products.

Basically, the method consists of loading crates of containers into an appropriately designed iron vessel (retort), closing the vessel, and heating the containers with steam. The temperature is regulated by a controller and the length of the process is determined by the rate of heat transfer into the containers. Cooling is accomplished by shutting off the steam and adding cold water to the retort. For large metal containers and glass jars with press-on lids, overriding air pressure must be used at the start of cooling because the pressure difference between the inside and outside of the container can otherwise cause, respectively, buckled cans and dislodged lids.

Introduction of steam into the retort should be done with care since it is necessary to displace all of the air in the retort. Presence of air during thermal processing can result in underprocessing since steam-air mixtures result in lower heat-transfer rates than steam or water alone.

Still retorts are either “horizontal” or “vertical” and are batch operated. A vertical retort is shown in Figure 6.13. Design and operation must meet approved standards and each canning plant must have personnel present at all times who have received specific training in retort operation. Procedures have been established for reprocessing food that has been underprocessed.

Improvements in batch-type retort systems have centered on the mechanics of handling the containers. In a conventional system, containers

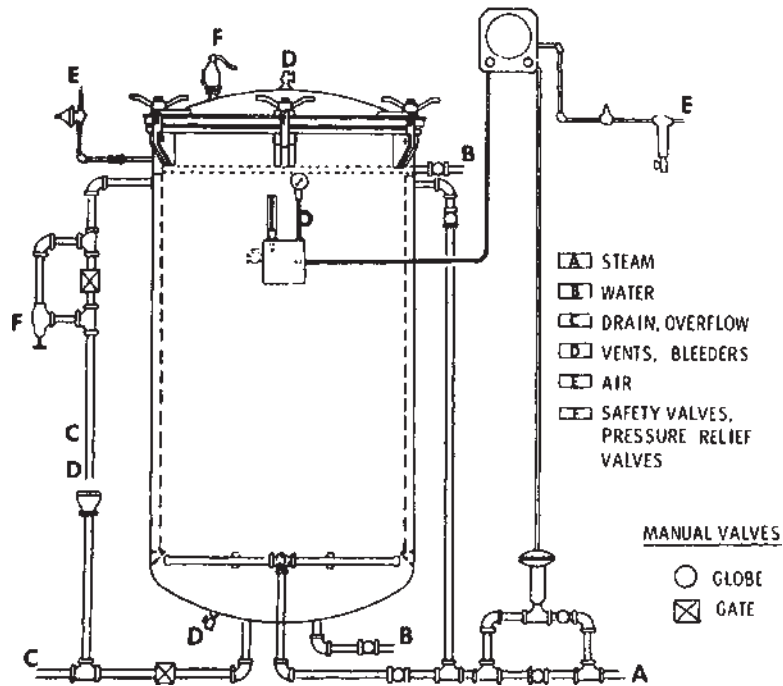


FIGURE 6.13 Vertical retort.

are loaded into crates for easy handling. To circumvent the container handling system, a "crateless" retort has been developed. The retort is filled with water which acts as a cushion for cans which are added by means of a conveyor. Steam is used to remove the water after the retort has been closed. After they are processed, the cans are deposited onto a shaking screen and are then conveyed to an unscrambler. The primary advantage of this system is the reduction in labor costs.

Continuous retorts offer two distinct advantages over batch-type retorts: (1) the production rate is greater and the labor cost is lower, and (2) the rate of heat transfer is greater in products which transmit heat energy primarily by convection. The second advantage occurs because the product is agitated as it moves through the retort.

There are currently at least four types of continuous retort systems that use steam as the heat transfer medium. Trade names or identifying terms for the processes are (1) Sterilmatic, (2) Orbitort, (3) Hydrostatic, and (4) Hydrolock.

In the Sterilmatic system cans are admitted into the retort through a mechanical pressure lock and are conveyed through the retort by means of

a horizontal, helical spiral. The cans remain at the periphery of the helix, and each can rotates about its own axis for a portion of each rotation. By operating the reel at 5 rpm each can rotates about 100 rpm around its own axis as it moves through the retort. This rotation provides the agitation and improved heat transfer mentioned above.

The Orbitort is similar to the Sterilmatic except it is used with more viscous products such as cream-style corn. Once the retort is loaded, each can is locked into position. That is, each can is prevented from rotating about its own axis. At a critical reel speed of about 35 rpm, the headspace bubble in the can follows an elliptical path through the center of the container significantly increasing the rate of heat transfer. This operation is particularly suited to retorting No. 10 (603 × 700) cans of cream-style corn since Sterilmatic or batch cookers result in long process times and relatively poor product quality.

The Hydrostatic cooker employs a unique method of confining high-pressure steam. Steam is confined and controlled by adjustable water legs at the entrance and exit of the retort (Fig. 6.14). For each 101.4 kPa (14.7 psi), a water column approximately 10.4 m (34 ft) high is required. In operation, a conveyor chain elevates the containers in air in the entrance leg and then lowers them through a U-shaped water leg. Water temperature at the entrance of the leg is close to 80°C and at the exit is 107–118°C. As the containers move down the leg, the temperature gradually increases, making this system particularly attractive for containers subject to thermal shock. After the containers pass the bottom of the U, they soon enter the steam chamber where they reside for the appropriate length of time. The can must travel at least two passes in the steam chamber (one up and one down) and then exit through another U-shaped water leg. To aid heat transfer, equipment manufacturers have provided means of agitating the containers as they travel through the cooker.

The Hydrolock system provides continuous agitation of containers by rolling them along tracks (Fig. 6.15). The containers enter and leave through the same pressure lock, which maintains pressure partly by a water seal and partly by a mechanical seal. The versatility of the Hydrolock system makes it suitable for either rigid containers or flexible pouches.

Direct flame sterilization of food in rigid containers has been successfully achieved with cans of small sizes. In this system the cans are conveyed on a live conveyor (each can rotates as it is conveyed) across a bank of gas burners operating at 1100°C. Since there is no overpressure, the containers must be able to withstand internal steam pressures of 170–270 Pa. Since cans larger than 211 or 300 diameter cannot withstand this amount of internal pressure, applications of this system are somewhat limited. With mushrooms, extremely high heat transfer rates are attained, resulting in decreased process times and improved product quality.

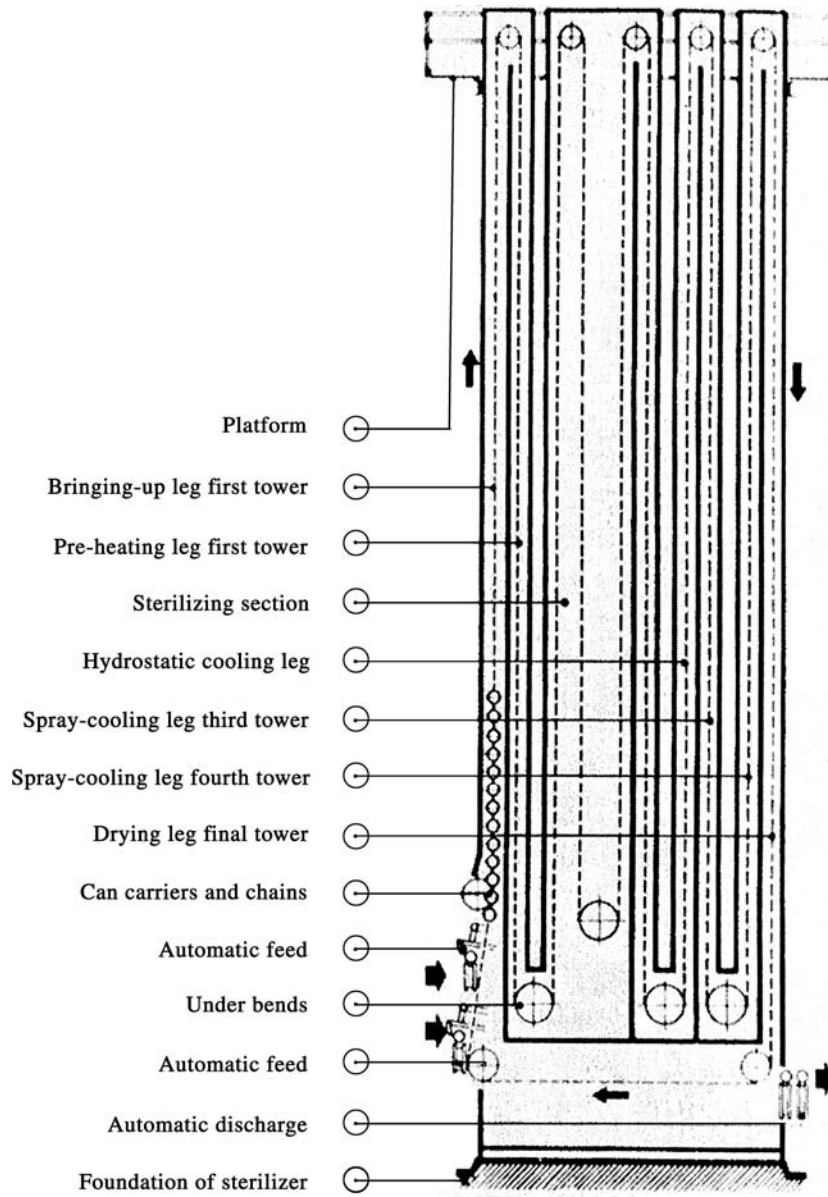


FIGURE 6.14 Hydrostatic cooker.

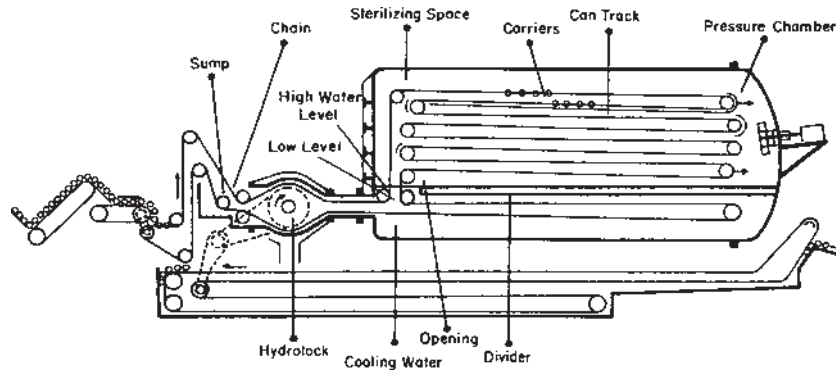


FIGURE 6.15 Hydrolock Sterilizer.

b. Aseptic Processing. Sterilizing product prior to packaging involves the same principles as discussed with respect to prior pasteurization prior to packaging. The only differences between aseptic commercial sterilization and pasteurization are the severity of the thermal process and the temperatures used. Since very high temperatures are employed (130–180°C) in aseptic commercial sterilization, these processes are generally referred to as *ultrahigh temperature* (UHT) processes. Although the process must accomplish commercial sterilization, processing at these temperatures usually requires that the process be based on enzyme inactivation since some enzymes exhibit greater heat resistance in this temperature range than do microorganisms.

Heat-exchange equipment used for aseptic processing include scraped surface heat exchangers, plate heat exchangers, tubular heat exchangers, and equipment involving direct steam injection. Systems have been developed for liquids, for liquids containing small particles, and for fluids that contain large particles. Since UHT processing is on the order of seconds, the residence time must be precisely controlled to avoid underprocessing. Detailed descriptions of these systems can be found in David et al. (1996).

In most aseptic processes, the product is pumped through a system consisting of heaters, a hold tube, and coolers. The pump design for the regulations state that a metering pump must be located upstream of the holding tube to ensure that the required residence time will be maintained. The metering pump, frequently referred to as the timing pump, is a positive displacement type (as distinguished from a centrifugal pump) because the delivery from this type of pump is less sensitive to pressure drop. However centrifugal pumps are generally used for initial sterilization of the system with hot water and for cleaning in place.

The type of positive displacement pump selected for aseptic application is dependent on product viscosity, presence of particulates, pressure drop, and cost.

Rotary displacement pumps are usually used when the pressure drop is less than 10 atm (1000 kPa) and particulates are less than approximately 3 mm maximum dimension. For higher pressure drop, a high pressure piston-type pump is used. For pumping fluid with particulates up to 7 cm maximum dimension, a reciprocating piston pump is used.

One of the most important system components in aseptic processing is the heating system. The objective is to elevate the temperature from room temperature or pasteurization temperature to the ultrahigh temperature processing range (up to 180°C) as rapidly as possible and with minimum fouling of the heat exchange surfaces. The systems are either direct heating or indirect heat-exchange systems.

For direct heating, either steam is directly added to the product (steam injection) or the product is exposed to an atmosphere of pressurized steam (steam infusion). For steam infusion, the product is either sprayed into the steam or is exposed as a free-falling film. Based on the enthalpy of condensing steam, a rule of thumb is that approximately 1 kg of steam will condense for every 10 kg of product that is heated 55°C. Thus the dilution rate for the product is approximately 10% for many aseptically processed products heated by direct steam. To remove this moisture, these products are generally cooled by spraying the product into a vacuum vessel so that water is evaporated and the heat of vaporization is extracted from the product as sensible heat.

The advantages over indirect heating include low initial cost, nearly instantaneous heating and cooling, minimum fouling, no moving parts, minimum floor space, and aeration of the product during flash cooling. Disadvantages include dilution of the product occurs by condensing steam, culinary steam is required, high shear can result from condensation of the steam potentially destabilizing disperse phase systems, volatile flavors may be removed from the product during flash cooling, and pressure and vacuum must be precisely controlled during heating and cooling, respectively.

For indirect heating and cooling the product is heated or cooled by indirect contact with a heating or cooling medium, i.e., heat is transferred through a heat transfer surface. Plate heat exchangers are used for nonviscous products such as milk or juices and consist of corrugated plates stacked in a press that allows steam or hot water to flow in alternating streams from the product. Hot water is generally used as the heating medium if the product is prone to fouling because the temperature difference across the plate wall can be minimized. Frequently, the hot product is cooled by using it to preheat the cold incoming product. This processes, called *regenerative heating*, requires that the pressure on the hot commercially sterile product side of the plate be at slightly higher pressure than the cold, unsterile product side so that any leakage will be from commercially sterilized to unsterilized product.

TABLE 6.10 Characteristics of Direct and Indirect Heat Exchange Systems for Aseptic Processing

| Equipment type | Product quality | Aroma retention | Energy saving | Capital cost | Space | Pulp capability | Fouling length of run | Turndown ^a |
|---------------------------|-----------------|-----------------|---------------|--------------|-----------|-----------------|-----------------------|-----------------------|
| Steam injection/in-fusion | Excellent | No | Poor | High | Fair | Fair-good | Excellent | Fair |
| Plate heat exchange | Good | Yes | Excellent | Low | Excellent | Limited | Limited | Good |
| Tubular: | | | | | | | | |
| Small tubes | Medium | Yes | Fair | Medium | Good | Good | Limited | Good |
| Large tubes | Poor | Yes | Fair | Low | Fair | Good | Good | Good |
| Swept surface | Good | Yes | Very Poor | Very High | High | Fair-Good | Good | Good |

^aTurndown is the capability of the system to process at different rates to accommodate different number of fillers or different package sizes. Source: From Dinnage (1983), with permission of the Food Processors Institute.

Advantages of plate heat exchangers include low initial cost, small hold up volume in the heat exchanger, easy inspection, and flexibility in sizing the system. Significant disadvantages include fouling tendencies of some products, high regasketing costs, and restriction to relatively low viscosity products. Tubular heat exchangers generally consist of concentric stainless steel tubes or tubes in a shell surrounded by an atmosphere of steam or water under pressure. The advantages of tubular systems are few gaskets to maintain, compact units, and no moving parts. Disadvantages include large pressure drops, difficult to inspect, fouling tendencies and restricted to products of relatively low viscosity and small particle size.

Scraped surface heat exchangers are more suited to viscous products including products with particles. Basically a unit consists of a jacketed tube with a scraper blade (called a *mutator*) positioned in the inner tube. The mutator generally has two to four blades and rotates at 40–400 rpm as product is pumped through the central tube. The blades mix the product increasing the heat transfer rate and reducing fouling. The heating or cooling medium flows on the outside of the central tube and may also be introduced thorough a tube on the centerline of the mutator. Advantages include processing of relatively viscous products including products with particulates, flexibility to expand the system, relatively low pressure drops, and ability to process at very high temperature with minimal fouling. Primary disadvantages are high cost per unit heat transfer area, high operating costs, large space requirements, and larger shear rates, which can damage particulates. The characteristics of the systems just described are shown in Table 6.10. There are several excellent books on aseptic processing that provide detailed characteristics of aseptic processing and packaging systems and cover the chemistry, microbiology, and packaging of aseptically processed products. Additional descriptions of hold tubes, deaerators, and surge tanks are also included (Sastry and Cornelius, 2002; Willhoft, 1993; David et al., 1996).

SYMBOLS

| | |
|-------|---|
| a | initial number of microorganisms |
| b | number of microorganisms after thermal processing |
| B | thermal process time (min) |
| c | concentration (number of organisms per unit volume or moles or grams per unit volume) |
| T_C | cooling water temperature (°F) |
| D | decimal reduction time (min) |
| E_a | Arrhenius activation energy (cal/mol or calories per organism) |
| f | time (min) for the heat penetration curve to traverse one log cycle (min) |

| | |
|----------|--|
| F | thermal death time (min) |
| F_o | thermal death time at 250°F for organisms with $z = 18F = 10C$ (min) |
| g | retort temperature-product cold point temperature at the end of the heating cycle (°F) |
| I | retort temperature – initial product temperature = $(T_R - T)$ (°F) |
| j_c | lag factor for cooling = $(T_C - T_{pic}) / (T_C - T_{ic})$ |
| j_h | lag factor for heating = $(T_R - T_{pih}) / (T_R - T_{ih})$ |
| k | first-order reaction rate constant (min^{-1} or h^{-1}) |
| l | lag time for heating the retort (min) |
| P_t | processor's time (min) |
| T_p | product temperature (°F) |
| Q_{10} | rate of reaction at $(T + 10)^\circ\text{C}$ /rate of reaction at $T^\circ\text{C}$ |
| R | gas law constant (cal/K mol) |
| T_R | retort temperature (°F) |
| s | Arrhenius frequency factor (s) |
| t | time (min or h) |
| T | temperature (°C, °F, K, or °R) |
| T_c | center or cold point temperature = T_p (°F) |
| T_i | initial product temperature (°F) |
| T_{pi} | pseudo-initial product temperature (°F) |
| T_s | surface temperature = T_R (°F) |
| TDT | thermal death time (min) |
| U | thermal death time at retort temperature (min) |
| z | F temperature change required to change the TDT by a factor of 10 (°F) |

Subscripts

| | |
|-----|-------------------------------|
| c | cooling, center or cold point |
| h | heating |
| T | temperature (°F) |

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7

Storage at Chilling Temperatures

I. INTRODUCTION

Storage of foods at temperatures above freezing and below 15°C (59°F) is known as refrigerated or *chilling* storage. Chilling storage is widely used because it generally results in effective short-term preservation by retarding the following:

1. Growth of microorganisms
2. Postharvest metabolic activities of intact plant tissues and post-slaughter metabolic activities of animal tissues
3. Deteriorative chemical reactions, including enzyme-catalyzed oxidative browning or oxidation of lipids and chemical changes associated with color degradation, autolysis of fish, and loss of nutritive value of foods in general
4. Moisture loss

Chilling is also used for such nonpreservative purposes as crystallization; aging of beef, wine, and cheese; and to facilitate such operations as pitting of cherries and peaches, cutting of meat, and slicing of bread.

This chapter is based on the original chapter by Owen R. Fennema, previously published as "Preservation of Food by Storage at Chilling Temperatures" in the previous edition of *Physical Principles of Food Preservation*.

II. CONSIDERATIONS

A. Normal Behavior of Food Stored At Chilling Temperatures

Most physiological processes in plant and animal tissue including growth of microorganisms at room temperatures are enzyme-catalyzed. Consequently, the effect of temperature on these reactions basically reflects the effect of temperature on enzyme-catalyzed reactions. In Chapter 2, the effect of temperature on reaction rates was characterized by temperature coefficients defined primarily by the temperature range. For reactions around 30°C the temperature coefficient is defined as the Q_{10} , i.e., the ratio of the reaction rate at $T + 10^\circ\text{C}$ to the reaction rate at temperature T . For enzyme-catalyzed reactions the Q_{10} is 2, i.e., the rate at 30°C is twice the rate at 20°C, which is twice the rate at 10°C, which is twice the rate at 0°C. Consequently, lowering the temperature from 30°C to 10°C can reduce enzyme-catalyzed reactions such as respiration, growth of microorganisms, and physiological reactions such as browning by a factor of four. The effect of temperature on reaction rates catalyzed by enzymes is so dramatic it is no wonder that temperature reduction is a method of choice for extending the shelf life of minimally processed foods.

1. Plant Tissues

The most important characteristic of harvested, intact plant tissues (fruits, vegetables, seeds, nuts) is the persistence of aerobic respiration throughout the storage life of the product. Aerobic respiration involves metabolism of carbohydrates and organic acids in the presence of atmospheric oxygen with the ultimate production of carbon dioxide, water, heat, and small amounts of organic volatiles and other substances. For maximum storage life of plant tissues at chilling temperatures, it is desirable that (1) aerobic respiration be allowed at a slow rate so that the maintenance processes associated with life continue to function and the natural protective coating which hinder invasion of microorganisms remain intact and (2) the temperature be suitably low so that major deteriorative reactions are slowed as much as possible. When the keeping qualities of various fruits and vegetables are compared, an association (not necessarily a cause and effect relationship) is often found between the rate of respiration and the rate of quality loss; i.e., commodities that normally respire rapidly often have short storage. This relationship is evident from the data in Table 7.1, where most of the rapidly respiring (expressed in terms of heat evolution) commodities on the left half of the table are highly perishable. Two other points about the data in Table 7.1 are worthy of comment: (1) at a constant temperature, species (and even varieties) exhibit large differences in rates of respiration, and (2) the amount of heat generated is sufficient to influence

TABLE 7.1 Respiration Rates of Fruits and Vegetables Based on Evolution of Heat^a

| Rapid (> 11,600 kJ) | Moderately rapid (5,800–11,600 kJ) | Moderately slow < 2,300–5,800 kJ) | Slow (< 2,300 kJ) |
|------------------------|---------------------------------------|--------------------------------------|----------------------|
| Asparagus | Beans, lime | Apples (yellow transparent) | Apples |
| Beans (green) | Brussels sprouts | Beets (topped) | Cabbage |
| Broccoli | Lettuce, leaf | Carrots (topped) | Cranberries |
| Corn, sweet | Raspberries | Cauliflower | Grapefruit |
| Okra | Spinach | Celery | Grapes |
| Peas (green) | Strawberries | Cherries (sour) | Lemons |
| | | Lettuce, head | Onions, mature |
| | | Potatoes, sweet | Oranges |
| | | Turnips | Peaches |
| | | | Plums |
| | | | Potatoes, mature |
| | | | Tomatoes |

^aFrom 1 metric ton (1000 kg) of product during a 24-h. period at 4.5°C (40°F).

Source: Hardenburg, Watada, and Wang (1986).

refrigeration requirements. Thus any calculation of refrigeration requirements for intact plant tissues must include heat of respiration, sensible heat of the product, and heat leakage into the storage facility.

When temperature reduction is used to slow the rate of aerobic respiration, this usually delays senescence and decay of plant tissues (except for those susceptible to chilling injury) and enables some fruits to be ripened at controlled rates.

In addition to large differences in the rates at which various plant tissues respire, a given tissue frequently does not respire at a constant rate when held at a constant temperature. This irregularity in rate of respiration is most apparent in fruits that undergo a *climacteric* (a relatively abrupt but temporary rise in the rate of respiration). This behavior is shown in the upper curve of Fig. 7.1. The climacteric maximum frequently but not always occurs at optimum ripeness of the fruit and the sharp decline in respiration rate following the maximum is often associated with over maturity, a stage referred to as senescence, a progressive loss of membrane integrity. Thus the climacteric maximum can be thought of as point dividing growth and maturation from deterioration and death.

The exact nature (time after harvest, duration, extent of rise) of the respiration curve produced by fruits that exhibit a climacteric varies greatly depending on species, variety, maturity, and environmental conditions (Biale, 1960).

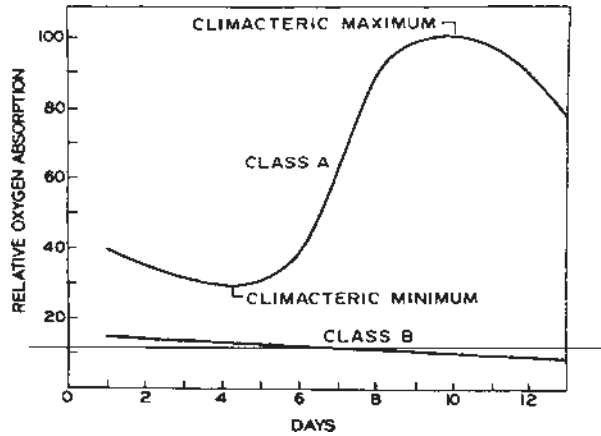


FIGURE 7.1 Respiratory behavior of climacteric and nonclimacteric fruits. Class A: Climacteric fruit; Class B: Nonclimacteric fruit. (From Biale, 1960.)

Vegetables do not exhibit the climacteric phenomenon, and it does not occur in some fruits. Table 7.2 contains a listing of fruits for which a climacteric has been conclusively demonstrated and fruits for which a climacteric has never been observed or is doubtful. Nonclimacteric fruits generally exhibit a decline in respiratory activity during storage, as illustrated by the lower curve of Fig. 7.1. The respiratory behavior of vegetables is similar to that of nonclimacteric fruits except that many vegetables undergo an abrupt decline in rate of respiration immediately following harvest, and then a more gradual decline in rate during storage (Platenius, 1942). Many members of the nonclimacteric group of fruits and vegetables respire more slowly than those of the climacteric group but there are exceptions to this behavior.

Fruits in general are harvested when fully mature and either ripe or unripe. Harvesting in an unripe state is often done with fruits that are capable of ripening during storage, or are soft when ripe, or retain optimum ripeness for only a relatively short period (e.g., bananas, avocados, pears). Some such as citrus fruits are not capable of ripening during storage. Vegetables are frequently harvested when immature, tender, and succulent.

2. Animal Tissues

Slaughter of an animal results in disruption of the natural protective coating and curtailment of most activities common to life. A major consequence is that the tissue is left with none of the life processes that formerly resisted deterioration. Lost is the ability to effectively resist invasion by microorganism—an ability so

TABLE 7.2 Classification of Some Edible Fruits According to Their Respiratory Behavior During Ripening

| Climacteric (fully demonstrated) | Nonclimateric (not demonstrated or doubtful) |
|-------------------------------------|---|
| Apple | Black berry |
| Apricot | Cacao |
| Avocado | Cashew |
| Banana | Cherry, sour |
| Biriba | Cherry, sweet |
| Bitter melon | Cucumber |
| Blueberry, highbush | Grape |
| Blueberry, lowbrush | Grapefruit |
| Blueberry, rabbiteye | Java plum |
| Breadfruit | Lemon |
| Cantaloupe | Litchi |
| Cherimoya | Mountain apple |
| Chinese gooseberry | Olive |
| Corossol sauvage | Orange |
| Feijoa | Pepper |
| Fig, common | Pineapple |
| Guava, "purple strawberry" | Rose apple |
| Guava, "strawberry" | Satsuma mandarin |
| Guava, "yellow strawberry" | Star apple |
| Guava | Strawberry |
| Honeydew melon | Surinam cherry |
| Kiwi | Tree tomato |
| Mammee-apple | |
| Mango | |
| Papaw | |
| Papaya | |
| Passion fruit | |
| Peach | |
| Pear | |
| Persimmon | |
| Plum | |
| Sapote | |
| Soursop | |
| Tomato | |
| Watermelon | |

Source: Yildiz (1994).

effective in living animals that many interior tissues exist in a sterile or near sterile condition. Also lost is the oxygen–carbon dioxide exchange system (breathing and blood circulation) which is necessary for normal aerobic respiration ($\text{glucose} + \text{O}_2 \rightarrow \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{energy}$). Following cessation of blood circulation, the internal supply of oxygen rapidly diminishes and aerobic respiration ceases. Anaerobic respiration ($\text{glycogen} \rightarrow \rightarrow \text{glucose} \rightarrow \rightarrow \text{lactic acid} + \text{energy}$) occurs in its place, causing the pH to fall from a physiological value somewhat above 7 to an ultimate value ranging from about 5.1 to 6.5. The exact ultimate pH depends on the type of muscle and how it has been handled before and after slaughter (De Fremery and Pool, 1960). All respiration ceases after a postmortem period of 1–36 h (the time for completion depending on the same factors just mentioned for ultimate pH).

At some point during the short-term course of anaerobic respiration (anaerobic glycolysis) the ATP content of muscle decreases to a level such that rigor mortis ensues (the muscle changes from a soft, pliable condition to an inextensible, generally firm condition). The diminished level of ATP and the lowering of pH tend to destabilize muscle proteins, especially sarcoplasmic proteins, and the muscle suffers a decrease in water-holding capacity. A normal lowering of pH in properly chilled muscle is desirable, however, since this helps retard growth of microorganisms and favor retention of a pleasing color. To achieve good qualities (tenderness, water-holding capacity, color), carcasses should be promptly cooled following slaughter and the handling practices should encourage slow respiration so that the muscle is cool when the desired ultimate pH value is attained.

Following onset of rigor, some muscles are stored for an additional period of time to allow for resolution of rigor and an associated improvement in tenderness and water-holding capacity (Lawrie, 1966).

3. Nontissue Foods

Since nontissue (milk, shell, eggs, manufactured foods) foods are physiologically inactive (the physiological activity of eggs, if it does in fact persist, is of no concern), the various complexities associated with the physiological activities of plant and animal tissues are not encountered. Although nontissue foods deteriorate at greatly different rates, effective short-term preservation can nearly always be accomplished by prompt cooling to near their respective freezing points. Highly perishably nontissue food, such as milk, must be handled under strict sanitary conditions and be promptly cooled.

B. Causes of Quality Loss

Loss of food quality during chilling storage can occur through several mechanisms.

1. Microbiological Activity

Growth of microorganisms is a major cause of spoilage of most natural and manufactured foods. Animal tissue are especially susceptible to spoilage by microorganisms (especially bacteria) since (1) slaughtering destroys the muscle's ability to combat microorganisms, (2) dressing and cutting operations disrupt the protective coating and contaminate previously sterile or near sterile tissues with microorganism from the intestines and exterior surfaces of the animal, and (3) muscle is an excellent substrate for growth of microorganisms. Plant tissues are moderately susceptible to spoilage by microorganisms, especially fungi.

2. Physiological and Other Chemical Activities

Depending on the product, quality loss resulting from physiological or other chemical activities can be slight, moderate, or severe. Fruits and vegetables, because of natural senescence, eventually become unacceptable under optimum conditions of chilling storage. Low nonfreezing storage temperatures can result in physiological disorders and damage to the quality of some fruits and vegetables (e.g., chilling injury). Unless proper precautions are observed, normal respiration can cause accumulation of carbon dioxide and depletion of oxygen to levels that instigate physiological disorders and quality defects in fruits and vegetables.

Autolysis is a major cause of damage in fish. Natural postslaughter metabolism of animal tissue, if improperly controlled, can result in excessive toughness, poor water-holding capacity, and poor color—the exact defects depending on the type of tissue and the conditions. Chemical reactions such as lipid oxidation, pigment degradation, protein denaturation, development of various off flavors, and vitamin degradation can reduce the quality of both tissue and nontissue foods. Furthermore, chemicals that are added intentionally or unintentionally to the product or its environment (e.g. food additives, sulfur dioxide, ozone, ammonia, carbon dioxide, and ethylene) can result in damage to some products. For example, ammonia is an unintentional additive (leaks in refrigeration equipment) the presence of which should be carefully avoided since it can cause severe damage to many food products.

3. Physical Damage

Bruising is a major cause of damage to fruits, a loss of product quality due to injury stress (Varoquaux and Wiley, 1994). Dehydration, if excessive, can cause substantial damage to most food products (e.g., wilting or shriveling of fruits and

vegetables, enlargement of air sacs in eggs). Excision of muscle prerigor can result in excessive contraction, toughness, and poor water-holding capacity.

C. Temperature

1. Desirable Consequences of Chilling Temperatures

Control of temperature in the storage facility is important because it has a profound effect on growth of microorganisms, metabolic activities, other chemical reaction, and moisture loss. Growth of pathogenic microorganisms occurs rapidly in the range 10–37°C (50–98°F) but only slowly in the range 3.3–10°C (38–50°F). Below 3.3°C (38°F) pathogenic microorganisms, can no longer grow. Growth of mesophilic and thermophilic microorganisms is greatly retarded at chilling temperature. Psychotrophic microorganisms, of course, grow well in the range 0–15°C (32–59°F), but in most instances their growth is much slower in this range than at temperatures of 15–45°C (59–113°F). Chilling temperatures therefore substantially retard spoilage caused by microorganisms.

Loss of quality resulting from physiological activity and other chemical reactions also can be effectively reduced by chilling storage. As the temperature is lowered within the range of chilling temperature, decreases occur in the rates of respiration of those fruits and vegetables that are not subject to chilling injury. This occurrence, illustrated for representative products in Table 7.3, effectively retards the process of senescence and results in an extension of storage life.

Similarly, the storage temperature can control the ripening of fruits. Within the range of chilling temperatures, the rate of ripening usually declines as the temperature is reduced, and ripening ceases at temperatures below about 4°C (39°F) (ripening ceases at higher temperatures for fruits subject to chilling injury). Below about 5°C (41°F) failure to ripen is associated with the absence of a climateric rise.

Figure 7.2 shows the prompt cooling of sweet corn is necessary for retention of its desirable sweetness. Data in Table 7.4 illustrate the general need for low handling and storage temperatures for retention of vitamin C in vegetables.

Surprisingly small changes in temperature sometimes result in marked changes in the rate of quality loss. For example, the storage life of cod and haddock is 22–29 days at –1 to –2°C (28–30°F) as compared to 13 days at the temperature of melting ice (Dassow and Slavin, 1971). Likewise, fresh poultry has a 41% longer (additional 12 days) storage life at –2°C (28°F) than at 0°C (32°F), and Williams pears have a 12-week storage life at –1.5°C (29°F) as compared to 10 weeks at –1°C (30°F), 9 weeks at –0.5°C (31°F), 7.5 weeks at 0°C (32°F), and 6 weeks at 1°C (34°F) (Fidler, 1970). Thus careful control of handling and storage temperatures is necessary in order to achieve maximum storage life and minimal loss of nutrients.

TABLE 7.3 Respiration Rates^a of Fruits and Vegetables Expressed as Rates of Carbon Dioxide Production (mg/kg(h), at Various Temperatures

| Commodity and source reference | Temperature | | | | | |
|--------------------------------|---------------|--------------------|----------------|----------------------|----------------------|----------------------|
| | 0°C (32°F) | 4–5°C (40–41°F) | 10°C (50°F) | 15–16°C (59–60°F) | 10–21°C (68–70°F) | 25–27°C (77–80°F) |
| Apples, summer | 3–6 | 5–11 | 14–20 | 18–31 | 20–41 | — |
| Apples, fall | 2–4 | 5–7 | 7–10 | 9–20 | 15–25 | — |
| Asparagus | 27–80 | 55–136 | 90–304 | 160–327 | 275–500 | 500–600 |
| Beans, snap | 20 | 35 | 58 | 93 | 130 | 193 |
| Blueberries | 2–10 | 9–12 | 23–35 | 34–62 | 52–87 | 78–124 |
| Cabbage | 4–6 | 9–12 | 17–19 | 20–32 | 28–49 | 49–63 |
| Peas, unshelled | 30–47 | 55–76 | 68–117 | 179–202 | 245–361 | 343–377 |
| Peas, shelled | 47–75 | 79–97 | — | — | 349–556 | — |
| Spinach | 19–22 | 35–58 | 82–138 | 134–223 | 172–287 | — |
| Sweet corn, w/husks | 30–51 | 43–83 | 104–120 | 151–175 | 268–311 | 282–435 |

^a Respiration rate often shown as a range. To compute heat evolution rates at harvest time, use either the highest figure or median one. To convert to Btu/ton (2000 lb)/24h day, multiply respiration rate by 220. To convert to kcal per 1000 kg/24 h, multiply by 61.2. Source: Hardenburg et al. (1986).

2. Undesirable Consequences of Chilling Temperatures

There are some instances where damage can occur if cooling is too fast or if the temperature is reduced to near freezing. For example, peaches undergo damage to quality if cooled too rapidly, a defect referred to as *wooly texture* (Fidler, 1970). Cold shortening of muscle, chilling injury of plant tissues, and staling of bread are additional types of injury that can result from low chilling temperatures.

a. Cold Shortening of Animal Muscle. Animal muscle that is excised immediately after slaughter (not common) can undergo a detrimental occurrence known as *cold shortening* if it is promptly cooled prerigor to the range 0–5°C (32–41°F). As the name implies, the excised muscle shortens greatly, resulting in poor water-holding capacity and usually excessive toughness. Cold shortening has been observed with prerigor excised muscle from poultry, beef, and lamb. It has been suggested that cold shortening results because low chilling temperatures impair the ability of the sarcoplasmic reticulum to regulate the distribution of calcium ions in muscle.

TABLE 7.4 Loss of Vitamin C in Fresh Vegetables During Storage

| Commodity | Temperature of storage (°C) | Total vitamin C | | |
|------------------|-----------------------------|-----------------|-----------------|------|
| | | Fresh (mg/100g) | Loss in % after | |
| | | | 24 h | 48 h |
| French beans | 4 | 25.6 | 22 | 34 |
| | 12 | | 26 | 40 |
| | 20 | | 36 | 52 |
| Peas | 4 | 36 | 7 | 10 |
| | 12 | | 18 | 29 |
| | 20 | | 23 | 36 |
| Spinach (spring) | 4 | 39.8 | 20 | 32 |
| | 12 | | 27 | 43 |
| | 20 | | 34 | 54 |
| Spinach (autumn) | 4 | 72.3 | 27 | 33 |
| | 12 | | 41 | 51 |
| | 20 | | 56 | 79 |
| Spinach (winter) | 4 | 120.5 | 5 | 8 |
| | 12 | | 5 | 8 |
| | 20 | | 14 | 20 |

Source: Zacharias (1962).

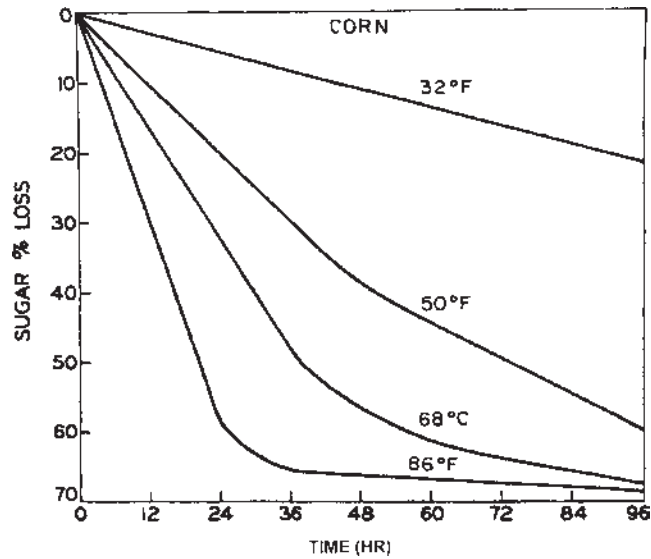


FIGURE 7.2 Effect of temperature on sugar loss in sweet corn. (From Appleman and Arthur, 1919.)

The possible adverse consequences resulting when freshly slaughtered animal carcasses are cooled very rapidly to 0–5°C are less well documented than with excised muscle. It has been demonstrated, however, that intact longissimus dorsi muscles of lamb carcasses cooled rapidly to 0–5°C are substantially tougher than similar muscles from carcasses which are cooled less rapidly (Marsh et al., 1968). Supporting evidence indicated that cold shortening was responsible for the toughening effect. Although the skeleton tends to restrict muscle shortening, Marsh and Leet (1966) indicated several means by which carcass muscles can undergo cold shortening.

1. Several muscles such as the sternomandibularis (neck muscle) are relatively free to shorten because the neck has been severed.
2. The economically important longissimus dorsi muscle is comparatively free to shorten because its fibers in the natural state are firmly attached to the skeleton at one end only.
3. A single muscle attached at both ends may maintain a constant total length while certain portions contract and other portions stretch. This can easily result because of temperature differentials within a muscle.

Muscles in prerigor carcasses of animal species other than lamb probably are susceptible to cold shortening, especially if they contain large quantities of the sensitive red fibers.

b. Chilling Injury. A substantial number of fruits and vegetables, especially those of tropical or subtropical origin, develop physiological disorders when exposed to temperatures below their optimum storage temperatures but above their freezing points. This type of disorder is known as *chilling injury*, *low-temperature injury*, or *cold injury*. Care must be taken to store these products at temperatures above their respective critical temperatures (lowest temperature at which chilling injury does not occur) if more than a brief storage period (depends on the product) is anticipated.

The symptoms of chilling injury differ depending on the product. Common symptoms include browning (external or internal or both), pitting or other skin blemishes, excessive rotting, and failure to ripen (fruits). One of the first indications of chilling injury in apples stored at a constant temperature is an abnormal increase in the rate of respiration (Fidler, 1968).

Factors that influence the onset of chilling injury are discussed below (Fidler, 1968).

1. Temperature. Different species and varieties exhibit different critical temperatures for chilling injury, ranging from a high of 14.4°C (58°F) for Lacatan bananas to a low of 1°C (34°F) for certain varieties of apples. Critical temperatures for various susceptible fruits and vegetables are listed in Table 7.5. Many critical temperatures fall in the range of 7–12°C (46–54°F). Generally temperate crops have lower critical temperatures (below 5–10°C) than crops grown in the tropical zone (Hardenburg et al., 1986).
2. Time at subcritical temperature. A certain time must elapse at subcritical temperatures for symptoms of chilling injury to develop. Minimum exposure times needed to induce chilling injury range from 12 h for bananas to 9–12 days for tomatoes to 2–3 months for citrus fruits (McColloch, 1953). The minimum time needed for symptoms of chilling injury to develop also depends on the subcritical temperature used (Fidler, 1970). Symptoms often develop more rapidly at high subcritical temperatures; however, given sufficient time, maximum injury occurs at the lowest nonfreezing temperature. This point was well illustrated by Van Der Plank and Davies (1937). They stored Marsh seedless grapefruit at temperatures ranging from –0.5°C to 10°C (31–50°F) and examined them at various storage times. Fruit stored at 10°C was not damaged during the storage period used. After 25 days, fruit stored at 7.5°C exhibited pitting of the surface, whereas fruit at –0.5°C exhibited no damage. After 33 days fruit stored at 5°C was most severely injured.

Once a product has been exposed to temperatures below the critical temperature, there are treatments that can alleviate chilling injury

TABLE 7.5 Fruits and Vegetables Susceptible to Chilling Injury When Stored at Moderately Low but Nonfreezing Temperatures

| Commodity | Approximate lowest safe temperature (°C) | Character of injury when stored between 0°C and safe temperature ^a |
|--------------------------|--|---|
| Apples certain cultivars | 2–3 | Internal browning, brown core, soggy breakdown, soft scald |
| Asparagus | 0–2 | Dull, gray–green, and lip tips |
| Avocados | 4.5–13 | Grayish–brown discoloration of flesh |
| Bananas, green or rip | 11.5–13 | Dull color when ripened |
| Beans (lima) | 1–4.5 | Rusty brown specks, spots, or areas |
| Beans (snap) | 7 | Pitting and russeting |
| Cranberries | 2 | Rubbery texture, red flesh |
| Cucumbers | 7 | Pitting, water-soaked spots, decay |
| Eggplants | 7 | Surface scald, alternaria rot, blackening of seeds |
| Guavas | 4.5 | Pulp injury, decay |
| Grapefruit | 10 | Scald, pitting, watery breakdown |
| Jicama | 13–18 | Surface decay, discoloration |
| Lemons | 11–13 | Pitting, membranous staining, red blotch |
| Limes | 7–9 | Pitting turning tan with time |
| Mangos | 10–13 | Grayish scald-like discoloration of skin, uneven ripening |
| Melons | | |
| Cantaloupes | 2–5 | Pitting surface decay |
| Honey Dew | 7–10 | Reddish-tan discoloration, pitting, surface decay, failure to ripen |
| Casaba | 7–10 | Same as above but no discoloration |
| Crenshaw and Persian | 7–10 | Same as above but no discoloration |
| Watermelons | 4–5 | Pitting, objectionable flavor |
| Okra | 7 | Discoloration, water-soaked areas, pitting, decay |
| Olives, fresh | 7 | Internal browning |
| Oranges | 3 | Pitting, brown stain |

(continued)

TABLE 7.5 Continued

| Commodity | Approximate lowest safe temperature (°C) | Character of injury when stored between 0°C and safe temperature ^a |
|---------------------------------|--|---|
| California and Arizona Papayas | 7 | Pitting, failure to ripen, off-flavor, decay |
| Peppers, sweet | 7 | Sheet pitting, alternaria rot on pods and calyxes, darkening of seed |
| Pineapples | 7–10 | Dull green when ripened |
| Pomegranates | 4.5 | Pitting, external and internal browning |
| Potatoes | 3 | Mahogany browning (Chippewa and Sebago), sweetening |
| Pumpkins and hardshell squashes | 10 | Decay, especially alternaria rot |
| Sweet potatoes | 13 | Decay, pitting, internal discoloration; hardcore when cooked |
| Tamarillos | 3–4 | Surface pitting, discoloration |
| Tomatoes | | |
| Ripe | 7–10 | Watersoaking and softening, decay |
| Mature–green | 13 | Poor color when ripe, alternaria rot |

^a Symptoms often apparent only after removal to warm temperatures, as in marketing.
 Source: Hardenburg et al. (1986)

symptoms. These consist of intermittent warming, temperature preconditioning, preconditioning, controlled atmosphere storage, pretreatments with calcium or ethylene, hypobaric storage, waxing, film packaging, and chemical applications (Hardenburg et al., 1986)

3. Metabolic state of the tissue. Susceptibility of fruits and vegetables to chilling injury frequently depends on maturity (some apples and bananas are most susceptible at the respiratory climateric), composition

(mineral and acid content of apples), and the growth environment (a given variety of apples can exhibit significantly different critical storage temperatures depending on the climatic conditions that prevailed during growth).

4. Composition of the atmosphere. Alterations in the carbon dioxide and oxygen contents of the storage atmosphere can influence the incidence of chilling injury, but reported results are inconsistent and generalization are not possible.
5. Rate of water loss. Rates of water loss from fruits and vegetable can influence susceptibility to chilling injury, but results vary depending on the product.

c. Staling of Bread. Bread represents a notable exception to the rule that all quality attributes of nontissue foods are retained for longer periods at chilling temperatures than at room temperature. It is evident from Fig. 7.3 that decreasing temperature in the range of 32–0°C (90–32°F) accelerates firming of bread (Pence and Standridge, 1955).

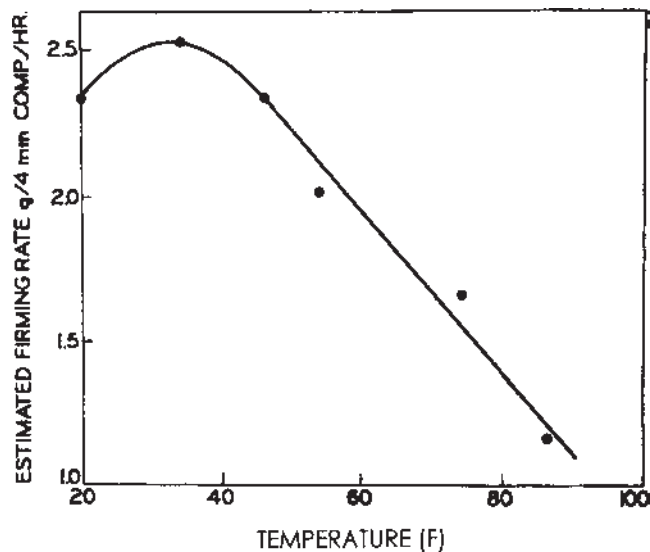


FIGURE 7.3 Firming rate of commercial white bread as influenced by temperature. (From Fence and Standridge, 1955.)

D. Relative Humidity

Control of relative humidity in the storage facility is essential if maximum storage life of foods is desired. Relative humidities that are greater than optimum (1) favor growth of microorganisms and result in excessive food spoilage or (2) result in abnormal splitting of some fruits (e.g., apples and plums) (Wilkinson, 1970).

Relative humidities which are less than optimum result in wilting or shriveling of fruits and vegetables, damage to the appearance of animal tissues, and unnecessary economic losses because of a reduction in product weight. Moisture losses of 3–6% will result in a marked loss in quality of many vegetables. Between the extremes discussed above, relative humidity can influence the severity of physiological disorders, especially flesh breakdown in apples and skin pitting of citrus fruits.

The relative humidity in the storage facility is determined primarily by the temperature difference between the air and the refrigerating coils. A small temperature difference (about 0.5–1°C (1–2°F)) during storage of a cool product is needed in order to maintain a suitably high relative humidity, and this is possible only if the surface area of the refrigerating coil is sufficiently large and air passage across the coil is sufficiently great to provide adequate heat transfer.

E. Air Circulation and Purification

Adequate circulation of air during chilling storage is necessary to (1) maintain a uniform temperature, (2) maintain a uniform composition of the atmosphere, (3) rapidly cool products which enter storage at temperatures warmer than desired, and (4) facilitate air purification when this treatment is desired.

Careful design of airflow patterns (size and location of air ducts, amount of product, and manner of stacking) is an absolute necessity if the above objectives are to be achieved. Moderate to rapid air circulation can result in some product dehydration, but this can be slight provided proper relative humidity is maintained.

Purification of air is sometimes accomplished to remove undesirable odors and to remove volatiles emanating from fruit. In some instances, removal of volatiles can retard ripening, and some claim that it retards the onset of apple scald. Stored apples sometimes develop this disorder, which is characterized by the surface formation of sharply defined brown patches that are often arranged in a ribbonlike pattern (Cook, 1971).

F. Adjuncts to Chilling Temperature

1. Light

As a general rule the storage facility should be dark except during period of product entry or removal. Darkness or reduced light delay the sprouting

of potatoes and onions and may, with certain products, help retard development of off flavors and discoloration.

Ultraviolet light, which is most effective as a bacteriocide at 2600 Å, can suppress growth of bacteria and molds on smooth surfaces, and for this reason it is sometimes used during rapid aging of beef at temperature well above freezing (Urbain and Campbell, 1971). However, care should be used in applying ultraviolet light since it catalyzes oxidative reactions and thus can hasten the onset of off flavors and discoloration.

Exposure to ultraviolet light is of no advantage for fruits and vegetables and is decidedly detrimental to the quality of many high-fat products (e. g., cheese, lard, butter, and cream). Thus longer term application of ultraviolet light is undesirable for most food products.

2. Pasteurization

Mild heat treatments (pasteurization) can be used to reduce the population of microorganisms on fresh fruits (mainly those on or near the surface) and thereby retard decay during chilling storage. As compared to chemical treatments, pasteurization has the advantage of not leaving an undesirable residue.

Pasteurization is sometimes advantageous for such fruits as lemons, papayas, nectarines, peaches, and plums. The treatment involves immersing the fruit in water at 46–54°C (115–130°F) for a period of 1–4 min.

3. Waxing or Oiling

Certain fruits and vegetables are waxed to either reduce dehydration (cucumbers, root crops) or to improve appearance. Waxing is common for rutabagas, cucumbers, mature green tomatoes, and cantaloupes and is not uncommon for peppers, turnips, honeydew melons, sweet potatoes, and certain other crops. The wax consists of paraffin or a vegetable wax/paraffin combination.

Dipping them in light mineral oil 12–24 h after laying can effectively extend the storage life of shell eggs. This treatment retards both dehydration and loss of carbon dioxide. Maintaining the original carbon dioxide content of eggs is an important factor in preserving the quality of the egg white.

4. Oxygen and Carbon Dioxide Contents of the Atmosphere

Altering the oxygen and carbon dioxide contents of the storage atmosphere is done to decrease the rates at which intact fruits and vegetable respire aerobically, to retard growth of microorganisms, and sometimes to inhibit oxidative reactions. The first two goals deserve further elaboration.

a. Retarding Aerobic Respiration of Plant Tissues by Altering the Composition of the Atmosphere. For maximum storage life of plant tissues it is desirable that aerobic respiration be sustained at a slow rate. For some products this can be satisfactorily accomplished by reducing the oxygen content of the atmosphere, increasing the carbon dioxide content of the atmosphere, and reducing the temperature to a suitable level. Shown in Table 7.6 are the effects of various levels of carbon dioxide and oxygen on the rate of respiration (carbon dioxide evolution and oxygen consumption) of apples stored at 3.3°C. Apples provide the most valuable example since they are by far the most important crop that is stored in atmospheres of controlled composition. Reducing the oxygen concentration from the normal value of 21% to 10% or lower decreases the rate of respiration, both in the presence and in the absence of carbon dioxide. Increasing the carbon dioxide concentration over the range of 0.03% (normal) to 10% also decreases the rate of respiration in the presence of a broad range of oxygen concentrations. At temperature above 3.3°C the results are qualitatively similar.

If the oxygen content of the storage atmosphere is reduced too drastically, the normal aerobic respiration is suppressed and at least partially replaced by anaerobic respiration. As a result, alcohol and other toxic end products of respiration accumulate in the plant tissues, the rate of respiration sometimes increases as compared to the rate obtained at oxygen levels just adequate to sustain aerobic respiration, physiological disorders eventually occur, and storage

TABLE 7.6 Rates of Respiration of Apples at 3.3°C (38°F), Relative to a Rate of 100 in Air^a

| %CO ₂ /%O ₂ | Rates, relative to air = 100 | |
|-----------------------------------|---------------------------------|----------------|
| | CO ₂ | O ₂ |
| Air | 100 | 100 |
| 0/10 | 84 | 80 |
| 0/5 | 70 | 63 |
| 0/3–2 | 63 | 52 |
| 0/1.5 | 39 | — |
| 10/10 | 40 | 60 |
| 5/16 | 50 | 60 |
| 5/5 | 38 | 49 |
| 5/3 | 32 | 40 |
| 5/1.5 | 25 | 29 |

^a Cox's Orange Pippin apples; other varieties exhibit similar behavior.

Source: From Fidler and North (1966).

life generally is shortened (Fidler and North, 1971). The threshold concentration for the onset of significant anaerobic respiration is dependent on temperature (oxygen needs are greater at higher temperatures), age of product (effect varies with different products), and the type of product (permeability of the tissue to oxygen, shape of the intact tissue, natural differences in respiration rate, etc.). Examples of approximate oxygen threshold concentrations for anaerobic respiration are 1.8% oxygen for Cox's Orange Pippin apples at 3.5°C (Fidler and North, 1971), 2.3% and 1.2% oxygen for asparagus at 20°C and 10°C, respectively; less than 1% oxygen for spinach at 20°; and 4% oxygen for carrots and peas at 20°C (Platenius, 1943).

Excessively high levels of carbon dioxide depress all metabolic activities (both aerobic and anaerobic respiration of plant tissues) either delay or eliminate the climacteric, and often result in rapid onset of quality defects (Brooks et al., 1932). The first changes in quality are generally off flavors, and these are eventually followed by discoloration, breakdown of the tissues, and decay (Biale, 1960; Smith, 1963).

b. Growth of Microorganisms As Influenced by the Carbon Dioxide Content of the Atmosphere. High levels of carbon dioxide (greater than 10%) can significantly retard growth of microorganisms that exist on the surface of foods. The minimum effective level of carbon dioxide depends on such factors as temperature (growth retardation can be achieved with less carbon dioxide at lower temperatures), exposure time, population of organisms, and nutritive quality of the food.

5. Other Chemicals

A variety of chemicals other than carbon dioxide and oxygen are used during the handling and storage of foods at chilling temperatures. These chemicals are applied in the form of vapors (or aerosols) or aqueous solutions or by addition to packaging materials (box liners, wrappers, or shredded packing materials). Ideally these chemicals should act quickly, be convenient to use and economical, and should have no undesirable effects on wholesomeness, nutritive value, or quality. These chemicals classed according to function, are listed below. Latest regulations should be consulted to determine legality of use and levels allowed.

1. Chemicals for controlling growth of microorganisms and insects. To retard or stop growth of microorganisms and insects, appropriate chemicals (e.g., chlorine, acetates, ozone, sulfur dioxide, diphenyl) are commonly applied to fruits, occasionally to vegetables and rarely to other foods.
2. Chemicals for controlling ripening of fruits. The ripening of bananas, pears, and some other fruits can be induced by adding small amounts

of ethylene (e.g., 1 m³ ethylene per 1000 m³ of air is sufficient for bananas) to the atmosphere.

3. Chemicals for controlling physiological disorders. Scald of apples can be retarded by applying diphenylamine (often applied to wrappers) or ethoxyquin prior to storage. Mineral oil added to the wrappers of apples also retard development of apple scald, presumably by absorbing volatile emanations.
4. Sprout inhibitors. Phenyl carbamates (isopropylphenyl carbamate, 3-chloro-isopropyl-*n*-phenyl carbamate), maleic hydrazide, or vapors of nonylalcohol are used to retard the formation of sprouts on such commodities as onions, potatoes, and carrots.
5. Antioxidants. Antioxidants, such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and L-ascorbic acid, are frequently used to inhibit oxidation of susceptible commodities.
6. Deodorizers. Ozone is sometimes used to oxidize odorous volatile compounds and render them innocuous. However, ozone must be used with care since it can promote undesirable oxidative reactions in susceptible products. Simple ventilation or absorption of odors on activated charcoal are safer procedures.
7. Color modifiers. Ethylene gas, because it degrades chlorophyll, is sometimes used at a level of 10 ppm in air to de-green citrus fruit.

6. Ionizing Radiation

Substerilizing doses of ionizing radiation (see Chapter 11) can effectively extend the storage life of some foods that are stored at chilling temperatures.

7. Vacuum

A popular process developed in the 1980s for application to minimally processed foods consists of raw product preparation, precooking if desirable, vacuum packaging, pasteurization in the sealed vacuum-package, and chilled storage. The process is called *sous vide* and has been particularly popular in Europe (Riley, 1994). Preservation principles are applied in the heat process given to the packaged product, the reduced oxygen atmosphere by applying a vacuum, and the reduced storage temperature. The entire process is subjected to Hazard Analysis and Critical Control Points (HACCP) since the reduced oxygen conditions could result in anaerobic conditions in the package ultimately allowing the outgrowth of anaerobic pathogenic microorganisms such as *Clostridium botulinum* and *Listeria monocytogenes*.

TABLE 7.7 Product Characteristics Which Influence the Selection of Conditions Used for Chilling Storage

| Class of food | Physiological characteristics ^a | | | | | Major trend in quality following harvest, slaughter, or manufacture | Common means by which quality becomes unacceptable |
|---------------|--|--|--------------|-------------------------|---|--|--|
| | Presence of natural protective coating | Normal type and duration of respiration | Climacteric | Heat generated | Possible injury caused by abnormal metabolism at chilling temp. | | |
| Fruits | Yes | Aerobic for entire storage life of product | Yes for some | Moderate to substantial | Some are subject to chilling injury | Some improve temporarily (ripen) then deteriorate; others start to deteriorate immediately after harvest | Microbiological, physiological and pathological physical |
| Vegetables | Yes | Aerobic for entire storage life of product | No | Moderate to substantial | Some are subject to chilling injury | Deterioration | Microbiological, physiological, and pathological |

(continued)

TABLE 7.7 Continued

| Class of food | Physiological characteristics ^a | | | | | | Common means by which quality becomes unacceptable |
|---|--|--|-------------|----------------|---|--|--|
| | Presence of natural protective coating | Normal type and duration of respiration | Climacteric | Heat generated | Possible injury caused by abnormal metabolism at chilling temp. | Major trend in quality following harvest, slaughter, or manufacture | |
| Animal Tissues | No | Anaerobic for about 24 hr, then complete cessation | No | Slight | Some are subject to cold shortening | Deterioration, except for temporary improvement of those meats which are aged. | Microbiological |
| Other products such as milk, eggs, and manufactured foods | No, except for shell of egg | None | None | None | None | Deterioration | Microbiological, chemical, physical |

^a Post-harvest if plant tissue, post-slaughter if animal tissue.
Source: Fennema (1975).

G. Summary of Product Characteristics That Influence Conditions Selected for Chilling Storage

Since behavioral characteristics of plant and animal tissues at chilling temperatures are discussed under several headings in the above discussion, it is appropriate to summarize the major points. This is done in Table 7.7.

III. APPLICATIONS AND PROCEDURES

A. Precooling

Precooling is a treatment administered prior to storage or long-distance shipping to promptly reduce the product temperature from that which exists at the time of slaughter or harvest to a chilling temperature that is approximately optimum. The purpose is to retard the rate of product deterioration and to reduce the refrigeration capacity needed in the transport vehicle or storage facility. Precooling is especially needed for products with short postharvest storage lives, such as most berries, asparagus, broccoli, sweet corn, and spinach and for products where growth of microorganisms must be promptly retarded to avoid toxicological problems and quality defects (animal tissues). The profound effect that a reduction in temperature has on the storage life of perishable food products was discussed earlier.

Precooling is less important for those fruits and vegetables that are only semiperishable and for those that require curing or ripening. This is especially true if the ambient temperature is relatively low at the time of harvest.

When precooling is recommended, it generally should be accomplished as rapidly as possible. Prompt cooling is nearly always advantageous, and the ultimate temperature ideally should be just above freezing for milk, eggs, those fruits and vegetables not subject to chilling injury, and those animal tissues not subject to cold shortening. The United States Department of Agriculture stipulates that poultry be chilled to less than 4.5°C (40°F) in accordance with the following schedule: (1) if 2 kg or less, less than 4 h; (2) if 2–4 kg, less than 6 h; and (3) if greater than 4 kg, less than 8 h.

Rates of cooling can be calculated using the techniques for unsteady-state heat transfer discussed in Chapter 3 on heat transfer. The only limitation is that the air temperature cannot be lower than the initial freezing point of the product. If the air temperature is lower than the freezing point of the product, then freezing can occur and the assumptions to solve the differential equations describing unsteady-state heat transfer are no longer valid.

1. Precooling with Moving Air

This method is widely used because it is simple, economical, sanitary and relatively noncorrosive to equipment. Major disadvantages of precooling with air

are the dangers of excessive dehydration and the possibility of freezing the product if air temperatures below 0°C are utilized. Products that are precooled in air include mammalian meat, citrus fruits, grapes, cantaloupes, green beans, plums, nectarines, sweet cherries, and apricots.

2. Hydrocooling

Hydrocooling is a common method of precooling because of its simplicity, economy (least expensive method for rapid precooling), and rapidity. The product to be cooled is immersed in, flooded with, or sprayed with cool water (often near 0°C) containing a mild disinfectant, such as chlorine or an approved phenol compound. Products such as celery, asparagus, peas, sweet corn, radishes, topped carrots, cantaloupes, peaches, and tart cherries are precooled by this method.

3. Precooling with Ice or Ice–Slush

Precooling with crushed ice or ice–slush is simple and effective if done properly. However, considerable labor is often involved when crushed ice is used. Products such as cabbage, cantaloupes, peaches, root crops (radishes, carrots), and fish are frequently cooled by direct contact with crushed ice.

Nearly all poultry and some fish are precooled by contact with an agitated mixture of ice and water (ice–slush). Precooling poultry in ice–slush is preferred to precooling in air because product weight is increased by the former method and decreased by the latter.

4. Vacuum Cooling

Vacuum cooling is extremely effective for products possessing the following two properties: (1) a large surface to mass ratio (leafy vegetables) and (2) an ability to readily release internal water. This method involves exposing the product to a pressure of about 4–4.6 mm Hg until evaporative cooling yields the desired temperature. Cooling times for suitable products, such as lettuce, are less than 1 h. The extent of cooling is proportional to the water evaporated (evaporation of 1 kg of water removes approximately 2200 kJ). Regardless of the product the temperature is lowered about 5°C for each 1% reduction in water content. Prewetting is beneficial for many products, especially those that have high initial temperatures and those with properties such that substantial amounts of the added water are retained on their surfaces until the vacuum is applied.

For suitable products, vacuum cooling is advantageous because it is rapid and economical as compared to direct icing, which is otherwise likely to be employed. The economy is derived from reductions in the cost of labor and packaging and from decreased product damage. The main disadvantage of vacuum cooling is the large capital investment required. Equipment needs are

a large, strong chamber (some are large enough to accommodate an entire railroad car), a device for reducing the pressure (a mechanical vacuum pump or steam ejectors), and a device for condensing water vapors that emanate from the product (needed only when mechanical vacuum pumps are employed).

Large amounts of lettuce and moderate amounts of celery, cauliflower, green peas, and sweet corn are vacuum cooled.

B. Conditions Recommended for Storage of Food in Ordinary Air at Chilling Temperatures

Shown in Tables 7.8 and 7.9 are temperatures and relative humidities recommended for attainment of maximum storage lives of various perishable foods stored at chilling temperatures (Fennema, 1975). When the optimum temperature of storage is substantially above the freezing point of the product, this indicates that product is susceptible to chilling injury. Air temperature should be maintained within 1°C of the recommended value. Total variation in relative humidity generally should not exceed 3–5%.

TABLE 7.8 Chilling Temperatures Yielding Maximum Storage Lives of Various Foods

| Temperature ^a | Product |
|--------------------------|--|
| Just above freezing | Animal tissues: mammalian meats, poultry, fish Fruits: apples (some varieties), apricots, berries, lemons (yellow), nectarines, oranges (Florida), peaches, pears, plums Vegetables: asparagus, beets (topped), broccoli, brussels sprouts, cabbage (late), carrots (topped), cauliflower, celery, corn (sweet), peas (green), radishes, spinach Milk (fluid, pasteurized, grade A) Eggs (shell) |
| 2–7°C (34–45°F) | Fruits: apples (some varieties), melons, oranges (except Florida), pineapple (ripe) Vegetables: potatoes (Irish, early) |
| Above 7°C (45°F) | Fruits: avocados, bananas, grapefruit, lemons (green), limes, mangoes, pineapples (mature, green), tomatoes Vegetables: beans (green), cucumbers, potatoes (Irish, late), potatoes (sweet) |

^a Atmosphere contains normal amounts of oxygen and carbon dioxide.
Source: Fennema (1975).

TABLE 7.9 Relative Humidities Recommended for Various Foods Stored at Optimum Chilling Temperatures

| Relative Humidity ^a | Product |
|--------------------------------|---|
| Less than 85% | Butter, cheese, coconuts, dates, dried fruits, eggs (shell), garlic, hops, nuts, onions (dry) |
| 85–90% | Animal tissues: poultry, mammalian meat except veal Fruits: bananas (yellow), citrus, melons, peaches, pineapples, plums, nectarines, tomatoes Vegetables: potatoes (sweet), potatoes (Irish, early) |
| 90–95% | Animal tissues: veal, fish Fruits: apples (90%), bananas (green), berries, pears Vegetables: beans, (green), corn (sweet), cucumbers, leafy vegetables, peas (green), potatoes (Irish, late), root crops (topped) |

^a Atmosphere contains normal amounts of oxygen and carbon dioxide.

Source: Fennema (1975).

TABLE 7.10 Approximate Storage Lives of Various Foods Stored at Optimum Conditions of Relative Humidity and Chilling Temperature

| Maximum storage life ^a | Product |
|-----------------------------------|--|
| Less than 2 weeks | Animal tissue: fish, poultry, mammalian meat except beef Fruits: apricots, bananas, berries, cantaloupes, tomatoes (firm, ripe) Vegetables: asparagus, beans (green), broccoli, corn (sweet), cucumbers, peas (green), spinach |
| 2–6 weeks | Animal tissues: beef Fruits: avocados, grapefruit, lemons (yellow), limes, nectarines, peaches, pineapples, plums, tomatoes (mature, green) Vegetables: lettuce, potatoes (early), radishes |
| 1–4 months ^b | Celery, lemons (green), oranges |
| Greater than 3 months | Fruits: apples, pears Vegetables: beets (topped), cabbage, carrots (topped, mature), potatoes (Irish, late), potatoes (sweet) Eggs (shell) |

^a Atmosphere contains normal amounts of oxygen and carbon dioxide. It is assumed that foods are fresh and of good quality when placed in storage.

^b Storage lives of individual products fall somewhere within the range stated.

Source: Fennema (1975).

In Table 7.10 products are grouped according to the approximate storage lives that can be expected, assuming optimum storage conditions prevail and the food is fresh and of good quality when it enters storage.

Not fully apparent from Tables 7.8 to 7.10 are the important influences that such factors as maturity, ripeness, date of harvest, variety, and origin can have on optimum storage temperatures and maximum storage lives for fruits and vegetables. For example, optimum storage temperature is influenced by the ripeness of bananas, lemons, pineapples, and tomatoes; the variety of apples and pears; the harvest date of potatoes; and the origin of tomatoes, grapefruit, oranges, cucumbers, and green beans. Similarly, the maturity of carrots; the ripeness of lemons, tomatoes, and bananas; and the harvest date of potatoes influence maximum keeping quality.

During transit over relatively short distances or during temporary storage in warehouses, it is usually not feasible to maintain optimum environmental conditions for each product because this necessitates an uneconomical number of separate storage and shipping units. A workable solution is arrived at by recalling that quality changes are dependent on time as well as temperature. Thus, during transit or temporary storage it is possible to deviate somewhat from optimum storage temperatures without incurring unacceptable changes in quality. A common course of action is to provide two storage environments, one at 0°C and 90% relative humidity and the other at 10°C (50°F) and 85–90% relative humidity. The 0°C facility accommodates eggs, milk, all animal tissues, and those fruits and vegetables not subject to chilling injury. The 10°C facility accommodates all fruits and vegetables that are subject to chilling injury. Normal precautions, of course, must be observed to avoid storing incompatible products in the same room (e.g., highly odoriferous products, such as fish and onions, should not be stored in the presence of odor-absorbing products, such as butter).

C. Conditions Recommended for Storage of Food in Chilled Atmospheres of Modified Composition

Lowering the level of atmospheric oxygen, raising the level of atmospheric carbon dioxide, or drastically reducing levels of both oxygen and carbon dioxide (nitrogen flushing), when used as supplements to low temperatures, can be significant aids to retaining marketable qualities of some products.

1. Controlled-Atmospheric Storage of Apples

Controlled-atmospheric (CA) storage involves the use of chilling temperatures combined with an atmosphere containing oxygen at an accurately controlled level substantially less than that of ordinary air and, containing carbon dioxide at an accurately controlled level substantially greater than that of ordinary air. Large

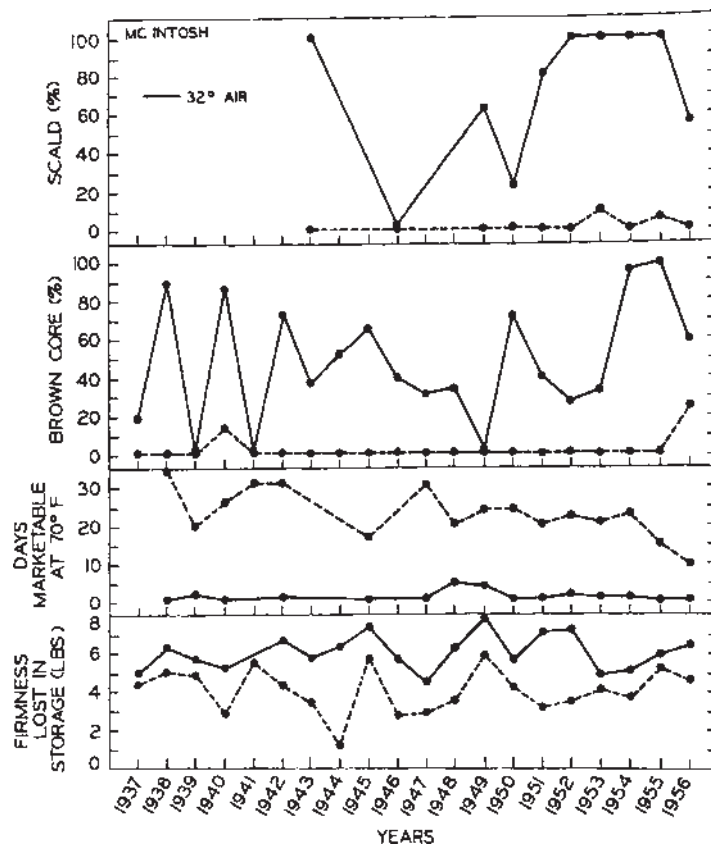


FIGURE 7.4 Comparative keeping quality of McIntosh apples in CA storage (5% CO₂ and 3% O₂ at 3.3–4.4°C [38–40°F]) and in conventional chilling storage (air at 0°C [32°F]). Measurements were made three a year after six months of storage. (From Smock, 1958.)

quantities of apples are stored under CA conditions, and this attests to the effectiveness and practicality of this approach. Controlled atmosphere storage is especially advantageous for apples (such as McIntosh) that must be stored several degrees above their freezing points in order to avoid the undesirable consequences of chilling injury. The desirable effect of CA storage on the keeping quality of apples is shown in Fig. 7.4. However, it is important to recognize that the quality of apples in CA storage generally does not exceed the quality of apples in conventional chilling storage until approximately 90 days or more have elapsed (Smock, 1964).

TABLE 7.11 Requirements for Controlled Atmosphere Storage of Apples

| Variety | Carbon dioxide (percent) | Oxygen (percent) | Temperature (°C) |
|------------------|-----------------------------|---------------------|----------------------|
| Cortland | 5 | 2–3 | 2.2 |
| | 2–3 | 2–3 | 0 |
| Delicious | 1–2 | 1.5–2 ^a | –0.5 to 0 |
| Empire | 2–3 | 2–3 | –0.5 to 0 |
| Golden Delicious | 1–3 | 1.5–2 ^a | –0.5 to 0 |
| Granny Smith | 1–3 | 2–3 | –0.5 to 0 |
| Idared | 2–3 | 2–3 | –0.5 to 0 |
| Jonathan | 0.5–5 | 2.5–3 | 2.2 one month then 0 |
| Macoun | 5 | 2–3 | 2.2 |
| McIntosh | 2–3 one month, then 5 | 2.5–3 | 2.2 |
| | 2–3 one month, then 5 | 2 | 3.3 |
| Northern Spy | 2–3 | 2–3 | –0.5 to 0 |
| Rome Beauty | 1–3 | 2–3 | –0.5 to 0 |
| Spartan | 2–3 | 2–3 | –0.5 to 0 |
| Stayman Winesap | 2–5 | 2–3 | –0.5 to 0 |
| Winesap | 1–2 | 2–3 | –0.5 to 0 |
| Yellow Newtown | 8 | 3 | 4.4 |
| | 5–6 | 3 | 2.2 |

^a1.5 percent oxygen not recommended for Delicious or Golden Delicious in New York because less than 2% oxygen is injurious.

Source: Hardenburg et al. (1986).

Recommended conditions for CA storage of apples are shown in Table 7.11 (Hardenburg et al., 1986). It is evident that recommended levels of oxygen and carbon dioxide depend not only on the species of fruit but also on the variety. Origin of the fruit is an additional factor influencing recommended levels of oxygen and carbon dioxide. Unfortunately, the most effective composition of the atmosphere can be determined only by trial and error.

a. Features of CA Facilities for Fruit. A facility for CA storage of fruit should have the following characteristics (Smock, 1958).

1. Air tightness. Rooms must be specially constructed and tested to assure that air leakage is reduced to a low level. Excessive leakage can seriously interfere with maintenance of the desired levels of oxygen and carbon dioxide or can result in excessive operating costs if the desired atmosphere is being maintained by gases not originating from the product.

2. Concentrations of oxygen and carbon dioxide. These gases must be accurately maintained at recommended levels. Instrumentation for measurement of O₂ and CO₂ concentrations is easily available and is used to control the action of O₂ and CO₂ scrubbers or absorbers or both.
3. Temperature. Air temperature should be controlled within 0.5°C (1°F) of the recommended value and in no instance should the product be allowed to fall below its freezing point.
4. Relative humidity. Relative humidity of the storage atmosphere should be about 90% for apples and 90–95% for pears.
5. Air circulation. The storage atmosphere should be circulated (1.6–2.4 m³/h/kJ) and evenly distributed to provide rapid cooling of incoming fruit and to assure uniformity of both the ultimate product temperature and the atmospheric composition.
6. Removal of volatile emanations. Removal of volatiles is sometimes recommended if the fruit is in a preclimacteric stage.

b. Methods for Establishing and Controlling the Concentration of Oxygen During CA Storage. Oxygen in the storage atmosphere can be reduced either by natural or by artificial means. The natural method relies on the ability of the stored plant tissue to consume oxygen. Excessively low levels of oxygen are avoided by introducing appropriate amounts of outside air. Advantages of the natural method are its simplicity and economy of operation. Disadvantages are (1) a long time is required to initially establish the recommended level of oxygen, especially if the fruit is quickly cooled (slows respiration); (2) the room must be exceptionally well constructed (otherwise too much oxygen leaks in); and (3) the room must be filled to capacity and should not be opened until the entire contents are removed (Pflug and Gurevitz, 1966).

Artificial methods (also referred to as *externally generated atmospheres*) for reducing the oxygen content of the storage atmosphere involve either flushing with pure nitrogen (liquid or compressed) or flushing with air from which most of the oxygen has been removed by catalytic combustion in the presence of added methane or propane. Advantages of the artificial method are (1) the desired level of oxygen can be established quickly (if liquid nitrogen is used, the rate of cooling also is increased); (2) the storage room need not be filled to capacity, and it can be partially emptied or refilled during the course of storage (this is possible because of the rapidity with which the desired level of oxygen can be reestablished); and (3) proper levels of oxygen can be maintained even in rooms that are somewhat leaky (provided the artificial atmosphere is continually added). This characteristic facilitates conversion of conventional storage units into units suitable for CA storage.

The main disadvantage of the artificial method is its high cost, especially if the storage rooms are moderately leaky.

Artificial methods of controlling the level of oxygen can be employed continuously (very expensive and usually not done) or as a supplement to the natural method (i.e., to speed establishment of initial conditions or to quickly reestablish desired condition if the room develops excessive leaks or the room is opened for removal or addition of product).

c. Methods for Establishing and Controlling the Concentration of Carbon Dioxide During CA Storage. Intact plant tissues evolve substantial amounts of carbon dioxide. Accumulation of carbon dioxide can be beneficial up to a point, but excessive levels of carbon dioxide can be controlled by simple ventilation or by methods which selectively remove carbon dioxide.

Simple ventilation removes excess carbon dioxide but simultaneously adds oxygen. In practice, of course, the extent of ventilation is restricted so that the carbon dioxide content of the storage atmosphere is much greater than that of normal air and the oxygen content is lower than that of normal air. The combined concentrations of carbon dioxide and oxygen always total 21% by this method. Since this value is far from ideal, the results are less satisfactory than those obtained when optimum levels of oxygen and carbon dioxide are employed.

Methods for selective removal of carbon dioxide from air (generally referred to as *carbon dioxide scrubbers*) can be classed as chemical or physical. Chemical methods involve an interaction between air and such chemicals as dry lime (calcium hydroxide), solutions of sodium hydroxide or ethanolamines, or suspensions of lime in water. Bagged dry lime is popular because it is effective, easy to handle, and relatively noncorrosive.

Physical methods for controlling the concentrations of carbon dioxide in air involve absorption in water and absorption on molecular sieves. Since the water method is effective, simple, economical to operate, noncorrosive, and in common use, it is considered further here.

A schematic representation of a water absorption apparatus for removal of carbon dioxide is shown in Fig. 7.5. Successful operation is based on two principles:

1. The solubility of carbon dioxide in water at constant temperature varies with the partial pressure of carbon dioxide in air.
2. The solubility of carbon dioxide in water at constant pressure varies inversely with temperature.

In the absorption section of the apparatus, water that has been equilibrated in normal air (0.03% carbon dioxide) is intimately mixed with air from the storage unit. This air, which contains a higher than normal amount of carbon

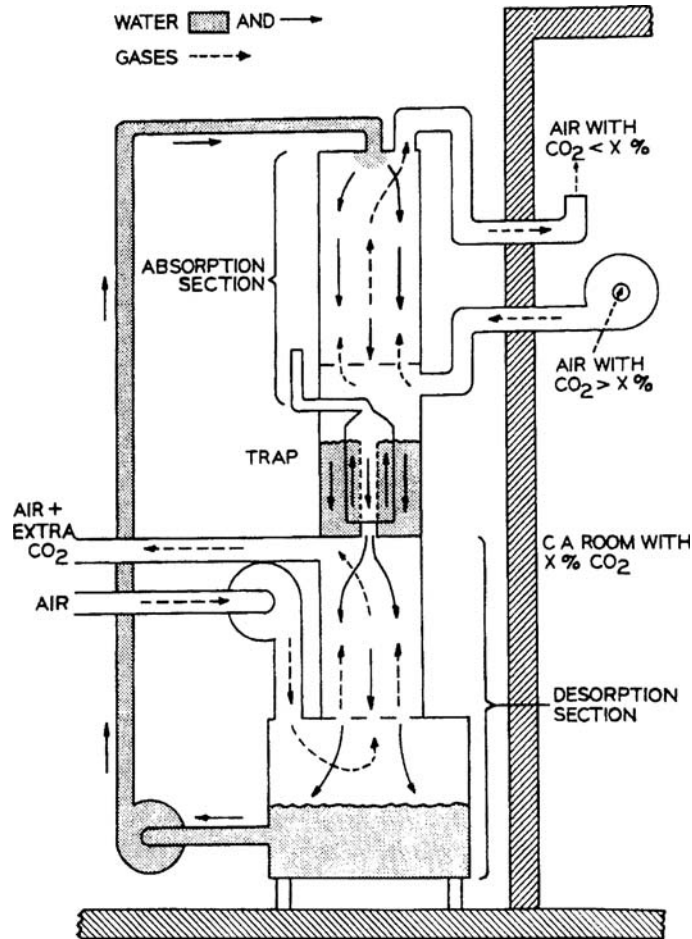


FIGURE 7.5 Water absorption apparatus for removal of carbon dioxide. (From Pflug, 1961. ©American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc.)

dioxide (perhaps 5%), yields part of its carbon dioxide to the water and then returns to the storage unit.

In the desorption section, water that is rich in carbon dioxide comes into contact with normal air, and the carbon dioxide previously acquired in the absorption section is now released from the water and discharged to the atmosphere. This water is then returned to the absorption section and the process is repeated. The trap located between the absorption and desorption sections

prevents interchange of air between the two sections. Concentrations of carbon dioxide in the storage unit is controlled primarily by the water temperature in the absorption unit and the duration of operation. A carbon dioxide concentration as low as 2% can be maintained by this method.

Major disadvantage of the water absorption system for removal of carbon dioxide are (1) a room with a very low rate of leakage is required and (2) initial establishment of a low oxygen concentration requires somewhat longer with the water absorption system than with an alkaline absorption system. This situation arises because the water absorption system adds small amounts of oxygen during the process of removing carbon dioxide.

Carbon dioxide removed by any of the methods discussed above is replaced by air or an artificial atmosphere, thereby providing control of the oxygen concentration. Regardless of how the desired levels of oxygen and carbon dioxide are controlled, it is important to arrive at the desired storage conditions (temperature, relative humidity, levels of oxygen and carbon dioxide) as soon as possible following loading of the storage unit. The adjustment period should not exceed 10 days for apples and 5 days for pears and ideally should be shorter.

2. Other Applications of Modified Atmospheres

Some plant and animal tissues are transported at low, nonfreezing temperatures in the presence of atmospheres that have been modified with respect to oxygen, carbon dioxide, and nitrogen concentrations. The effect of various modified atmospheres on the quality of foods other than apples and pears are reviewed briefly below.

a. Mammalian Meat and Meat Products. The storage lives of meats and meat products often can be extended by the presence of greater than normal amounts of carbon dioxide in the atmosphere. Moran (1937) and Moran et al. (1932) found that the storage life of chilled beef can be increased significantly by using an atmosphere containing 10–20% carbon dioxide rather than ordinary air. The desirable effect occurs primarily because the high level of carbon dioxide suppresses growth of microorganisms. An atmosphere containing 10% carbon dioxide is used commercially during shipment of beef by sea from Australia and New Zealand to Great Britain. At a temperature of -1 to -1.5°C (29 – 30°F) this treatment increases the storage life of beef to approximately 70 days as compared to about 45 days in air (Hales, 1963; Smith, 1963).

Oxidative rancidity and microbiological spoilage of fresh pork can be greatly reduced by using an atmosphere containing 50–100% carbon dioxide as compared to air (Callow, 1933). However, this treatment can result in some

TABLE 7.12 Suggested Atmospheres for Transport and Storage of Tropical Fruits

| Commodity | Intended use | Beneficial atmosphere | | Best temperature (°C) | Degree and character of benefit | Injurious atmospheres |
|------------|-------------------------------|---|---------------------|-----------------------|---------------------------------|---------------------------------------|
| | | O ₂ (%) | CO ₂ (%) | | | |
| Avocados | Fresh storage | 2-3 | 10 | 7 | Major, extends life | 1% O ₂ 15% CO ₂ |
| Bananas | Fresh storage | 2 | 2-5 | 15 | Major, extends life | 1% O ₂ 7% CO ₂ |
| | LP | 150 mm Hg | | 15 | Major, extends life | |
| | Fresh transport | MA polyethylene bag + C ₂ H ₄ absorbent | | 15 | Major, extends life | 10 ppm C ₂ H ₄ |
| Limes | Fresh storage | 21 | 7-10 | 10 | Slight, slows green color loss | 5% O ₂ 10% CO ₂ |
| | | LP, 150 mm Hg | | 10 | Major, extends life | 114 mm Hg |
| Mangos | Fresh storage | LP, 150 mm Hg | | 13 | Moderate | 76 mm Hg (some split) low RH |
| | Fresh transport with 5-10% CO | 5 | 5 | 13 | Slight | 12.5% CO, explosive 1% O ₂ |
| Cherimoyas | Fresh | 2 | 10 | 8 | — | — |
| Papayas | Fresh | 10 | 21 | 18-20 | Moderate | 10% CO ₂ |
| Sapodillas | Fresh | 5-10 | 21 | 20 | Moderate | — |

Source: Hatton and Spalding (1990).

TABLE 7.13 Summary of Controlled Atmosphere (CA) and Modified Atmosphere (MA) Requirements and Recommendations for Selected Vegetables

| Vegetable | Temperature ^a (C) | Atmosphere ^b | | Potential benefit | |
|---------------------|---------------------------------|-------------------------|---------------------|----------------------|-----|
| | | O ₂ % | CO ₂ (%) | | |
| Artichokes | 0 | (0–5) | 2–3 | 2-3 | + |
| Asparagus | 2 | (1–5) | Air | 10–14 | +++ |
| Beans (green snap) | 8 | (5–10) | 2–3 | 4–7 | + |
| Processing | 8 | (5–10) | 8–10 | 20–30 | ++ |
| Braissicas | | | | | |
| Broccoli | 0 | (0–5) | 1–3 | 5–10 | +++ |
| Cabbage | 0 | (0–5) | 2–3 | 3–6 | +++ |
| Cauliflower | 0 | (0–5) | 2–3 | 3–4 | + |
| Celery | 0 | (0–5) | 2–4 | 3–5 | + |
| Chinese cabbage | 0 | (0–5) | 1–2 | 0 | + |
| Cucumbers (fresh) | 12 | (8–12) | 1–4 | 0 | + |
| Pickling | 4 | (1–4) | 3–5 | 3–5 | + |
| Leeks | 0 | (0–5) | 1–6 | 5–10 | + |
| Lettuce (crisphead) | 0 | (0–5) | 1–3 | 0 | ++ |
| Cut salad | 0 | (0–5) | 1–3 | 0 | +++ |
| Lettuce (leaf) | 0 | (0–5) | 1–3 | 0 | ++ |
| Mushrooms | 0 | (0–5) | Air | 10–15 | ++ |
| Okra | 10 | (7–12) | Air | 4–10 | + |
| Onions (bulb) | 0 | (0–5) | 0–1 | 0 | + |
| Onions (bunching) | 0 | (0–5) | 2–3 | 0–5 | + |
| Parsley | 0 | (0–5) | 8–10 | 8–11 | + |
| Pepper (bell) | 12 | (8–12) | 2–4 | 0 | + |
| Pepper (chili) | 12 | (8–10) | 3–5 | 0–5 | ++ |
| Processing | 5 | (5–12) | 3–5 | 15–20 | ++ |
| Radish (topped) | 0 | (0–5) | 1–2 | 2–3 | + |
| Sweet corn | 0 | (0–5) | 2–4 | 5–10 | + |
| Sweet potatoes | 13 | (13–16) | 6–7 | 3–5 | + |
| Tomatoes | 12 | (12–20) | 3–5 | 0–3 | + |
| Witloof chicory | 0 | (0–5) | 3–4 | 4–5 | + |

^aOptimum and usual and/or recommended range of temperatures (a RH of 90 or 95% is usually recommended).

^bSpecific CA recommendations depend on cultivar, temperature, and duration of storage.
Source: Leshuk and Saltveit (1990).

brown discoloration (formation of methemoglobin and metmyoglobin). Levels of carbon dioxide ranging from 25–50% provide some protection against growth of microorganisms but do not retard oxidative rancidity.

Using an atmosphere of 100% carbon dioxide rather than air approximately doubles the storage life of bacon at 5°C (41°F) (Callow, 1933). The storage life of frankfurtes increases as the carbon dioxide content of the atmosphere is increased up to 50% (Nelson, 1970).

For beef and pork stored for 6–8 days at either 3 or 7°C (37 or 45°F), the following atmospheres provide better preservation than air (Partmann et al., 1971): (1) nitrogen (with oxygen less than 0.5%), (2) 70% carbon dioxide and 30% air, and (3) 90% nitrogen and 10% carbon dioxide. Similarly, red meats apparently deteriorate less rapidly when transported in an atmosphere of nearly pure nitrogen at an accurately controlled temperature (0.5°C) than they do when transported in air at the same but less well-controlled temperature (Dixon and Robe, 1966).

b. Poultry. Microbiological spoilage of poultry occurs at a decreasing rate as the carbon dioxide content of the atmosphere is increased up to 25%. However, discoloration and off flavors can occur at carbon dioxide levels above approximately 15% (Ogilvy and Ayres, 1951).

c. Fish. The keeping quality of chilled postrigor haddock is reportedly doubled by storage in an atmosphere containing 50–100% carbon dioxide as compared to air at the same temperature (Standby and Griffiths, 1935). This effect can be explained largely on the basis that 20% carbon dioxide at 0°C effectively retards growth of those bacteria responsible for spoilage of fresh fish.

d. Eggs. Quality attribute of chilled shell eggs are apparently retained better in an atmosphere containing 0.55% carbon dioxide than in ordinary air (Sharp, 1937). However, oiling of eggs is more practical and achieves similar benefits (Cook, 1971).

e. Fruits. Deterioration of some freshly harvested fruits can be significantly reduce by brief exposure (1–2 days) to atmospheres containing at least 20% carbon dioxide. This technique has resulted in decidedly favorable experimental results (less decay and firmer and fresher than controls in air) with sweet cherries, plums, peaches, Barlett pears, raspberries, dewberries, blackberries, figs, grapefruit, and oranges. However, off flavors can result if the carbon dioxide concentration is too high or the exposure time is too long. For many other fruits the carbon dioxide treatment described above offers no advantage or is injurious (e.g., green tomatoes fail to ripen following removal from the modified atmosphere).

Fruits such as tomatoes, strawberries, grapes and melons apparently deteriorate less rapidly when transported in an atmosphere of nearly pure nitrogen at an accurately controlled temperature (0.5°C) than they do in air at

the same but less well-controlled temperature. Other gases have been investigated for improvement of quality storage life of fruits and vegetables. Varoquaux and Wiley (1994) reviewed the application of gases such as carbon monoxide, sulfur dioxide, ethylene oxide, propylene oxide, and ozone on growth of microorganisms on chilled fruits and vegetables. Table 7.12 presents selected conditions for transport and storage of tropical fruits (Hatton and Spalding, 1990).

f. Vegetables. Quality loss of some vegetables can be slowed by short-term (1–7 days) exposure to atmosphere containing 5–50% carbon dioxide. On an experimental basis this treatment has been shown to benefit carrots, cauliflower, sweet corn, and asparagus. However, many vegetables are either not benefited or are injured by treatment described above.

D. Handling of Food Following Removal from Chilling Storage

When food products are moved from chilling storage to a warm environment, the product temperature frequently is below the dew point of the air, condensation occurs and growth of microorganisms is encouraged. Occurrence of undesirable condensation can be predicted from the temperature and relative humidity of the warm air and the temperature of the product. Condensation can be avoided by warming the product gradually, but this is often not practical. If condensation does occur, ventilation should be adequate to warm and dry the product, or alternatively, the product should be consumed without undue delay.

A summary of recommended conditions for controlled or modified atmosphere storage of selected vegetables is shown in Table 7.13. Controlled atmosphere storage is not recommended for the specific root crops of carrots, garlic, horseradish, and radishes. Furthermore, the benefits of CA storage of beets, Chinese cabbage, Lima beans, potatoes, spinach, squash, sweet potatoes, and yellow snap beans have not been conclusively demonstrated (Leshuk and Saltveit, 1990).

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8

Freezing

I. INTRODUCTION

A. Objectives of Freezing of Foods

The primary objective of freezing of foods, as well as cells, vaccines, protein preparations, and other bioactive materials is the preservation of their functionality. In the case of foods preservation of optimal organoleptic characteristics and of nutrient content while assuring absence of microbial growth are the preservation objectives. The great advantage of freezing as a method of preservation is its ability to achieve stability without damaging initial quality.

Freezing attains the preservation objectives by combining two key factors:

1. *Concentration of solutes*, achieved through crystallization of water as ice, increases the osmotic pressure of the concentrated nonfrozen solution, thus preventing microbial growth. The mechanisms by which this is achieved were discussed in Chapter 5. The high viscosity of the concentrated solution reduces the mobility of reactants and may contribute to maintenance of quality by minimizing rates of deteriorative reactions. The effects or reduction of water activity on rates of reactions were discussed in Chapter 5.
2. Maintaining a *low temperature of storage* is the most important factor in controlling biochemical and chemical reactions resulting in

deterioration of quality. The low temperature also has a contributory effect to the prevention of microbial growth. Freezing of foods is also used for purposes other than preservation. The following applications deserve mention:

Freeze concentration in which solutions are frozen and the ice separated by in a centrifuge or in a sedimentation wash column

Freezing as a step in *freeze drying*, in which the ice is removed by sublimation

Freezing as a step in *cryocomminution*

Freeze–thaw processes for *texturizing*, based on the principle that formation of crystals disrupts the original cell and tissue structure

B. Size of the Food Industry

Freezing is expensive because it requires the maintenance of low temperatures throughout the shelf life of the frozen food. For this reason freezing is most prevalent in the more prosperous regions of the world. The significance of freezing in the United States is apparent from the data shown in Table 8.1 based on data reported by the American Frozen Food Institute (AFFI). According to AFFI frozen foods accounted for 33% of the value of food service sales and 7% of supermarket sales.

II. PHYSICOCHEMICAL PRINCIPLES OF THE FREEZING PROCESS

A. Introduction

The objectives of freezing preservation are optimally achieved by the following steps:

1. Induce freezing by lowering the temperature below the point at which

TABLE 8.1 Frozen Food Sales (United States, 1999) (Billions of Dollars)

| Category | Food service | Retail |
|-------------------|--------------|--------|
| Bakery products | 3.0 | 3.2 |
| Dairy products | 5.3 | 5.5 |
| Fruits/vegetables | 5.7 | 4.0 |
| Meat/fish/poultry | 22.5 | 3.3 |
| Prepared meals | 2.5 | 5.3 |
| Other products | 2.0 | 6.0 |
| TOTAL | 41.0 | 27.3 |

nucleation occurs. Nucleation refers to the formation of crystal embryos which serve as the nucleus for growth of crystals. (Depending on composition and other factors, this temperature may be substantially below the melting point of water.)

2. Lower the temperature further to promote crystallization of a sufficient fraction of the total water to achieve a high concentration of solutes in the nonfrozen part of the food.
3. Store the frozen food at low temperature, preferably below the T_g of nonfrozen concentrated solution.

B. Water and Ice

Freezing is synonymous with crystallization of water. Within the range of pressures normally encountered in our experience water exists depending on temperature as vapor, liquid, or solid. The phase diagram of water is shown in Fig. 8.1. The transition of water into ice is accompanied by release of the latent heat of fusion ΔH_F because the water–ice transition is a first-order transition involving a discontinuity in the thermodynamic quantity enthalpy. Enthalpy at a temperature T is the total energy absorbed by a given amount of the substance as its temperature is raised from a reference temperature to T and is measured in kJ/mol or kJ/kg.

Figure 8.2 shows the enthalpy changes in raising the temperature of water from below the melting point to above the boiling point. The molecular arrangement of water molecules in ice is shown in Fig. 8.3, and the resulting crystal structure is shown in Figs. 8.4 and 8.5. In reality this ideal structure contains defects, three types of which are shown in Figs. 8.6 to 8.8.

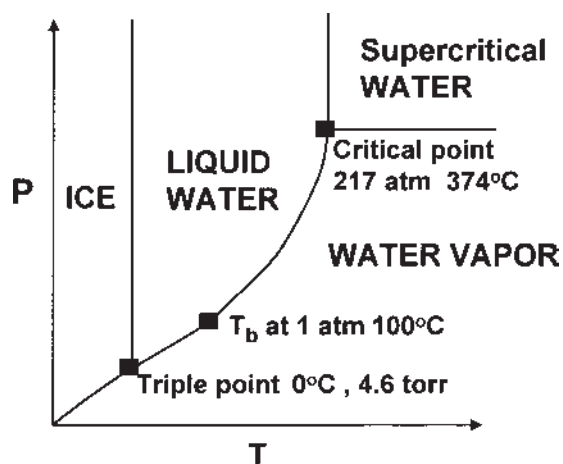


FIGURE 8.1 Phase diagram for water.

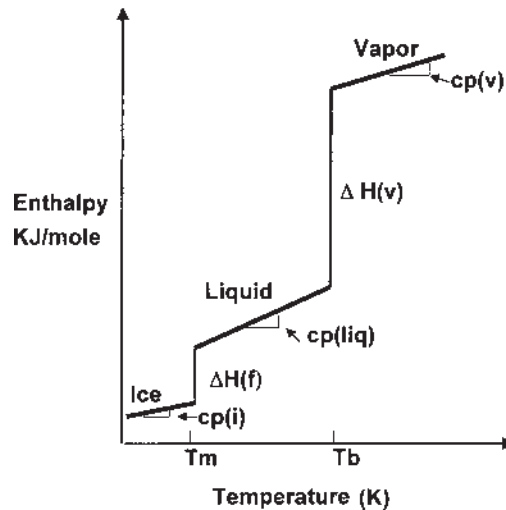


FIGURE 8.2 Temperature-enthalpy diagram for water.

These defects have an impact on properties of ice, in particular on its electrical properties. Water is an exceptional substance in many respects (Ball, 2000). Table 8.2 shows a comparison between the properties of water and of other small molecules. Liquid water has an unusually high boiling point, and its heat of vaporization is very high, indicating a highly bonded liquid state. The currently accepted view of water structure is that most of the 4 hydrogen bonds per water molecule that exist in ideal ice structure are retained in the liquid state, even at

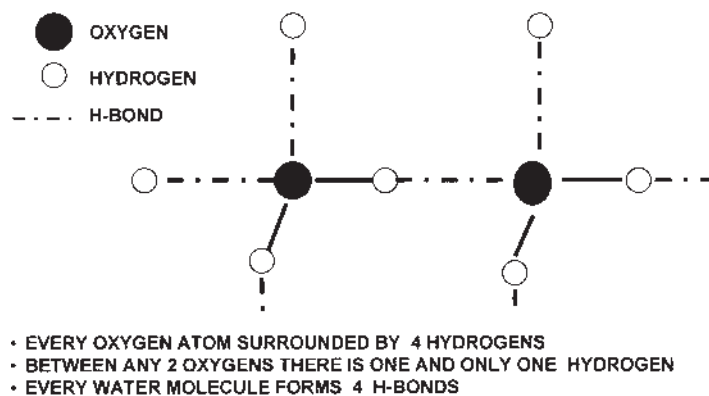


FIGURE 8.3 Ideal structure of ice.

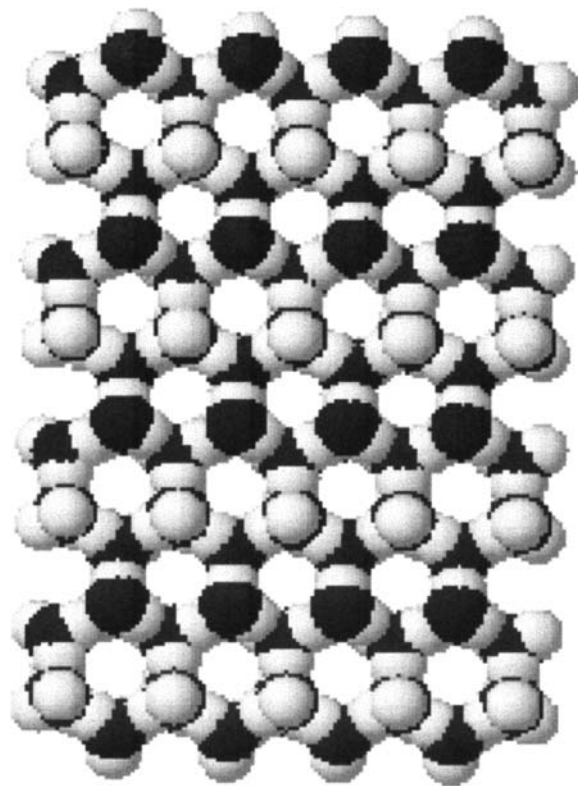


FIGURE 8.4 Molecular model of ice.

temperatures close to the boiling point. However this conclusion fails to explain the relatively low viscosity and the relatively high self-diffusion coefficient of liquid water. The paradox of a high degree of bonding while a high mobility exists in the liquid is resolved by assuming that the bonds have an extremely short half-life in the liquid state, so that the location of the breaks in H bonds is constantly changing. A schematic two-dimensional representation of bonding in liquid water is shown in Fig. 8.9. At the same time the transfer into the vapor phase in which there are essentially no water–water bonds (at very high pressure a very small dimer fraction may exist) require the breaking of all H bonds, resulting in a high enthalpy of vaporization (Stanley, 1999).

Another unusual aspect of water–ice transition is the change in density. In contrast to other liquids ice has a lower density than liquid water. The highly bonded structure of water provides an explanation since the relatively more open

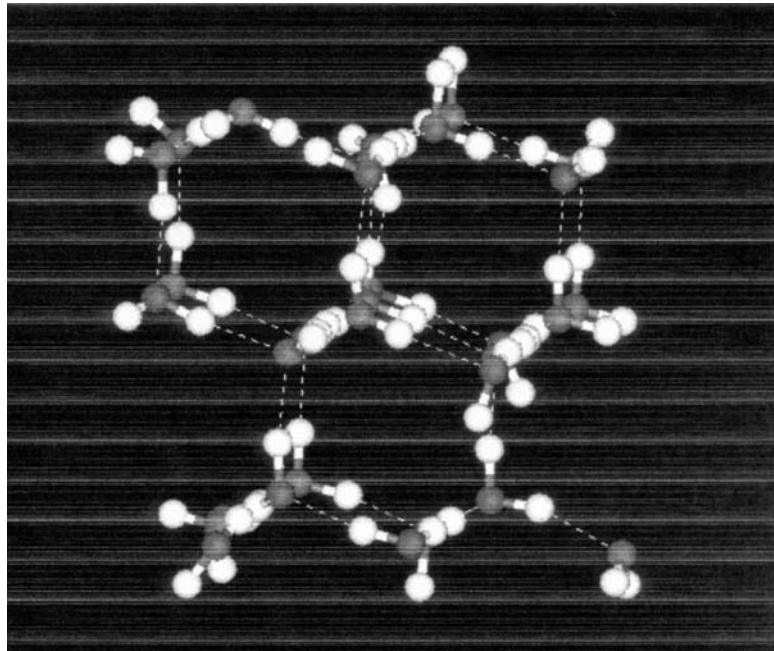


FIGURE 8.5 Representation of structure of ice crystals.

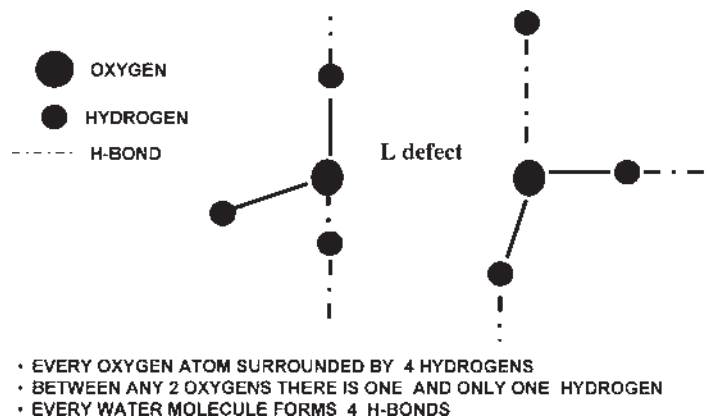


FIGURE 8.6 Defects in ice (L defect).

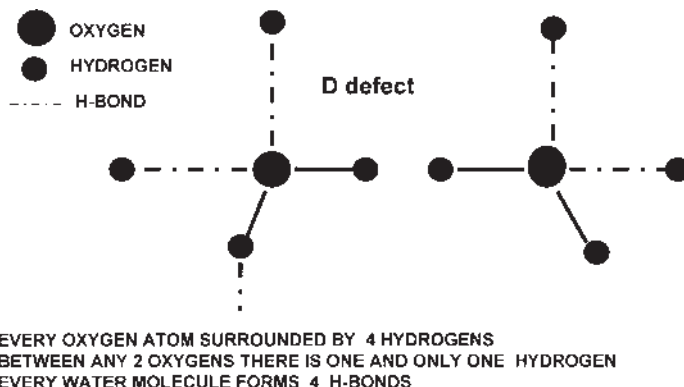


FIGURE 8.7 Defects in ice (D defect).

structure of ideal ice is allowed to “contract” when some of the H bonds are broken in the transition. It should be noted, however, that the low density of ice applies only to the ice structure existing at relatively low pressures (ice I). Figure 8.10 shows the phase diagram of ice and water, and the existence of several other forms of ice (Atkins, 1990). The high-pressure forms of ice have densities higher than the density of liquid water as shown in Table 8.3 (Kalichevsky et al., 1993).

The transition to ice I, which is the transition we deal with at the pressures existing on earth has another important consequence of the unusual volume change behavior: as shown in Fig. 8.10, the melting point *decreases* with

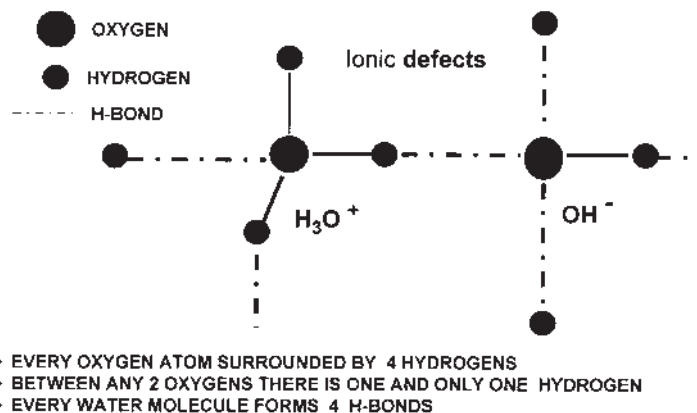


FIGURE 8.8 Defects in ice ionic (defects).

TABLE 8.2 Properties of Water Compared to Those of Other Small Molecules

| | MW Daltons | Melting Pt K | ΔH (fusion) Kcal/mole | Boiling Pt K | ΔH (vapor.) Kcal/mole |
|------------------|---------------|-----------------|----------------------------------|-----------------|----------------------------------|
| CH ₄ | 16 | 90 | 0.22 | 111 | 1.95 |
| NH ₃ | 17 | 195 | 1.35 | 239 | 5.58 |
| H ₂ O | 18 | 273 | 1.43 | 373 | 9.73 |
| HF | 20 | 190 | 1.09 | 306 | 7.46 |
| Ne | 20 | 24 | 0.08 | 27 | 0.44 |
| Na | 23 | 371 | 0.63 | 1187 | 23.12 |

pressure. The fact that imposing pressure makes ice I melt has an impact on various phenomena ranging from glacier flow to iceskating. For the other ice forms an increase in pressure *increases* the melting point.

C. Nucleation in Pure Water

The transition from ice to liquid water occurs at a temperature at which the free energy per mole of water (G/n), which decreases with increasing temperature, is equal in the two states, namely at the melting point T_m . This is illustrated schematically in Fig. 8.11. The reverse transition, from water to ice, is usually initiated at a temperature lower than T_m due to the phenomenon known as *supercooling*. The basis for this phenomenon is the fact that the total free energy

Cartoon of liquid water in a continuum model

100 Water Oxygens at vertices of a square lattice

43% of water molecules have 4 H bonds ~ 80% of H bonds in ice are intact

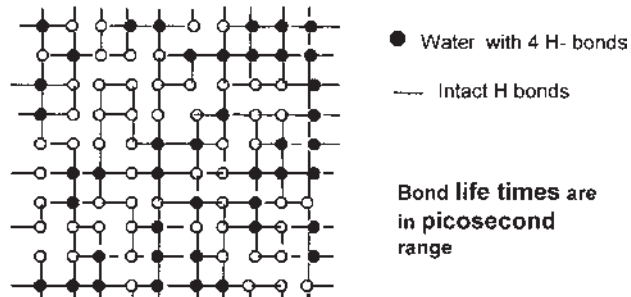


FIGURE 8.9 Representation of liquid water structure. (From Stanley, 1999.)

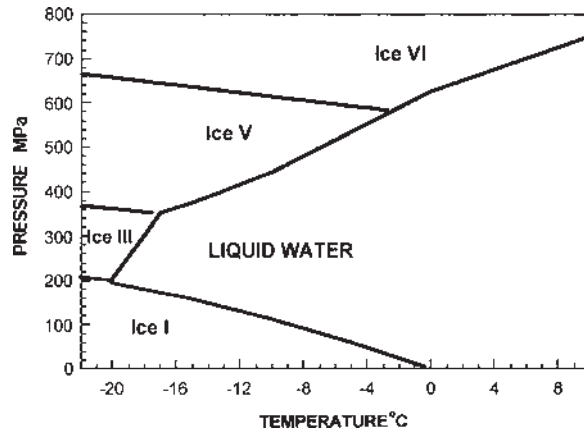


FIGURE 8.10 Extended phase diagram for water and ice.

of a particle, such as a crystal, has a contribution from *surface free energy*, illustrated schematically in Fig. 8.12.

The total surface free energy per particle is equal to the interfacial energy γ (between ice and the surrounding liquid water) multiplied by the surface area of the particle. The area per unit mass is inversely proportional to particle radius (approximating the particle shape as a sphere). Therefore small particles have a significant free-energy contribution from surface energy, and as shown in Fig. 8.12 their melting point is below the melting point of bulk water. The process

TABLE 8.3 Thermodynamic Properties During Phase Transition of Water

| Transition | Temperature (°C) | Pressure (MPa) | ΔV (m ³ /kg) | ΔH (kJ/kg) |
|-------------------|------------------|----------------|---------------------------------|--------------------|
| Liquid to ice I | -20 | 193 | +0.131 | -241 |
| | -10 | 110 | +0.112 | -285 |
| | 0 | 0.1 | + 0.090 | - 334 |
| Liquid to ice III | -20 | 246 | -0.040 | -226 |
| Liquid to ice V | -20 | 308 | -0.082 | -253 |
| | 0 | 624 | -0.060 | -293 |
| Liquid to ice VI | 0 | 624 | -0.092 | -295 |
| | +20 | 883 | -0.075 | -320 |

Source: Kalichevsky et al. (1995).

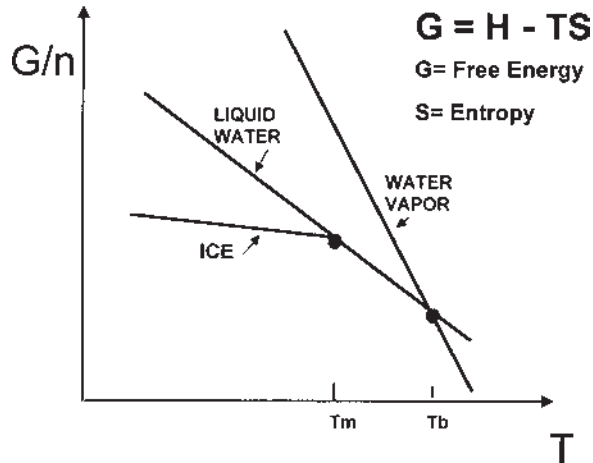


FIGURE 8.11 Free-energy temperature diagram for water.

of crystallization in the absence of pre-existing crystals (seeds) starts with small clusters of water molecules forming the basis for crystal-initiating nuclei, and this process is known as *homogeneous nucleation*. As the temperature is decreased below the melting point, the difference between the free energy of liquid water and ice (ΔG) based on bulk conditions (ignoring surface free energy) increases providing an ever higher the driving force for the transition. This driving force is, however, opposed by the surface energy of the small nuclei, which have a large

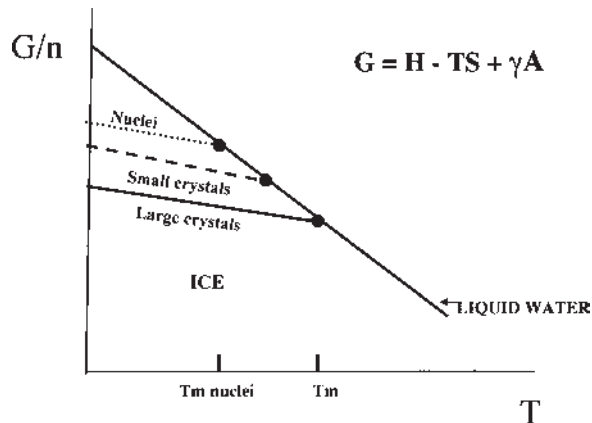


FIGURE 8.12 Effect of crystal size on free energy of nuclei and crystals.

surface area per unit mass. The balance between the driving force for and against formation of nuclei is expressed by Eq. (1):

$$\Delta G_r = 4\pi r^2 \gamma - \frac{4\pi r^3 \Delta G_v}{3v_m} \quad (1)$$

where

ΔG_r = total free energy difference between crystalline and liquid state for a nucleus of radius r .

ΔG_v = molar free energy difference between crystalline and liquid state ignoring the surface energy.

γ = interfacial free energy between ice and surrounding liquid

v_m = molar volume of ice.

ΔG_r is dependent on temperature (since as seen in Fig. 8.11, ΔG_v increases with decreasing temperature) and on r .

We can calculate a critical radius r^* by letting $d\Delta G_r/dr = 0$. At this point ΔG_r is at a maximum, and nuclei with a radius $> r^*$ will continue to grow, while those with $r < r^*$ will melt. The corresponding ΔG_r we will designate by ΔG_v^* .

$$r^* = \frac{2\gamma v_m}{\Delta G_v} \quad (2)$$

Since ΔG_v is a function of temperature, we can readily obtain the temperature T^* at which r^* occurs.

$$T^* = T_F - \frac{2\gamma v_m T_F}{\Delta H_F r^*} \quad (3)$$

where ΔH_F is the latent heat of fusion. The calculated T^* for homogeneous nucleation of water is -40°C . The value of ΔG_v^* is estimated by

$$\Delta G_v^* = \frac{16\pi\gamma^3 v_m^2}{3\Delta H_F^2 (T_F - T)^2} \quad (4)$$

The rate of nucleation J is given by

$$J = K_1 \exp \frac{-\Delta G_v^*}{kT} \quad (5)$$

where K_1 = pre-exponential constant and k = Stephen-Boltzman constant.

The rate of homogeneous nucleation increases with the degree of supercooling. Homogeneous nucleation is almost never the mechanism of freezing, even in "pure" water. To observe homogeneous nucleation, extraordinary precautions are necessary to avoid contamination, such as emulsification of tiny water droplets so that only a fraction of them might contain

contaminating “motes.” Water contains various “impurities,” tiny motes that produce local regions of reduced surface energy which acts as a preformed focus for the aggregation of water molecules into nuclei and eventually crystals. Walls of containers are a common source of this nucleation, since they contain rough or pitted surfaces able to provide nucleation sites. A great number of inorganic and organic substances can serve as nucleators. During the recent decades research into nucleating properties of bacteria and their molecular components has disclosed the existence of biological promoters and inhibitors of nucleation. Heterogeneous nucleation requires supercooling as well, but to a very much reduced extent because the effective ΔG_v^* is much reduced since the quantity $4\pi r^2\gamma$ is reduced at the surface of the nucleator. The possibility of attaining a glassy state of water by cooling it very rapidly below its glass transition temperature (*vitrification*) has been the objective of a number of studies. Vitrifying pure water is extremely difficult but has been achieved by several investigators. The values of T_g obtained in these studies were between -143 and -134°C (Roos, 1995).

D. Freezing Point Depression in Solutions, Biological Systems, and Foods

In aqueous solutions the free energy of water is depressed by the presence of solutes. As discussed in Chapter 6, Raoult’s law is useful in estimating this depression in ideal solutions. Figure 8.13 shows the depression of free energy and the resulting freezing point depression in ideal solutions. The freezing point decreases with increasing solute concentration, and since water crystallizes as a pure substance, the concentration of the solute in the unfrozen solution increases

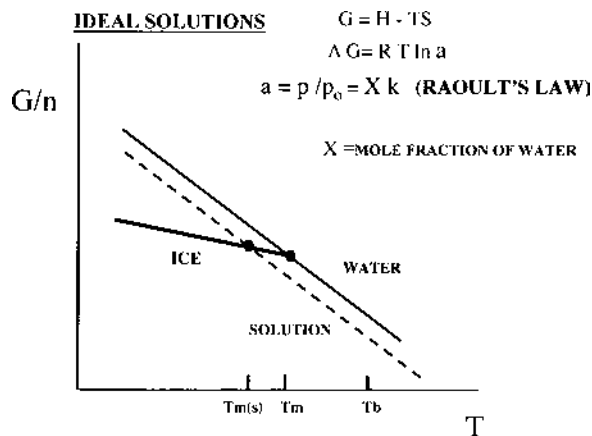


FIGURE 8.13 Freezing point depression by ideal solutes.

as freezing progresses, and the freezing point fall continuously. Freezing curves of water and of a solution or a typical food are shown schematically in Fig. 8.14.

The line in the temperature vs concentration plot (state diagram) which represents the equilibrium freezing condition is known as the *liquidus line* and is shown in Fig. 8.15 for a simple aqueous solution. Ideally the freezing point ceases to fall when the eutectic point is reached, located at the intersection of the liquidus line and the solubility line. Beyond that point the solutes precipitates while water continues to crystallize, so that the concentration in the unfrozen solution, and consequently the freezing point, remains constant. Very often, however, and especially in solutions which have a high viscosity at concentrations approaching the solubility limit, the solute fails to crystallize because its nucleation and crystallization are prevented by this high viscosity. In those cases, theoretically the liquidus line would be followed until the T_g line is reached. The intersection of the liquidus and the T_g lines represents the maximum possible concentration achievable by freezing out the solvent water and is known as C_g' . The corresponding temperature is known as T_g' .

However, as the viscosity increases with increasing concentration, crystallization of water as well as that of the solutes becomes impeded and in industrial freezing C_g' is almost never achieved. In Fig. 8.16 we show a typical freezing process in which the concentration of the unfrozen solution at the end of the process is well below the equilibrium freezing line. The material is then often cooled to temperatures below T_g , to maximize storage stability. This final cooling usually fails to bring the solution very much closer to C_g' , and the frozen material is a mixture of ice and a solute concentration in the glass (C_g) well above C_g' , as

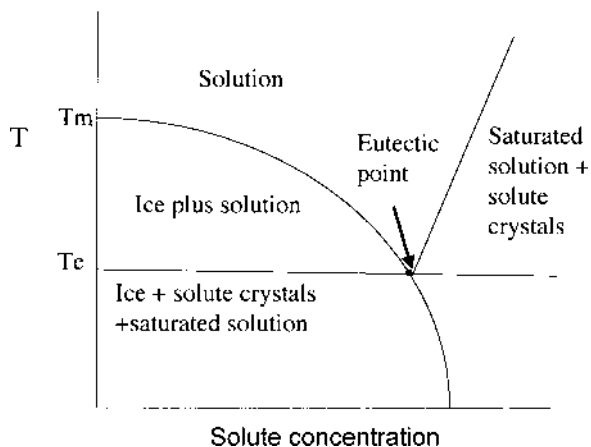


FIGURE 8.14 Temperature concentration diagram for a simple solution.

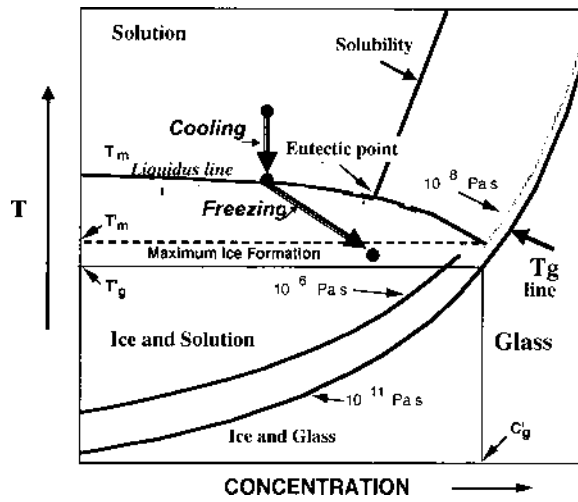


FIGURE 8.15 Freezing process represented in a state diagram for an aqueous solution.

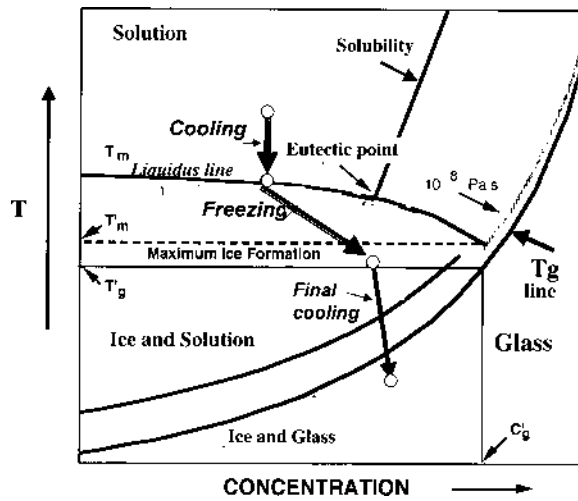


FIGURE 8.16 Freezing and subsequent cooling represented in a state diagram.

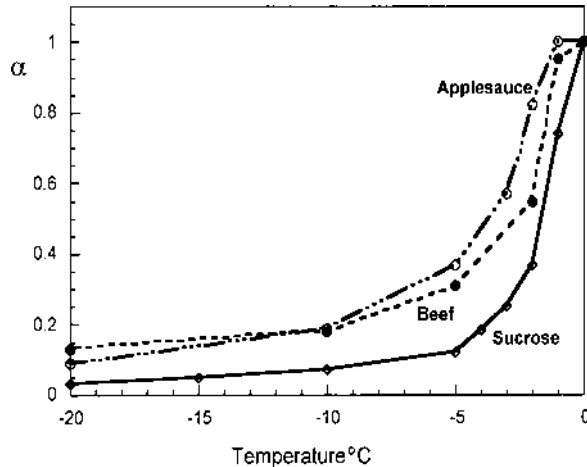


FIGURE 8.17 Fraction of freezable water remaining unfrozen as a function of temperature of two foods and an aqueous solution.

shown in Fig. 8.17. The amount of ice may, however, be maximized by an annealing process, consisting of repeatedly cooling and warming the solution within the range of maximum ice formation, shown in Figs. 8.16 and 8.17 (Roos and Karel, 1991a). Using this methodology it is possible to attain concentrations very close to Cg' .

The freezing point depression and the resulting liquidus line may be readily estimated for ideal solutions using the Raoult's law to calculate the water activity of the unfrozen solution in equilibrium with ice. The vapor pressure of ice is determined only by temperature, and at equilibrium the unfrozen solution must have a partial pressure equal to the vapor pressure of ice. The activity is therefore defined as the ratio of the vapor pressure of ice to the vapor pressure of liquid water at a given temperature. The freezing point depression ΔT may also be calculated by the relation $\Delta T = 1.86 M$, where M is molality of dissolved molecules or, if dissociated, ions. Table 8.4 shows the water activities at temperatures below freezing. Since the Raoult's law assumes that $a(w) = X$ the mole fraction of unfrozen water can be obtained directly and the weight fraction can be readily calculated if the molecular weight of the solute is given. An approximate relation for the unfrozen fraction α is given by Fennema (Karel et al., 1975):

$$\alpha = \frac{1.86 M_1}{T_{FI} - T} \quad (6)$$

where M_1 is the molality of the solution before freezing (mol/kg water) and T_{FI} is the initial freezing point (°C).

TABLE 8.4 Water Activity of Ideal Solutions in Equilibrium with Ice

| Temperature (°C) | Vapor pressure of ice (torr) | Vapor pressure of water (torr) | Water activity | Molality (mole/kg) |
|------------------|------------------------------|--------------------------------|----------------|--------------------|
| 0 | 4.58 | 4.58 | 1.000 | 0 |
| -1 | 4.22 | 4.26 | 0.990 | |
| -1.86 | | | 0.982 | 1.00 |
| -2 | 3.88 | 3.96 | 0.981 | |
| -3 | 3.57 | 3.67 | 0.971 | |
| -3.7 | | | 0.964 | 2.00 |
| -4 | 3.28 | 3.41 | 0.962 | |
| -5 | 3.01 | 3.16 | 0.953 | |
| -5.6 | | | 0.947 | 3.00 |
| -6 | 2.77 | 2.93 | 0.943 | |

Foods contain a variety of solutes, as well as insoluble water-sorbing compounds, and it is very difficult to estimate unfrozen water content on the basis of composition. However, calorimetric measurements have been conducted on the key food types, and tables and nomographs relating enthalpy and nonfrozen water content in various foods to temperature have been compiled (Dickerson, 1969). Curves of nonfrozen water fraction vs temperature for two foods are compared in Fig. 8.18 with the curve for a 12% sucrose solution.

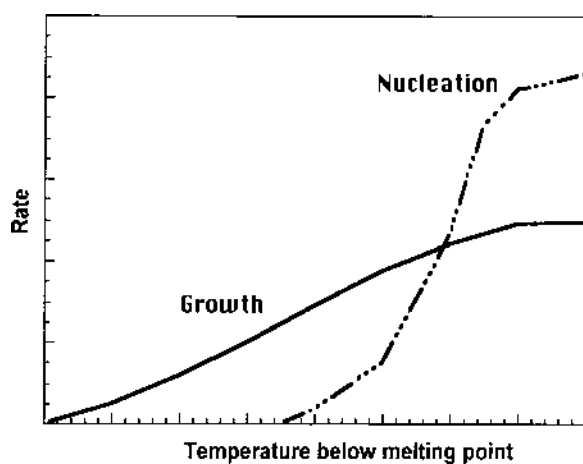


FIGURE 8.18 Effect of temperature on relative rates of nucleation and of crystal growth.

The estimation of nonfrozen water curves by calculating an apparent molecular weight of solute from the known moisture content and the initial freezing point depression, as shown below, was described by Heldman and is very convenient since (initial) freezing point depression for practically all foods are readily available in literature (Heldman, 1992).

$$\ln X' = \frac{\Delta H_P}{R} \left(\frac{1}{273} - \frac{1}{T'} \right) \quad (7)$$

In this equation the observed freezing point T' is given in Kelvin, and X' is the effective mole fraction of water in the initial (prefreezing) state of the food. If the weight fraction of water (w) is known, the apparent molecular weight MW' may be calculated using

$$X' = \frac{w/18}{(w'/18) + (1 - w')/MW'} \quad (8)$$

In foods, in solutions and in tissues freezing is initiated by heterogeneous nucleation due to indigenous nucleators, and in many freezing operations it is due to ice existing on the surfaces of the freezing equipment. In biological cells intracellular nucleation is inhibited (Toner, 1993). The nucleation and crystallization occur readily in solutions and in tissues surrounding the cells, and the water activity outside the cells falls below that inside them, resulting in a flux of water across the cell membranes. The end result of this process depends on conditions of freezing. If the cooling rate is slow, the concentration of solutes inside the cells increases due to water removal, and it is possible to attain vitrification without any formation of ice inside the cells. In rapid freezing ice crystals do form inside the cells and result in cell death. The preservation of cells and tissues by freezing will be discussed in later section.

E. Crystal Growth

Growth of crystals follows the nucleation. The rates of crystal growth are controlled by the rates of mass and heat transfer. The heat transfer is required to remove the heat of fusion from the sites of crystal growth. Mass transfer includes the transport of water molecules to crystal boundaries, and the transport of solute molecules away from these boundaries. Heat transfer is the rate-controlling transport process in almost all situations, until most of the freezable water is crystallized and the extremely high viscosity of the highly concentrated amorphous substrate surrounding the crystals drastically reduces water diffusivity.

Both heat transfer and mass transfer are promoted by increasing temperatures, heat transfer primarily because of the increase in the driving force (temperature difference between the crystal surfaces and the cooling medium), and mass transfer because of reduced resistance (reduced viscosity).

Consequently, significant rates of growth occur at close to the melting point, in contrast to rates of nucleation calculated using Eq. (5).

Figure 8.18 compares the relative rates of heterogeneous nucleation and of crystal growth as a function of temperature below the melting point. The difference between the dependence of rates of nucleation and growth on temperature is responsible for the large effect of cooling rates on crystal size distribution:

1. At low cooling rates (slow freezing) relatively few nucleation sites provide the nuclei for growth of large crystals.
2. At rapid cooling rates (rapid freezing) there are numerous nucleation sites, each competing as the site for addition of water molecules. The end result is the initial formation of many small crystals.

In foods and in other complex systems (tissues, cell suspensions, emulsion, and dispersions) the size and the location of crystals is strongly affected by factors beyond temperature. In particular geometric consideration, such as cell orientation, location of dispersed particle and emulsion droplets, location of large protein micelles, and location of crystals of precipitating solutes, may dictate the location, patterns of growth, and size of ice crystals. Rapid cooling results in very small crystals and absence of mechanical disruption of cell and tissues. The rapid cooling also minimizes transport of water from inside the cells (in which nucleation is inhibited) to the surrounding extracellular spaces. This is because the time of transition from the nucleation temperature to the temperature range close to the glass transition temperature in which viscosity is very high and growth slowed is short. As a result the morphological features of tissues and foods are best preserved by rapid freezing. This is not necessarily the condition for optimal preservation of food quality or preservation of viability of biological cells.

As will be discussed later, preparation of foods for freeze drying is often optimal when freezing rates are moderately slow, and there is an optimal range of freezing rates maximizing cell survival. While structure of frozen foods is best retained by rapid freezing, optimal texture may occasionally be achieved by modifying or disrupting the original structure. The effects are complex, and freeze-thaw cycles may make foods tougher by promoting aggregation and cross-linking of protein systems or more tender by breaking up structural elements contributing to toughness. "Texturizing" food by freezing treatment is used commercially in some meat product technologies.

F. Recrystallization

The crystal size distribution existing immediately after completion of freezing is not necessarily stable. The processes by which the number, size, shape, and orientation of crystals are changing during storage after freezing are known

collectively as *recrystallization*. The driving force for recrystallization is the tendency of all systems to minimize their free energy. As discussed previously the free energy of crystals has a component related to surface conditions, γA . The free energy may be minimized if a crystal form with lower free surface energy γ is obtained or if the total surface area of the crystals A is minimized. In the case of ice recrystallization this tendency is manifested primarily by the increase in crystal size and widening of the crystal size distribution. The most important mechanism of this recrystallization is migratory recrystallization. The surface area to volume ratio of crystals increases with decreasing crystal size—for spherical crystals this ratio varies directly with $1/r$, where r is the radius of the sphere. As a consequence the melting point of small crystals is lower than that of larger crystals

$$T_F - T(r) = \frac{2\gamma v T_F}{\Delta H_F r} \quad (9)$$

where T_F is the melting point for flat surfaces (very large crystals), $T(r)$ is the melting point for a crystal with radius r , and v is the specific volume of ice. The other symbols have been defined previously. It should be noted that the latent heat of fusion and the specific volume must be expressed in consistent terms, that is, either as molar quantities or quantities per unit weight. Equation (9) may be simplified to give the expression shown in

$$T_F - T(r) = \frac{A}{r} \quad (10)$$

In studies on ice cream, Hartel (1998) considered A to be $0.047^\circ\text{C } \mu\text{m}$. Other values reported in literature were 0.03 and $0.015^\circ\text{C } \mu\text{m}$. The differences are due in part to different freezing points of different solutions and the corresponding differences in latent heats of fusion. The most significant impact on value of A , however, is the value chosen for γ , the interfacial tension between ice and surrounding solution. The value used by Hartel was 25 mJ/m^2 , but values between 15 and 35 were reported for ice cream, and the interfacial tension may depend strongly on solution composition.

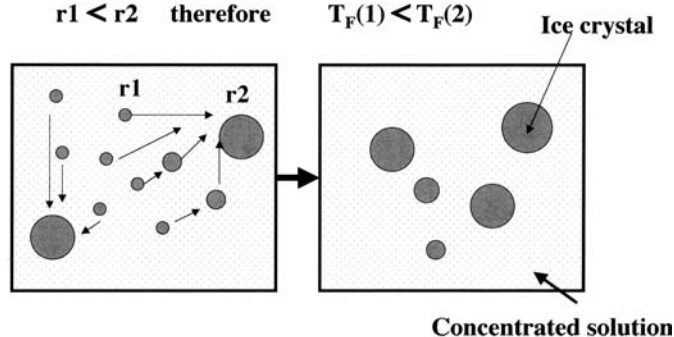
There are two major processes in migratory recrystallization: Oswald ripening and isomass rounding. In *Ostwald ripening* small crystals disappear as large ones, grow because as a result of the difference in their melting points, small crystals melt, and the melted water recrystallizes on larger crystals. As a consequence the number of crystals decreases with time and their mean size increases with time as shown schematically in Fig. 8.19.

The mean crystal sizes increases with time as given by eq. (10).

$$r'(t) = kt^n$$

Small crystals have lower melting points

$$r_1 < r_2 \quad \text{therefore} \quad T_F(1) < T_F(2)$$



$$T_F(2) - T_F(1) = K \left\{ \frac{1}{r_1} - \frac{1}{r_2} \right\}$$

$$K = \frac{2\gamma v T_F}{\Delta H_F}$$

FIGURE 8.19 Schematic representation of Ostwald ripening.

Recrystallization rates are increased with increasing temperatures. The recrystallization rates in frozen aqueous sucrose-hydrocolloid model systems was found to increase with temperature in the range of 259 to 267K in accordance with Arrhenius equation. The activation energies were found to be between 68 and 115 kJ/mol. In his studies on recrystallization in ice cream Hartel found that the rates of crystallization depend on initial crystal size distribution (controlled primarily by freezing rates), on post-freezing hardening (annealing) process, and on temperature as well as on temperature fluctuation. Hartel found that both the WLF and Arrhenius equations could be used in relating rates of recrystallization to temperature. The activation energies reported by Hartel for ice cream were between 112 and 125 kJ/mol.

Fluctuating temperatures greatly enhance the process of recrystallization. As the temperatures fluctuate the equilibrium between ice and solution follows the liquidus line, and as temperatures increase some crystals melt. When the temperature decreases again, there is usually little nucleation of new crystals and the equilibrium is reestablished by crystal growth. The effect of temperature fluctuation on recrystallization is shown in Fig. 8.20 (Hartel, 1998).

The effect of composition of ice cream on recrystallization rate was found to be primarily due to differences in freezing point. At the same concentration sugars with lower molecular weight (e.g., fructose) depress the freezing point more than those with higher MW (e.g., sucrose). At a given temperature, therefore, the amount of unfrozen water is higher in ice creams made with

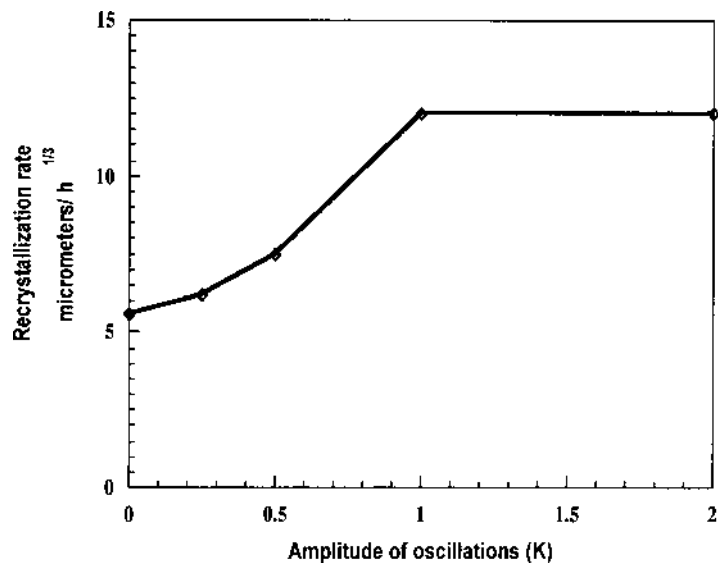


FIGURE 8.20 Effect of temperature oscillations on rate of recrystallization.

the lower MW sugars, and the recrystallization rate was found to be directly proportional to the amount of unfrozen water. The effect of polymeric stabilizers was more complex: they had little effect on rates of recrystallization, but the perception of “iciness” by the consumer was modified by the increased viscosity due to the stabilizers. It seems therefore that these stabilizers used to reduce iciness do not work primarily by reducing average ice crystal size.

Hartel suggests the following equation as useful in relating mean crystal size to time of storage:

$$\frac{r'(t)}{r'(0)} = \left(1 + \frac{t}{\tau}\right)^{1/3} \quad (11)$$

where $r'(t)$ and $r'(0)$ are mean sizes at time t and time $= 0$, respectively, and τ is a constant.

In addition to Ostwald ripening migratory recrystallization may occur by a process known as *isomass rounding*. In Ostwald ripening the tendency to minimize surface area is achieved by growth of crystal size. Isomass rounding is based upon differences in melting points of different regions in single crystals due to differences in radii of curvatures at different points. The crystals undergoing rounding tend toward becoming spherical since a sphere is the geometric shape with minimum surface to volume ratio. A schematic representation of isomass rounding is shown in Fig. 8.21.

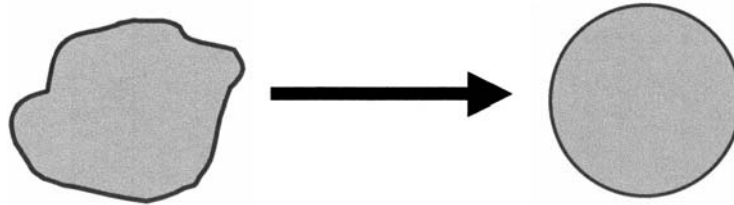


FIGURE 8.21 Schematic representation of isomass rounding.

Another mechanism of recrystallization of ice is due to accretion, or *fusion* of crystals. In this mechanism, contact between two growing crystals results in bridging between them, followed by their fusion into a single crystal, which then may undergo isomass rounding. This mechanism may be predominating in systems with many crystals.

III. GLASSY STATE AND PRESERVATION BY FREEZING

Freezing of dilute solutions of readily crystallizing solutes (e.g., salt) results in precipitation of the solute at the eutectic point, and the maximum amount of ice is formed at the eutectic temperature, as shown schematically in Fig. 8.15.

However, this is not the case with important food and biomaterial systems, including sugars and biopolymers. In these systems the crystallization of ice leads to concentration of solutes and to the formation of a highly viscous concentrated amorphous matrix. The rapid attainment of high matrix viscosity prevents the crystallization of the solutes, and the solute concentrations greatly exceed the solubility limits. Eventually, as the viscosity reaches very high levels; the crystallization of water is also impeded. It has been suggested that ice formation ceases at viscosities of 10^8 Pa s. As a result, equilibrium ice formation is prevented, and the process leads to formation of a glass surrounding the ice crystals. The state diagrams in Figs. 8.16 and 8.17 show the T_g lines. Each solute has a specific glass transition line. Mixtures of solutes have a glass transition line which depends on the solute mixture.

The state of the frozen material after a given nonequilibrium freezing procedure is very much dependent upon conditions of freezing (including initial concentration) and the time-temperature profile of the freezing process. This is demonstrated by the experiments on sugar solutions conducted by Roos and Karel. By a laborious annealing process it is possible to reach the true maximum

TABLE 8.5 Maximum Freeze Concentration Conditions for Sugars

| Sugar | $Tg(\text{anh.})^{\text{a,b}}$ (°C) | $T'g$ (°C) | $C'g$ (%) | $T'm$ (°C) |
|----------|--|---------------|--------------|---------------|
| Fructose | 5 | − 58 | 78.8 | − 47 |
| Glucose | 31 | − 57 | 79.2 | − 46 |
| Lactose | 101 | − 40 | 82.5 | − 29 |
| Maltose | 87 | − 41 | 81.5 | − 31 |
| Sucrose | 82 | − 46 | 79.5 | − 34 |

^a All Tg values refer to onset temperatures.

^b $Tg(\text{anh})$ is Tg for anhydrous sugar.

Source: Roos and Karel (1991a).

freeze concentration points, shown as points $C'g$ and $T'g$ in Fig. 8.17. The values of $C'g$ and $T'g$ are shown in Table 8.5 for several sugars.

The values of $C'g$ and $T'g$ are expected to be independent of starting concentrations. In studies on sucrose solutions, we found this to be case for annealed solution with 60% sucrose or less (Roos and Karel, 1991b). However, the higher the initial concentration, the more difficult it is to achieve the maximum concentration. For sugar concentrations above 60% in particular, the annealing process required long times of holding the temperature range of range of maximum ice formation. This zone lies between $T'g$ and $T'm$, where $T'm$ is the equilibrium melting point of ice in solution with a solute concentration equal to that of the maximally freeze-concentrated unfrozen matrix $C'g$. Sucrose solution with initial sucrose concentration of 65% required annealing for 30 min at -35°C , or just 1 degree below $T'm$.

Sucrose solution with initial sugar concentrations of 68% required 300 min annealing at the same temperature. Figure 8.22 shows the effect of annealing on the fraction of freezable water, which remains unfrozen. *Freezable* water is defined here as the water content in maximally freeze-concentrated solutions ($W'g$). For fructose $C'g$ is 78.8% and $W'g$ 21.2%; for glucose $C'g = 79.2\%$ and $W'g = 20.8\%$.

Table 8.6 list $C'g$, $T'g$, and $T'm$ values for carbohydrates. It is interesting to note the $C'g$ values calculated on weight basis are almost constant for many different carbohydrates and lie in the range of approximately 2–3 mol of water per monosaccharide unit. Since this value is close to a ratio of 1 mole of water per $-\text{OH}$ group available for H bonding, it seems that the idea that nonfreezable water corresponds to water H bonded to solutes and to sorbents may have some merit.

It should also be noted that the temperature difference between $T'm$ and $T'g$, and therefore the width of the maximum ice formation zone, varies with

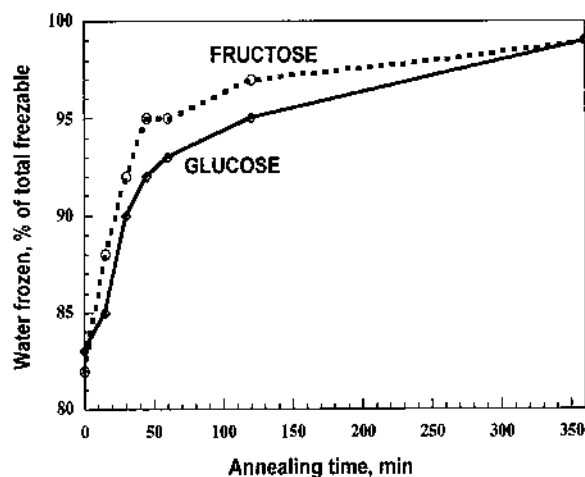


FIGURE 8.22 Effect of annealing on freezing out of water in concentrated sugar solutions.

the material being frozen. For starch (the data shown in Table 8.6 are for amylopectin) $T'g$ and $T'm$ coincide. Our results led us to the conclusion that in materials such as starch with extremely narrow zones of “maximum ice formation,” freezing to the maximal freeze-concentration level is not feasible (Roos and Karel, 1991c). The magnitude of nonfrozen but theoretically freezable water in starch may be estimated if we assume that in common with other carbohydrates, the starch system could be maximally concentrated to a $W'g$ of 20%, that is, 0.25 g/g solids. The actually achievable $W'g$ is 25% (Table 8.6) or

TABLE 8.6 Values of $C'g$, $T'g$ and $T'm$ for Different Carbohydrates

| Carbohydrates | $C'g$ (% w/w) | $T'g$ (°C) | $T'm$ (°C) |
|---------------|---------------|------------|-------------|
| Pentoses | 79–82 | –65 to –67 | – 53 |
| Hexoses | 78–83 | –62 to –56 | – 48 to –44 |
| Disaccharides | 81–82 | –46 to –40 | – 34 to –30 |
| Raffinose | 84.1 | –36 | – 28 |
| Sorbitol | 81.7 | –63 | – 49 |
| Xylitol | 80.2 | –72 | – 57 |
| Maltodextrins | | | |
| MW ~ 500 | ~80 | – 30 | – 15 |
| MW ~ 1000 | ~80 | –18 | – 10 |
| Starch | ~75 | –6 | –6 |

0.33 g/g solids. It seems therefore that 0.08 g of water/g solids that are potentially freezable do not freeze in polymer systems such as starch.

IV. BIOLOGICAL ASPECTS OF FREEZING

A. Cryopreservation of Cells and Other Biomaterials

Freezing is an important method for preservation of living cells, their constituents as well as of organs. Peter Mazur, one of the key pioneers in the field, expressed the paradox of cryopreservation in 1970 as follows: "Freezing is lethal to most living systems: yet it can also preserve cells and their constituents, and it may some day permit long-term storage of whole viable organs" (Mazur, 1970). The advances made since the 1970s have been spectacular, and cryopreservation is an important tool of modern biomedical engineering and is used widely in medical procedures.

Preservation of blood has been one of the earliest applications in medicine, but the scope of cryopreservation is now very broad. The 37th Annual Meeting of the Society for Cryobiology was held in August of 2000 at MIT in Cambridge, Massachusetts. Besides a large number of scientific papers on theory and practice of cryopreservation, there were numerous papers, posters, and exhibits on current applications. These included preservation of blood, various cells, cell constituents, as well as tissues and organs. Among tissues being cryopreserved are skin, corneal tissue, liver tissue, arteries, and veins. An extremely active field is preservation of semen, ova, and embryos. It has very wide application in animal husbandry and within the past decade became important in human reproduction.

It is of considerable importance therefore to understand the mechanisms of injury to cells during freezing in order to develop optimal preservation procedures. The following two key aspects of cell injury and death are known to characterize cell behavior:

1. Ice formation within a cell (intracellular ice formation) is lethal.
2. Intracellular nucleation is inhibited.

According to Steponkus, in plant cells nucleation inside the cells does not occur above -5°C . In various animal and single-cell systems nucleation inhibition was observed to extend to even lower temperatures. Furthermore the inhibition was particularly pronounced when external ice formation was absent (Toner, 1993). Table 8.7 demonstrates this effect.

The generally accepted view is that heterogeneous nucleators within the cytosol, or solution within the cells, are very much less effective than those external to the cell. There is no agreement however about the mechanism for the apparent increase in intracellular nucleation temperature in the presence

TABLE 8.7 Intracellular Ice Formation (IIF) in Isolated Cells

| Cell type | Temperature of IIF (°C) | |
|-----------------|-------------------------|---------------------|
| | External ice present | External ice absent |
| Sea urchin eggs | -4 to -8 | < -15 |
| Spirogyra | -7.7 | < -12.4 |
| Yeast | -10 to -15 | -40 |
| Erythrocytes | -10 to -15 | < -35 |
| Mouse oocytes | -12.3 | < 20 |
| Drosophila eggs | -10.2 | -28.5 |

Source: Toner (1993).

of external ice. One of the earliest mechanism explanations is that advanced by Mazur in a series of pioneering papers (Mazur, 1977; Mazur, 1965; Mazur, 1970). He noted that the rates of survival of frozen cells depended very strongly on freezing rates. Very rapid freezing resulted in very low survival rates. In some cell types, slowing the rate of cooling substantially improved survival. Very slow cooling rates however resulted in lowering the survival rates again. Each cell type appeared to have optimal survival rates at a type-specific cooling rate.

He proposed that a necessary (but not sufficient) condition for survival was prevention of formation of ice inside the cell. This postulate was confirmed in many subsequent studies. Toner analyzed a large number of studies published during the period of 1963 and 1992 on a variety of cells, including red blood cells, lymphocytes, granulocytes, HeLa tumor cells, yeast, hepatocytes, and mouse and hamster oocytes, and plotted the cooling rate resulting in 50% survival against the cooling rates resulting in the presence of microscopically observable ice in 50% of the cells. The cooling rates giving the 50% survival varied from cell to cell. For example, the 50% yeast survival occurred at a cooling rate of 10°C/min but with red blood cells at over 1000°C/min. However a plot of rates giving the 50% survival vs rates resulting in 50% cells with ice gave an excellent linear correlation with a 45° slope. This observation suggests very strongly, perhaps conclusively, that cells which show presence of intracellular ice do not survive (Toner, 1993).

Starting with the assumption that intracellular nucleation is unlikely and with experimental results on a variety of cells of different sizes, Mazur postulated that external ice seeds initiate intracellular nucleation at a temperature at which very small ice clusters become thermodynamically stable. These small clusters were assumed to be capable to penetrate the cell through pores. Until these temperatures are reached, the cells undergo dehydration. Since cell membranes

are permeable to water but not to most solutes present inside the cells, the supercooled solutions inside the cell have a higher vapor pressure than that of the ice in the exterior, and this pressure difference drives the water out of the cell. If the rates are not too rapid, the dehydration results in very high solute concentrations, which prevent freezing within the cells even when the assumed penetration temperature is reached and the cells survive. Mazur estimated cell permeabilities and calculated the magnitudes of water loss. He found the results of these calculations consistent with his postulated mechanism, and these calculation also explained some of the differences between optimal cooling rates for different cells. These could be related to differences in permeability and most importantly to differences in size. Large cells have lower surface-to-volume ratios; for a given cooling rate less water would permeate for a given extent of cooling.

Mechanisms other than that proposed by Mazur have been described in literature. In a paper published in 1990 we proposed that the initiation of intracellular freezing does not require seeding by external ice but may be due to nucleation by membrane sites, which in turn are activated by interaction with external ice (Toner et al., 1990). The group of Steponkus at Cornell and others are of the opinion that cell membrane damage occurs at low temperatures unless sufficient solute concentration is achieved within the cells. The membrane failure allows the external ice to penetrate. This theory discounts the role of external ice as a nucleator.

Whichever mechanism is accepted, the conclusion one reaches is that a dehydration of cells, and therefore a low cooling rate promotes survival. This conclusion must be modified, however, because if cooling rates are too slow, then vital cell components, including proteins, are exposed for significant periods of time to very high concentrations of solutes, at temperatures which have still not reached low enough levels to reduce or even prevent interactions between solute and biological components.

Two additional factors must be considered at this point:

1. The possibility of modifying the *composition*, as well as concentration of both extracellular and especially of intracellular solutes, by solute addition prior to freezing
2. The role of *thawing*

In practical biomedical applications cell freezing requires the use of *cryoprotectants*. Cryoprotectants are divided into two major groups: permeating and nonpermeating. Cryopreservation is greatly facilitated by the addition of permeating cryoprotecting solutes. Many cryopreservation protocols include the addition of 1.0 to 2.0 M of compounds such as dimethyl sulfoxide, glycerol, propane diol, and ethylene glycol. Sugars and especially sucrose are the most widely used nonpermeating cryoprotectants. The stabilizing solutes include

glycerol, glycols, glucose, sucrose, inositol, glycine, sodium acetate, and trehalose. Trehalose is known to be particularly effective in cryopreservation, and its use is investigated in many laboratories.

These compounds form solutions with a high viscosity and readily attain the glassy state, which stabilizes biomolecules. Equally important is their ability to protect the sensitive biomolecules during the process of concentration, prior to attainment of the glassy state. The mechanisms of this protective function are not fully understood. In a review of this subject Crowe and his co-workers (Crowe et al., 1990) noted various theories proposed for cryoprotection during concentration and concluded that the dominant mechanism is due to preferential exclusion of these solutes from the hydration shell of proteins. For thermodynamic reason this exclusion tend to prevent proteins from unfolding and therefore stabilizes their configuration. While the validity of this theory remains to be accepted by all researchers, what is not in dispute is the effectiveness of the compounds listed above, especially of sugars.

It is established on both theoretical grounds and from studies on various sugar-accumulating organisms that sugars are excellent cryoprotectants and that their presence within the cells enhances survival. However, cells are not permeable to sugars, and their addition was not possible until recently. A recent development is the use of a hemolysin from of a genetically engineered strain of *Staphylococcus aureus*. This toxins forms 2-nm transmembrane pores in cells. Furthermore these pores can be toggled between open and closed states by removal or addition of micromolar quantities of Zn^{2+} ions, thus achieving reversible permeabilization of cells to sugars. At present this is a laboratory technique used for investigating the effect of freezing cells containing added internal sugar concentrations. Studies have shown that introduction of sugars greatly improved cells survival after freezing and thawing. Trehalose was particularly effective giving 80% survival of fibroblasts and 70% survival of human keratocytes after reversible permeabilization resulting in addition of 0.2 M trehalose, rapid freezing in liquid nitrogen, and thawing in a + 37°C bath (Eroglu et al., 2000).

The major functions of cryoprotectants are

1. Lowering the freezing point, and promoting medium to be supercooling.
2. Protecting cell membranes from freeze-related injury.
3. Decrease the deleterious effects of high salt concentrations during freeze-concentration of cell contents.

If the internal concentrations of potentially glass-forming solutes are high enough it is possible to rapidly lower the temperatures of the biological preparations to achieve vitrification (formation of glassy state). In applications to preservation of human embryos very high concentrations of cryoprotectants (e.g., 3–4 molar DMSO) were used to permeate embryos. After permeation, the embryos were

plunged directly into liquid nitrogen, resulting in ultrafast freezing and avoidance of ice formation, precluded. This is still an experimental subject, although pregnancies from previously vitrified human embryos have been reported (Shabanowitz, 1997).

Survival is dependent upon controlled thawing, which allows for a gradual rehydration of cells as they are warmed. In order to prevent recrystallization of water within a cell with resultant cell damage, successful cryopreservation requires a proper match between the freeze and thaw programs. Thawing rates depend upon how cells were initially frozen. According to Shabanowitz, if cells were subjected to a rapid freeze, a rapid thaw is required, typically by direct immersion in a $+37^{\circ}\text{C}$ water bath with warming rates in excess of $+200^{\circ}\text{C}/\text{min}$. On the other hand, a slow thaw may be required for slowly frozen materials and requires the use of a programmable cell freezer. In this method, embryos are slowly warmed at controlled rates of approximately $+8.0^{\circ}\text{C}/\text{min}$ to about 4°C .

Cryoprotectants must also be removed after thawing embryos. Transfer of the embryos through stepwise dilutions of the cryoprotectant typically accomplishes this. The use of thaw solutions containing nonpermeating solutes, such as sugars, but no permeating cryoprotectant has been found helpful. The presence of extracellular sugars in the thaw medium acts as a counter solute to prevent the rapid influx of water into the cells while at the same time, the permeating cryoprotectant is effectively removed from the cell.

B. Biological Ice Nucleation

Research into frost damage to various crops in California and other areas subject to occasional temperatures below freezing during the growing season has resulted in discovery of several bacterial species capable of increasing the damage potential by facilitating ice formation at minimal supercooling. The organisms were found to exist on plant leaves of many plants. *Pseudomonas syringae* and strains of *Erwinia* and *Xanthomonas* were found to be affective promoters of frost damage. It was found that the effect is due to the ability of proteins present in the outer membranes of these bacteria to nucleate ice. The nucleators are very effective, and initiate freezing at temperature as high as -2°C . Their nucleation capacity exceeds substantially that of inorganic nucleators such as silver iodide (Lindow, 1998).

Subsequent research has characterized the bacterial proteins responsible for ice nucleation. The nucleation property is apparently expressed by a single gene which codes the nucleating protein. The proteins have an amino acid repeating structure, which is characteristic for all of them. This structure includes the repeating unit Ala-Gly-Tyr-Gly-Ser-Thr-Leu-Thr (Li and Lee, 1995).

The nucleating capability, however, also depends on size of the protein. Larger proteins have a greater nucleating potential, and it is believed that

aggregation of protein units result in units with different nucleating temperatures. The nucleator size ranges from 150,000 Da (active at -12°C) to 8,700,000 Da (active at -3°C). Theoretical considerations based on surface thermodynamics appear to explain the effect of size on the nucleating effectiveness (Burke and Lindow, 1990).

It has been suggested that bacterial protein nucleators have the potential to produce desirable effects in food technology. The following applications have been suggested:

1. Producing desirable texture by controlled nucleation freezing (freeze-texturing)
2. Improving efficiency of freeze concentration procedures
3. Freezing in the presence of the nucleators to reduce freezing time
4. Producing crystal structures facilitating freeze-drying

The applications are hampered by the fact that only one organism with some nucleating potential (*Xanthomonas campestris*) is considered to be food grade.

Future applications would be greatly aided by purification of the proteins in active form, which has not as yet been achieved, or by expression of the nucleating gene in organisms recognized as safe. Work is currently in progress in both areas.

C. Antifreeze Proteins

Research in the 1950s resulted in recognition that various fish species have proteins enhancing their capability to survive at low temperature. These proteins were originally isolated from blood of perchlike fish species surviving in cold waters at temperatures of -2°C . Subsequently similar proteins were found in many species of fish and in insects. There are a number of structurally related protein types having the antifreeze function (Lillford and Holt, 1994).

Glycoproteins (AFPG) represent one of the types. They range in MW from 2.6 to 33 kDa with the higher MW units being more effective. They have a repeating unit Ala-Ala-Thr with glycosylation at the threonine residue.

There are several other types and their characteristics are shown in Table 8.8, (based on personal communication from Dr. M. Erison of A/F Protein, Inc.). Types I-IV are extracellular proteins isolated from various fish species. Types s-AFP is an intracellular protein isolated from skin of flounder.

Type I is alanine rich, has a MW of 3.3-4.5 kDa and is found in winter flounder. Type II is cysteine rich and contains several S-S bonds. The most recently discovered type IV is glutamine rich. As shown in Table 8.8 there are also several AFP types isolated from insects.

In spite of considerable research since their discovery, the exact mechanism by which antifreeze proteins is not established. It is generally agreed

TABLE 8.8 Biochemical Characteristics of Fish and Insect Antifreeze Proteins

| | Type I | Type II | Type III | Type IV | AFGP | sAFP | sbwTHP |
|----------------------|--|---|------------------------|------------------|--|--|---|
| Sub-isotypes | 7 | 2-6 | 12 | nd | 8 | 8 | nd |
| M _r (kDa) | 3-5 | 14-24 | 7 | 13 | 3-33 | 12-13 | 8-9 |
| Composition | > 60% Ala (Tx ₂ Nx ₇) _n | Cys-rich | Unremarkable | Glu, Gln-rich | Ala, Thr-rich (AAT) _n , (PAT) _n | Ala-rich (Tx ₁₀) _n | Thr, Cys-rich (CTXS ₂ Cx ₂ AXT) _n |
| rep-Sequence | None | None | None | None | O-linked sugar | N-term MDAP | Disulfide linked |
| Other features | None | Disulfide linked | None | N-term blocked | Coil only | Mostly α-helix | β-sheet & coil |
| 2° structure | 100% α-helix | α-helix, β-sheet | Short β-strands | Mostly α-helix | nd | 65% helical | Globular |
| 3° structure | Helical rod | Globular | Globular | 4-helix bundle | Extracellular | Intracellular | Extracellular |
| Properties | Extracellular | Extracellular Ca ⁺⁺ dependent | Extracellular | Extracellular | Extracellular | Found in skin | |
| Homology | nk | C-type lectins | nk | Lipoprotein-like | nk | Antimicrobials | nk |
| Gene copies | 80-100 | 12-15 | 30-150 | nd | nd | 30-40 | nd |
| Native source | Flounder Sculpin | Smelt, Herring Sea raven | Ocean pout Wolffish | Sculpin | Nototheniids Northern cods | Flounder | <i>C. fumiferana</i> |

nk, not known; nd, not defined.

Source: From A/F Protein, Inc.

that the proteins function by inhibiting growth of ice crystals by concentrating at the ice crystal surfaces. It is further agreed that this inhibition exceeds that expected from inhibition of bulk diffusion, and that the effects occur at the ice crystal–solution interface (Ewart et al., 1999).

The major differences of opinion among researchers concern the type of binding and the orientation of the proteins at the crystal surfaces. The prevailing theories attribute the hydrogen bonding of polar residues to ice. Most antifreeze proteins possess a planar face able to form regularly spaced hydrogen bonding patterns with the neatly ordered water molecules of nascent ice crystals. Potential sites for hydrogen bonding are the hydroxyl groups of the carbohydrates in the antifreeze glycoproteins and the polar amino acids (such as aspartic acid, asparagine, glutamic acid, glutamine, serine, and threonine) in the antifreeze proteins. This hydrogen bonding of the antifreeze protein to ice crystals, including potential hydrophobic effects from other regions of the protein, is thought to inhibit crystal growth (Lillford and Holt, 1994).

A different view of the binding is expressed by Haymet and co-workers (Haymet et al., 1999), based on work using analogues of antifreeze proteins, in which the hydrogen–bonding threonine residues were replaced by other residues. They concluded that the hydrophobic interactions are primarily responsible for binding to ice surfaces. Several companies are involved in exploring the potential for utilization of AFP in commerce. As shown in Table 8.9, the AFPs have potential applications in several fields (Fletcher et al., 1999). Genetic engineering of organisms containing AFP is considered to offer advantages in agriculture and in aquaculture:

1. Aquaculture (extending the range of suitable waters to colder areas)
2. Agriculture (reducing losses of frost–sensitive crops)

Isolated ATPs may have potential in cryopreservation of biological materials, and in medicine. It has also been suggested that they may be used to improved texture of food products (including ice cream) by preventing growth of large ice crystals associated with iciness.

V. FREEZING TECHNOLOGY

Freezing is primarily a heat transfer operation. Once nucleation is achieved the limitation on crystal growth is primarily due to limitations on rates of heat removal. The industrial equipment for freezing may therefore be classified according to the type of heat transfer.

Industrial freezing systems are as diverse as heat transfer systems, and they differ by the type of cooling medium used, by the methods of contacting the food to be frozen with the cooling medium, and by the methods of conveying the foods through the freezers. In the context of our discussion

TABLE 8.9 Market Potential for Antifreeze Protein and for Plants and Fish Genetically Engineered for Increased AFP Content

| Freeze resistance | Total market, \$ millions | Potential annual revenues, \$ millions |
|---|---------------------------|--|
| Fish | 400 | 20 |
| Plants | | |
| Soybeans | 500 | 30–50 |
| Coffee | 2,000 | 100 |
| Fruit | 200 | 10 |
| Citrus | 360 | 18 |
| Cold preservation or cryopreservation of cells, tissues, and organs | 4,000 | 150–200 |
| Cold preservation of platelets | 1,000 | 75–100 |
| Cryosurgery | — | 50 |
| Ice cream | 30,000 | 90–100 |
| Salmon growth | 2,500 | 125 |

here we consider the term *cooling medium* to mean the medium actually contacting the food, or food packages, rather than the refrigerants within the various freezing systems. However, in some systems food is exposed directly to refrigerants and then the term cooling medium will apply to the refrigerants.

A. Air Freezers

Air is the medium most commonly used to freeze packaged as well as unpackaged foods. The performance of air freezers depends very much on velocity of air in the freezer. As discussed previously in the Chapter 3 on heat transfer, the heat transfer coefficient (h) of air increases is approximately proportional to $vel^{0.8}$, where vel is the linear velocity of air. The overall coefficient of heat transfer U depends of both internal and external resistance. In the case of freezing the internal resistance is due to the resistance of the frozen layer through which the heat is removed. Assuming one-dimensional transfer, we can consider that resistance equal to x/k , where x is the thickness of the frozen layer, at a given time, and k , is the thermal conductivity of frozen food in $W/(m^{\circ}C)$. Frozen food is a good heat conductor, and the Biot number ($Bi = hx/k$) is often very small indicating that the external resistance to heat transfer is limiting. The value of h is of crucial importance in freezing in air. In still air (natural convection) h is typically $5-10 W/(m^2 \text{ }^{\circ}C)$; in blast freezers with very rapid air movement h may be $20-30$.

Given the thermal conductivity of frozen food in the range of $2 \text{ W}/(\text{m}^\circ\text{C})$, we can calculate the thickness of frozen food which gives a Bi value of 1.0, that is a condition at which the internal and external resistances are equal by setting $x = \text{Bi}k/h$. If we assume an h of 20 (typical of a blast freezer with a velocity of air of 3 m/s), we obtain $x = 1.0 (2)/20 = 0.1 \text{ m}$. We find therefore that the external resistance is equivalent to that of a 10 cm slab of frozen food.

The acceleration of air to extremely high velocities is only moderately effective, however, when freezing packaged foods. For comparison it may be noted that thermal conductivity of cardboard is approximately $0.07 \text{ W}/(\text{m}^\circ\text{C})$, some 30 times lower than that of frozen food. Thus a 3 mm thick cardboard would offer a resistance of $0.043 (\text{m}^2\text{ }^\circ\text{C})/\text{W}$, which is of the same order of magnitude as that of the air in an air freezer. Packages may also entrap air layers at food package interfaces, which result in very high heat transfer resistances. Shrink wrapping and vacuum packing may alleviate these problems of added resistance to heat transfer.

The use of very high velocities is however very effective when freezing unpackaged foods, especially when they can be completely surrounded by flowing air, as is the case in fluidized bed freezers. h values of over $100 \text{ W}/(\text{m}^2\text{ }^\circ\text{C})$ may be attained in these freezers.

The following listing of types of air freezers demonstrates the great versatility of these systems. The major companies producing these freezing systems, such as Frigoscandia in Europe and FMC Corporation in the United States have web sites which display many of their systems and their characteristics.

Types of air freezers:

Batch freezers:

Walk-in cold rooms

Stationary tunnels

Push-through tunnels for carts conveying food products batchwise

Continuous

Belt freezers

Continuous carrier freezers (e.g., for carts continuously moving through)

Spiral belt freezers

Fluidized bed freezers

Fluidized bed freezers are suitable for individually quick-frozen (IQF) foods, such as peas, but have been applied to larger items such as fish sticks.

B. Indirect Contact Freezers

In these freezers the refrigerant or the cooling medium is separated from the materials to be frozen by a conducting materials, often a steel plate. The conductivity of metals used for the contact plates is good, even though their

choice is governed primarily by sanitary requirements, rather than the best thermal conductivity available in materials (As an example, it may be noted that the food equipment grade stainless steel has a conductivity some 20 times lower than that of copper.) The major heat transfer problem arises from the difficulty in maintaining good contact between the materials being frozen and the heat exchange surfaces. In so-called plate freezers good contact may be maintained with flat packages or with flat food portions (blocks of fish flesh are a typical example) by maintained pressure upon the plates during the freezing process thus enforcing contact with the packages. Plate freezers may be apparent in a batch mode or in a continuous mode in which the product is contained between the plates at one end of the freezer, moves in this position, and is released at the exit from the freezer. Overall heat transfer coefficients for plate freezers are in the range of 50 to 100 W/(m²°C) in systems maintaining good contact.

A very efficient utilization of indirect freezers is possible for partial freezing of liquids. These freezers use scraped surface heat exchangers and achieve extremely rapid heat transfer. They are used in production of ice cream (Hartel, 1996). The ice cream process is shown schematically in Fig. 8.23. The initial nucleation and crystal formation is achieved in a scraped surface rotary heat exchanger with an extremely high heat transfer coefficient. The temperature difference available for heat transfer between the ammonia vaporizing on the inside of the heat exchanger barrel (typically at -30°C) and the thin layer of ice cream mix on the outside is large, and a very large degree of supercooling favors nucleation and proliferation of many small ice crystals. The mechanism of nucleation is not entirely established. The dendritic crystals formed on the barrel surface are rapidly moved to the film of ice cream mix where they ripen in block-shaped ice crystals. The ice cream is discharged from the first freezer at -5 to -6°C , and has a low enough viscosity to allow it be pumped into the containers for packaging. At that point approximately half of the freezable water has been actually frozen. The residence time in the scraped surface freezer is typically less than a minute.

Most of the crystal growth, and freezing out of remaining water occurs in the second freezer (Fig. 8.23), typically an air blast freezer at -30°C , where the packages are cooled to -18°C in a process taking several hours. The size distribution of crystals is affected primarily by the initial crystallization, but also by the formulation of the mix. The polymeric stabilizers used increase viscosity and may impede diffusion of water to crystal surfaces. Recrystallization during storage and development of iciness can be prevented by storage at low temperatures and avoidance of temperature fluctuations (Hartel, 1996). The stabilizers are also effective in reducing the likelihood of crystallization of lactose which is supersaturated in ice cream. Lactose crystallization can occur under very undesirable storage conditions (high and fluctuating temperatures). It results in defects known as sandiness or grittiness.

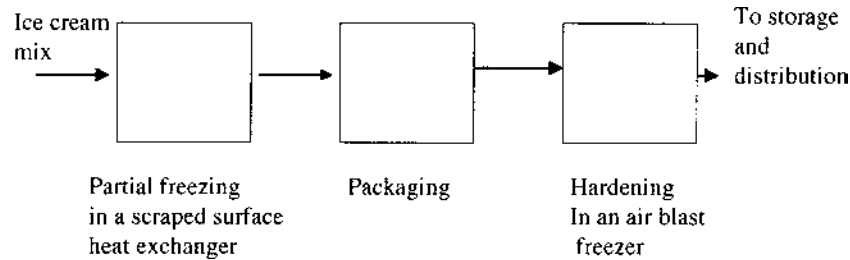


FIGURE 8.23 Flow chart for ice cream freezing.

It is considered likely that polymeric stabilizers not only reduce the post storage crystal sizes, but also reduce the undesirable sensory impact of a given crystal size, possibly by adsorbing on crystal surfaces.

C. Immersion Freezing

Foods may be frozen by immersion in cold liquids media suitable for immersion cooling are primarily aqueous solutions. Solutions of all of the following have been used as cooling media: glycols, glycerol, sodium chloride, calcium chloride, and mixtures of salt and sugars. The advantage is the improved heat transfer coefficient for brine (sodium chloride or calcium chloride solutions) the coefficient (h) may be as high as $85 \text{ W}/(\text{m}^2\text{C})$. The disadvantages lie in the undesirable effects of contacts of these media with foods. When these cooling media are used to freeze packaged foods, some of the advantages of improved heat transfer are lost because of resistance of the package, and additional technical difficulties, and costs arise from the need to wash or otherwise remove the media form package surfaces. The media may also exert corrosive effects on metallic packages.

D. Cryogenic Freezing

Cryogenic freezing refers to processes in which the material to be frozen, either packaged or unpackaged, is exposed directly to a liquid boiling at a very low temperature or a solid subliming at a very low temperature. The cooling media which have been used for this purpose include liquid and solid CO_2 , N_2 , N_2O , and Freon 12 (CCl_2F_2). The important thermal properties of these media are shown in Table 8.10.

Cryogenic freezing has the advantage of being capable of achieving very rapid heat transfer. Heat transfer from boiling liquids can achieve heat transfer coefficients in excess of $1000 \text{ W}/(\text{m}^2\text{C})$. These high values of h are however difficult to achieve in practice since the gas to which the liquid is converted depresses the values considerably by blanketing the materials being frozen.

TABLE 8.10 Properties of Cryogenic Cooling Media

| Cooling medium | Boiling point (°C) | Latent heat (kJ kg ⁻¹) | Specific heat (gas) (kJ kg ⁻¹ °C ⁻¹) |
|-------------------------|-----------------------|---------------------------------------|---|
| Liquid N ₂ | -196 | 199 | 1.04 |
| Solid CO ₂ | -79 | 571 | 0.85 |
| Liquid CO ₂ | -79 | 342 | 0.85 |
| Liquid N ₂ O | -89 | 376 | 0.85 |
| Freon 12 | -30 | 165 | 0.63 |

Nevertheless h values of the order of 200 to 400 W/(m²°C) are often reported for cryogenic freezers. Cryogenic freezing with liquid nitrogen and with carbon dioxide is also very convenient for seasonal, or occasional freezing since it can be conducted without the need for constructing permanent refrigeration installations. Cryogenic freezing with these gases is used widely, and successfully, in spite of the somewhat higher cost than that for other methods of freezing. The application of N₂O has been proposed but uses, if any, are extremely limited. Freon 12 freezers were used in a number of application in the 1960s and 1970s, including in freezing IQF vegetables and shrimp. The systems were developed by DuPont and the equipment was designed to minimize losses of Freon to the environment and to avoid contamination of foods with the refrigerant. However, the recognition that fluorinated hydrocarbons were the cause of damage to the atmospheric ozone layer has resulted in complete abandonment of this method of direct freezing.

The use of solid carbon dioxide (dry ice) is also fairly limited to small-scale applications. Where it is used, the dry ice is applied as powdered material (snow) to maximize contact with the material to be frozen.

E. High Pressure Applications in Freezing Technology

Recent developments in the use of high pressure in food preservation (cf. Chapter 13) have also renewed an interest in high pressure applications in freezing technology. As shown in Fig. 8.10, the freezing point of water, and the types of ice formed depend on pressure. It is possible therefore to affect the ice–water transition by controlling pressure rather than temperature (Kalichevsky et al., 1993).

The applications in freezing technology include maintenance of nonfrozen materials at low temperatures and high-pressures, high-pressure shift freezing, and pressure-assisted thawing.

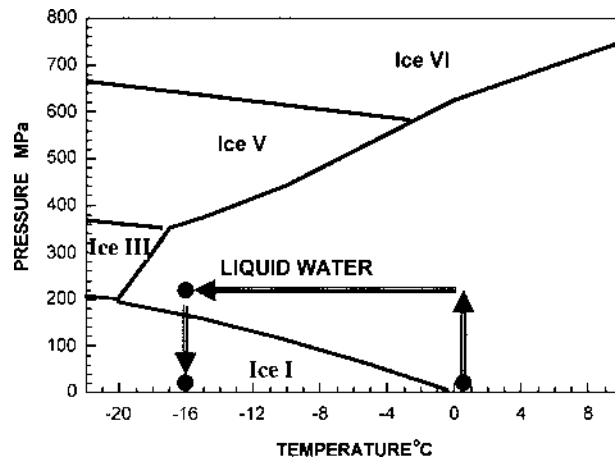


FIGURE 8.24 Extended phase diagram for water and ice.

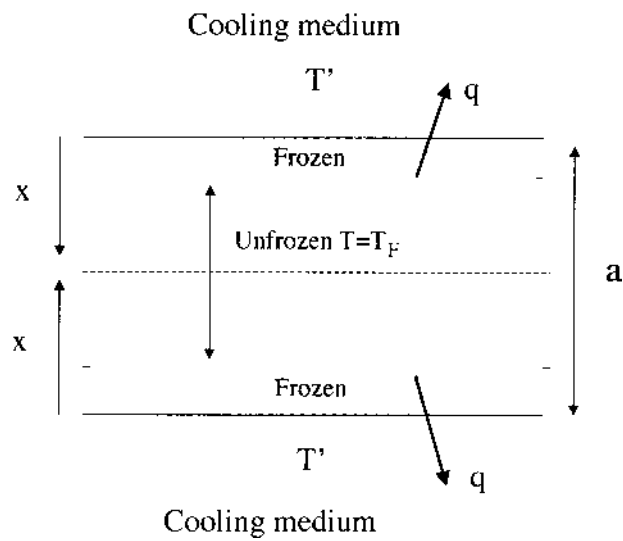


FIGURE 8.25 Heat transfer during freezing of a slab.

It is possible to maintain nonfrozen materials at temperature in the range of 0 to -20°C without freezing by maintaining pressure at appropriately high levels (20 to 200 MPa). Several food materials were stored under these conditions. In several cases an extension of shelf life or improvement of post-storage was observed, but the results do not seem to justify the procedure as a substitute for freezing preservation. A recently investigated application is that of high-pressure shift freezing. In this process a water-containing material is maintained at a low temperature (subfreezing at atmospheric pressure) and at a high pressure which maintains water in the liquid state. The pressure is then reduced rapidly, resulting in very substantial supercooling, which promotes nucleation of ice throughout the material. A schematic and idealized representation of the process is shown in a temperature–pressure phase diagram for water in Fig. 8.24.

The characteristic distribution of granular crystal throughout the product confirms the occurrence of nucleation throughout the depressurized material, due to the very high degree of supercooling achieved instantaneously, which is due to the instantaneous pressure drop. The maximum amount of ice produced just after the expansion depends on the maximum applied pressure and the temperature and has been calculated to be as much as 36% of the total water available for freezing (Otero and Sanz, 2000). The major impediment to the achieving of the rapid crystallization theoretically implied by the diagram in Fig. 8.25 is heat transfer. The huge latent heat of fusion overwhelms the heat capacity of initially cold unfrozen portion and the temperature rises rapidly toward the freezing point corresponding to atmospheric pressure. The supercooling effect is lost rapidly, terminating nucleation, and the small crystals formed initially melt and contribute to growth of large crystals. To achieve the potential benefits of high-pressure shift freezing (often claimed as formation of small, uniformly distributed ice crystals) very efficient heat transfer removing the latent heat is required. This can only be achieved with very small sample and limits the applications. The use in microscopy where samples are extremely small and an efficient cooling medium (liquid nitrogen) can be applied conveniently has been reported (Kalicevsky et al., 1993).

The use of high pressure has also been suggested in thawing. It has been reported that the use of pressures of 100 to 200 MPa may reduce the time required for thawing. Both positive and negative effects on quality have been reported (Kalicevsky et al., 1993). At present these applications require further research to establish their potential value.

VI. DESIGN CALCULATIONS

The choice of equipment and the design of the process require knowledge of freezing time and of the total heat removal required.

A. Heat to Be Removed

The total amount of heat to be removed during the process is readily obtained from the following heat balance for product entering the process at an above-freezing temperature of T_1 and leaving at a temperature below freezing T_2 . The heat balance below is based on 1 kg of product.

$$q(\text{removed}) = [c_{ps}w_s + c_{pw}(w_{uw} + w_{fw})](T_1 - T_2) + \Delta H_F W_i + c_{pi}w_i(T_F - T_2)$$

The symbols are c_p = specific heat in kJ/kg and w = weight fraction of product; subscripts are as follows: s = solids, uw = nonfreezing water, fw = freezable water, and i = ice. It is assumed that specific heats of liquid water, of solids, and ice are independent of temperature, and the latent heat of fusion is constant.

The amount of nonfrozen water at various temperatures is available in most food engineering texts, in form of tables or nomographs. These nomographs also allow the direct estimation of enthalpy difference between the initial and final state of the product being cooled, hence an estimate of the cooling requirement (Charm, 1971; Heldman, 1992). The reader is also referred to the review by Dickerson (1969).

B. Calculation of Freezing Time

The simplest and best known equation for determining the freezing time for solids is that of Plank, developed originally in 1913, and still very useful as a starting point for calculations. As shown in Fig. 8.25 for the case of a slab, being frozen from two sides, it is based on the following simplified assumptions:

1. The freezing medium remains at a constant temperature T' .
2. All the freezable water freezes at a single freezing point T_F .
3. The latent heat of fusion ΔH_F is constant.
4. The heat transfer coefficient of the freezing medium h is constant.
5. The thermal conductivity of the frozen material (k') through which heat is removed is constant.
6. As long as water remains to be frozen all the heat removed is due to latent heat of fusion.

It may be instructive to consider the derivation of the Plank equation. The rate of heat removal (q in kJ/s) is given by

$$q = \Delta H_F \frac{dw'}{dt} \quad (12)$$

where w' is water converted to ice.

$$\frac{dw'}{dt} = \left(\frac{dV'}{dt}\right)\rho = A\left(\frac{dx}{dt}\right)\rho \quad (13)$$

where V' is volume frozen (m^3), x is thickness of slab frozen (on each side) (m), and ρ is mass of ice per unit volume of frozen material.

As a consequence we can write

$$q = A\rho\Delta H_F\left(\frac{dx}{dt}\right) \quad (14)$$

Given the last assumption (6) above, it follows that q must be continuously transferred from the slab into the freezing medium

$$A\rho\Delta H_F\frac{dx}{dt} = A(T_F - T')\left(\frac{1}{h} + \frac{x}{k'}\right)^{-1} \quad (15)$$

We can now separate the terms and integrate between time limits of 0 to t' , where t_F is time to freeze the slab, thickness of ice limits are 0 to $a/2$, and a is the slab thickness. (Once the ice reaches the center of slab at $a/2$ the freezing is complete.)

$$\int_0^{a/2} \left(\frac{1}{h} + \frac{x}{k'}\right) dx = \frac{T_F - T}{\Delta H_F\rho} \int_0^{t_F} dt \quad (16)$$

The integration yields the Plank equation:

$$t_F = \frac{\Delta H_F\rho}{T_F - T} \left(\frac{a}{2h} + \frac{a^2}{8k'i}\right) \quad (17)$$

The equation may applied to freezing shapes other than slabs by introducing constants P and R into the following general equation:

$$t_F = \frac{\Delta H_F\rho}{T_F - T} \left(\frac{Pa}{h} + \frac{Ra^2}{k'}\right) \quad (18)$$

The values of P and R depend on geometry as shown in Table 8.11.

The assumptions of the Plank equation are greatly simplified and the calculations based on it can only serve as first approximations. In particular, the equation does not consider the contributions of the sensible heat to the net heat transfer during freezing when the frozen portion of the food increases in temperature. Furthermore the assumption of constant latent heat and constant thermal conductivity introduce errors. More sophisticated equations and numerical methods of calculation are available in literature of freezing and of heat transfer.

TABLE 8.11 Constants P and R in the Plank Equation for Different Geometric Shapes

| Geometric shape ^a | P | R |
|--|-------|--------|
| Infinite slab (a = thickness) | 0.5 | 0.125 |
| Infinite cylinder (a = diameter) | 0.24 | 0.0625 |
| Sphere (a = diameter) | 0.167 | 0.0417 |
| Parallopipeds (a = shortest length) | | |
| $\beta_1 = 3, \beta_2 = 3$ | 0.3 | 0.085 |
| $\beta_1 = 3, \beta_2 = 8$ | 0.34 | 0.095 |
| $\beta_1 = 5, \beta_2 = 5$ | 0.36 | 0.097 |
| $\beta_1 = 5, \beta_2 = 8$ | 0.38 | 0.103 |
| $\beta_1 = 5, \beta_2 = 3$ | 0.33 | 0.091 |

^a β_1 and β_2 are the ratios of lengths of the thickness of other two sides to that of the shortest (thinnest) side.

C. Illustrative Examples

1. Using Plank's Equation

We shall first compare the results of use of Plank's equation with more sophisticated estimates. Heldman used the more realistic Cleland and Earle equation to calculate freezing time in a hypothetical example (Heldman, 1992). We shall calculate the freezing time for his hypothetical situation using the Plank equation and ignoring the sensible heat removal. We shall then compare the results to illustrate the errors inherent in our use of the simplified equations.

The example is as follows: Lean beef steaks ($0.1 \text{ m} \times 0.06 \text{ m} \times 0.02 \text{ m}$) are frozen in air at -20°C . Initial temperature is $+10^\circ\text{C}$ and the final temperature -10°C .

Heldman calculates the thermal properties of the material on the basis of composition. For our simplified approach, however, we will use data from the literature (Earle, 1983). We will take $k' = 0.0023 \text{ kJ}/(\text{ms}^\circ\text{C})$, which is the conductivity of ice in the range of temperatures involved in freezing in this example. For the beef, we take the values as follows: $T_F = -2^\circ\text{C}$, $\Delta H_F = 225 \text{ kJ}/\text{kg}$, and $\rho = 1000 \text{ kg}/\text{m}^3$. For the values of h we will also use a typical literature value for air freezing, namely $h = 20 \text{ (W/mK)} = 0.020 \text{ (kJ m}^{-2} \text{ s}^{-1} \text{ m}^{-2}\text{C}^{-1})$.

The slab of beef has β_1 and β_2 values of $0.1/0.02 = 5$ and $0.06/0.02 = 3$, respectively, and the corresponding Plank equation constants are $P = 0.33$ and $R = 0.091$. Ignoring sensible heats completely (including times to cool from $+10^\circ\text{C}$ to the freezing point, and cool from freezing point to -10°C), we

substitute these values in Eq. (18) in the units cited above, which are consistent with each other:

$$t_F = \frac{255(1000)}{-2(-20)} \left(\frac{0.33(0.02)}{0.02} + \frac{0.091(0.0004)}{0.0023} \right)$$

We obtain a freezing time of 4900 s or 1.36 h. The value obtained by Heldman using the more accurate Clernand and Earle equation is 1.43.

Obviously the simplified assumptions were quite satisfactory for this example, in part because the sensible heats involved were small compared to the latent heats. Assuming a specific heat for beef above freezing of $3.2 \text{ (kJkg}^{-1}\text{°C}^{-1}\text{)}$ and of 1.67 below the freezing point, the sensible heat to cool to the freezing point is $3.2 \text{ (kJkg}^{-1}\text{°C}^{-1}\text{)} \times 12\text{°C}$, equal to 38.4 kJ/kg . The sensible heat for cooling the frozen beef to -10°C is $1.67 \text{ (kJkg}^{-1}\text{°C}^{-1}\text{)} \times 8\text{°C}$, equal to 13.3 kJ/kg . The total sensible heat of 51.8 kJ/kg is relatively small compared to the latent heat of 255 kJ/kg . Nevertheless it should be clearly understood that the simplifying assumptions of the Plank equation can lead to substantial deviations in many cases, perhaps even in most cases.

Where estimation of freezing time is critical, engineers must rely on numerical methods or on experimental determination of the time. Calculation of both the cooling requirement and of the freezing time are needed to estimate size of equipment for a given throughput and the refrigeration requirements. It may also be useful to consider some illustrative examples of freezing calculations.

2. Freezing in a Blast Freezer

Chicken cubes (0.5 cm each side) are frozen in belt blast freezer. Their moisture is 60% ($w = 0.6$). To achieve good contact the product is maintained at 6 kg/m^2 of belt area. Total surface area of belts within the freezer is 33 m^2 . The air providing the cooling in the freezer is cooled in an air cooler by flowing over heat exchangers in which the refrigerant is maintained at -60°C . The flow chart is shown schematically in Fig. 8.26. The overall head transfer coefficient (U) in the air cooler is $100 \text{ Wm}^{-2} \text{ °C}^{-1}$.

It is desired to estimate the flow throughput of product in kg/h , the flow rate of air $V(a)$ in m^3/h , and the heat exchanger area A in the air cooler.

The following data and estimates are obtained from technical literature: Heat transfer coefficient in freezer $h = 10 \text{ Wm}^{-2}\text{°C}^{-1}$. For simplification we assume that all the water in the chicken freezes, and the weight fraction from $wf = 0.6$. Specific heats in kJ kg^{-1} yield solids (cs) = 1.2, air (ca) = 1; water (cw) = 4.2, ice (ci) = 2.1, and air (ca) = 1.0. The freezing point (T_f) is equal to -2°C . Assume the density of product as 1000 kg/m^3 latent heat of fusion of water (ΔH) = 330 kJ/kg of water frozen, and thermal conductivity of frozen chicken

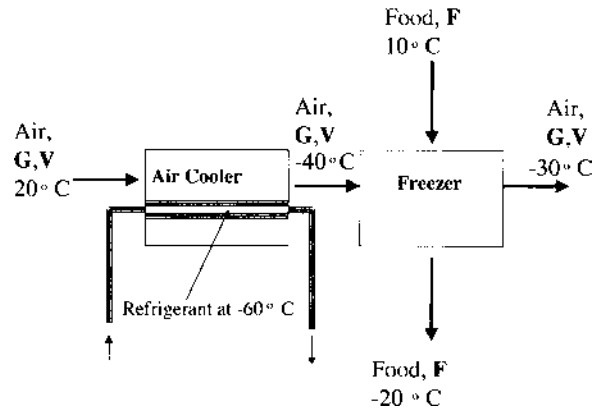


FIGURE 8.26 Freezing in a blast freezer.

(k) = $1.6 \text{ Wm}^{-1}\text{C}^{-1}$. Heat losses to walls and in pipes may be neglected in an initial estimation.

The estimation is conveniently done as follows: Let T_i be entering food temperature and the exit temperature be T_e . For convenience we convert all quantities to consistent units in kJ, m, s, kg.

1. Calculate the cooling required to cool and freeze the product: per kg of product (since $wf = w$, w will be the symbol used).

$$\begin{aligned} H' &= w\Delta H + ws(cs)(T_i - T_e) + cw(w)(T_i - T_p) + ci(w)(T_F - T_e) \\ &= 0.6(330) + 0.4(0.0012)(30) + 0.6(0.0042)(12) \\ &\quad + 0.6(0.0021) = 198 \text{ kJ/kg} \end{aligned}$$

We have included the sensible heat load, but a very quick calculation shows that the sensible heat is entirely negligible.

2. Calculate freezing time using the Plank equation (for cubes $P = 1.67$; $R = 0.041$). Substituting the correct values into

$$t_F = \frac{198(1000)}{33} \left(\frac{0.167(0.005)}{0.01} + \frac{0.041(0.000025)}{0.0016} \right) = 505 \text{ s} = 0.14 \text{ h}$$

3. Calculate throughput of product:

$$F = \frac{(\text{area of belt})(\text{loading per unit area})}{\text{freezing time}} = \frac{33(6)}{0.18} = 1100 \text{ kg/h}$$

4. We can now calculate the requirements for air throughput: The heat to be removed per hour (q) is equal to (F) (H'). $q = 1100 \times 198 = 217,800 \text{ kJ/h} = 60.5 \text{ kJ/s}$
 The heat picked up by 1 kg of air $H'' = c(a) \times \Delta T = 1(10) = 10 \text{ kJ/kg}$.
 Air flow needed is therefore $G = q/H'' = 21,780 \text{ kg}$. The volumetric flow is $V(a) = G/\rho(\text{air}) = 21,780/1.29 = 16,880 \text{ m}^3$.
5. The heat exchange area needed in air cooler is the remaining estimate to be made. The well-known heat transfer equation

$$q(\text{cooler}) = UA\Delta T_{\text{mean}}$$

Therefore, $A = q/(U\Delta T_{\text{mean}})$. For simplicity we can choose the arithmetic average for ΔT_{mean} :

$$\Delta T_{\text{mean}} = [20 - (-60)] + [-40 - (-60)] \times \frac{1}{2} = 50$$

$$A = \frac{60.5 \text{ kJ/s}}{0.1 \text{ kJ m}^{-2}\text{s}^{-1} \text{ } ^\circ\text{C}^{-1}} \times 50^\circ\text{C} = 12.1 \text{ m}^{-2}$$

3. Freezing in a Liquid Nitrogen Freezer

It is desired to freeze beef patties in a liquid nitrogen (LN) belt freezer, with LN being sprayed directly onto the patties. The proposed flow chart is shown Fig. 8.27. In order to maximize the utilization of the LN, the cold nitrogen gas leaving the spray freezer is to be used to further cool the frozen beef in a secondary freezer, and this discharged gas from that freezer is to be used to precool the beef in the precooler.

It is desired to have very rapid freezing, and for this reason the gas exists the spray freezer while still at a very low temperature (-90°C), thus providing a good temperature difference for freezing. The gas leaving the secondary freeze is also chosen to at the low temperature of -40°C for similar reasons.

It should be noted that for some products the extremely rapid cooling and crystallization resulting from direct spraying of the liquid nitrogen are not desirable because they may cause stresses, which produce texture defects. Where liquid nitrogen spray is still to be used for such products the exposure shock may be tempered by exposing the food to cold nitrogen gas prior to the spraying in a flow pattern as shown in Fig. 8.28 The quantities to be calculated are

1. LN = the amount of liquid nitrogen required per kg of beef patties.
2. T_e = the exit temperature of the beef (from the secondary freezer).
3. T_{eN} = the exit temperature of the nitrogen gas from the precooler.

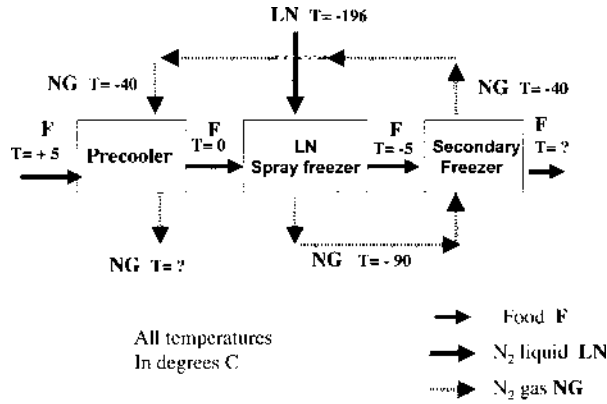


FIGURE 8.27 Freezing in a liquid nitrogen freezer (flow pattern 1).

For the estimation we will use literature values for properties of beef and of nitrogen:

Nitrogen:

Latent heat of vaporization (ΔH_v) = 199 kJ/kg.

Specific heat of gas $c(N) = 1 \text{ kJ kg}^{-1}\text{°C}^{-1}$.

Beef:

Latent heat of fusion (based on 1 kg of beef) (ΔH) = 255 kJ/kg.

Specific heat unfrozen $c(u) = 3.2 \text{ kJkg}^{-1}\text{°C}^{-1}$.

Specific heat frozen $c(f) = 1.67 \text{ kJkg}^{-1}\text{°C}^{-1}$.

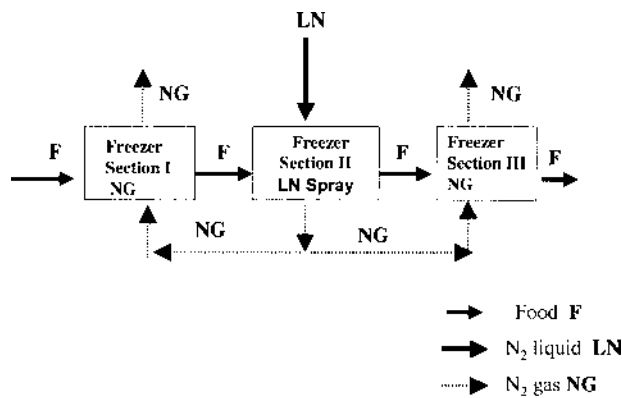


FIGURE 8.28 Freezing in a liquid nitrogen freezer (flow pattern 2).

By an energy balance on spray freezer per 1 kg of beef and ignoring the sensible heat change of beef in the spray freezer as negligible, but including the very significant the temperature change in nitrogen gas ($\Delta T = 106^\circ\text{C}$),

$$\text{LN} = 1 * \Delta H_v \{ \Delta H_v + \Delta T [c(N)] \} = 225/199 + (106 \times 1) = 0.87 \text{ kg}$$

The exit temperature of beef T_e is obtained by energy balance on secondary freezer. Let $\Delta T(N)$ be change in gas temperature, and $\Delta T(F)$ be the corresponding temperature change in beef.

$$\text{LN}[\Delta T(N)][c(N)] = 1[\Delta T(F)][c(f)]$$

$$0.87(50)(1) = 1[\Delta T(F)](1.67)$$

$$\Delta T(F) = 0.87(50)(1)1(1.67) = 26^\circ\text{C}$$

$$T_e = -5^\circ\text{C} - 26^\circ\text{C} = -31^\circ\text{C}$$

The exit temperature of nitrogen is obtained by a similar energy balance on the precooler Note that the beef is unfrozen hence the relevant specific heat is $c(u)$.

$$\text{LN}\Delta T(N)[c(N)] = 1[\Delta T(F)][c(u)]$$

$$0.87[\Delta T(N)](1) = 1(5)(3.2)$$

$$\Delta T(N) = 1(5)(3.2)1(0.87) = 18.4^\circ\text{C}$$

$$T_{eN} = -40 + 18.4 = -21.6^\circ\text{C}$$

The calculations do not consider the time needed in each section: however, they provide guidance in the following respects:

1. Minimum amount of liquid nitrogen needed.
2. Assurance that the specified criteria provide adequate driving forces in secondary freezer and precooler (Minimum exit ΔT s values of 9°C in secondary freezer and 21°C in precooler).
3. Reasonable efficiency of LN utilization. The useful cooling capacity not utilized, and discharging with LN exiting precooler is less than 5% of maximum.

VII. EFFECTS OF FREEZING, STORAGE, AND THAWING ON FOOD PROPERTIES

The primary objective of freezing is the preservation of functionality of the materials frozen so that they can be utilized at a later time. The functionality

includes viability in the case of cells, and retention of activity in the case of enzymes, vaccines, antibiotics, and other biological preparations, and in the case of foods it means primarily the retention of organoleptic and safety characteristics. Freezing is one of the most effective preservation methods in this respect, but it is not invariably effective in eliminating all undesirable changes in functionality. It may be useful to consider the following aspects of quality of frozen materials and in particular of foods since some quality aspects of preservation of biomaterials were discussed previously.

Effects of freezing per se
Effects of storage in the frozen state
Effects of thawing

A. Effects of Freezing

Phase transition of water to ice has two consequences with potentially significant effects on structure and properties of foods.

1. Growing ice crystals may disrupt structures such as cell membranes and various polymer aggregates (micelles) and may have a direct effect on disrupting emulsions, foams, and other colloidal components of foods.
2. Separation of water as pure ice freeze-concentrates the nonfrozen solution. Initially the effect is limited to increasing concentrations of all solutes; however, as solvent water is depleted further, the solute composition of the solution changes as well since some of the solutes precipitate out of solution. These changes affect such important parameters of importance to food properties as pH, ionic strength, and redox potential.

The effect of freezing out the solvent on rates of chemical reactions is complicated, and various patterns of deviation from the Arrhenius relation have been observed, including increases in reaction rates below freezing, as well as decreases greater than those expected due to lowered temperature.

The magnitude of the concentration effects is readily estimated if very simplified assumptions are made (Pincock and Kiovsky, 1966).

The simplest case is one in which the reactants, products of the reactions as well as inert solutes, remain in solution, and ice has no catalytic effects. Consider a simple bimolecular reaction:



In the unfrozen state the reaction rate r is given by

$$r = dD/dt = k[A][B]$$

[A] and [B] are concentrations in mol/l. In the partially frozen state we can expect the rate to be r' given by

$$r' = k[A]'[B]'$$

where $[A]' = [A](V/V')$, $[B]' = [B](V/V')$, and $r' = k[A][B](V/V')^2$. V is the total volume of water (ice plus liquid) and V' is the volume of water remaining unfrozen. We may assume that the fraction of unfrozen water at any one temperature depends on total concentration of all solutes C (C is initial concentration, C' concentration in partially frozen solution):

$$V' = VC/C'$$

Therefore, r' is proportional to $(C'/C)^2$,

$$C = [A] + [B] + [D] + [I]$$

where I is the concentration of inert solutes.

We come to the conclusion therefore that not only the concentrations of reactants but also those of inert solutes affect the reaction rates in partially frozen system because they affect the amount of nonfrozen water at any given temperature. The consequences of the concentration effect are of significance primarily in the range of temperature of a few degrees below freezing. As the temperature decreases further and solute concentration become very high, reaction rates slow down because of low temperatures as well as the very high viscosity. The calculated viscosity of partially frozen sucrose solution is shown in Fig. 8.29 and demonstrates this effect.

A major conclusion that may be reached from inspection of the characteristics of the effects of mechanical damage due to crystals and of the concentration effect is rapid freezing is most beneficial. It produces small crystals that cause less disruption, and it reduces the residence time in the temperature range, which produce acceleration of reaction rates.

Fennema considers the concentration effect to be of most importance in nonenzymatic reaction at high subfreezing temperatures, primarily during thawing. Enzymatic reactions are affected much more by enzyme dislocations due to freezing than by concentration effects (Fennema, 1975).

B. Effect of Storage in the Frozen State

Storage in the frozen state is generally maintained under conditions minimizing changes. Well-controlled commercial storage results in substantial high quality life (HQL). Fennema (1966) lists the following values for HQLs:

At -10°F (-23°C)
 Frozen vegetables: 16–36 months

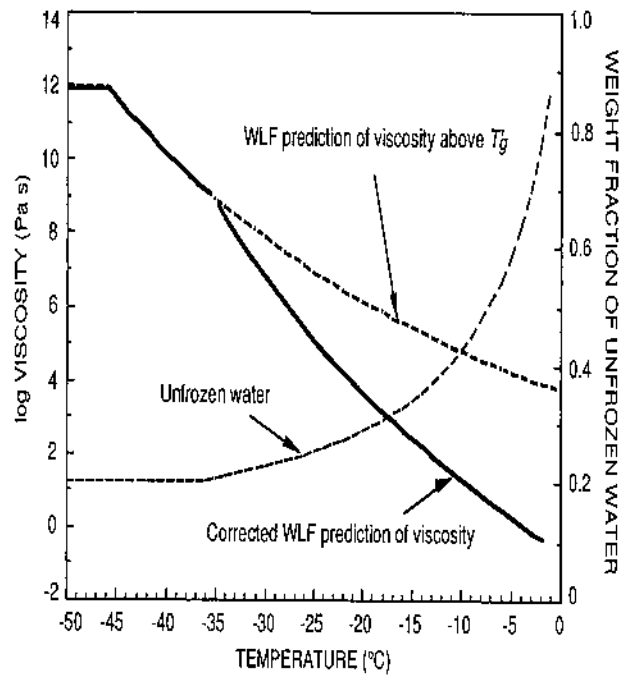


FIGURE 8.29 Viscosity of freeze-concentrated sucrose solutions. (From Roos, 1995.)

Forzen fruit: 24 months
 Frozen fish: 10–16 months
 At -0°F (-18°C),
 Frozen vegetables: 8–24 months
 Frozen fruit: 18–24 months
 Frozen fish: 6–12 months
 Frozen meats: 4–14 months
 At $+10^{\circ}\text{F}$ (-12°C),
 Frozen vegetables: 4–12 months
 Frozen fruit: 6–10 months
 Frozen fish: 4–10 months

Oxidative reactions and insolubilization of proteins are the reactions most likely to cause deterioration in the range of temperature of frozen storage. The recent studies on effect of glass transition have led to considerable discussion on the role of these transitions in optimizing frozen storage. It is generally agreed

that storage at temperatures maintaining maximal freeze concentration (below Tg', Cg') may be optimal. However, these are difficult to achieve in practice because maximal concentration is not consistent with the rapid freezing required to achieve good quality during freezing. Furthermore temperatures corresponding to the range below Tg' are difficult to maintain in the distribution chain from factory to the consumer storage. Fennema (1996) reports the following values for Tg' values in foods:

Fruit juices: -43 to 37.5°C
 Fresh fruits: -41 to -35°C
 Vegetables: -27 to -8°C
 Meat and fish: -18 to -6°C

There is, however, no agreement on the relation between rates of deterioration above Tg' and temperature. The changing unfrozen water content, and therefore solute concentrations, complicate viscosity estimates above Tg , and the effect of diffusional limitations due to increased viscosities varies with different reactions. (See discussion of the effect of water content on diffusion limited reactions in Chapter 5.)

Arrhenius relations are often found to be useful in correlating effects of temperature on storage in the frozen state, in spite of the changing viscosity relations (Simatos et al., 1989).

It should be noted again that temperature fluctuation may be detrimental beyond its effect on raising temperature average, because they promote recrystallization and associated texture defects.

C. Effects of Thawing

The effects of thawing are often more damaging than those of freezing. This is due to the fact that residence time in the most damaging temperature zone just below the freezing point is very much longer than in freezing. The reason for this phenomenon is due to the heat transfer occurring through unfrozen portions, and the heat transfer through these is much slower than the heat transfer through the frozen layer occurring in freezing. Under unsteady-state conditions, as they exist in the unfrozen portion, the heat transfer is proportional to thermal diffusivity α .

$$a = k/(c_p\rho)$$

where k is thermal conductivity, c_p is specific heat, and ρ is density.

The k value for frozen food is 4 to 5 times higher than for unfrozen; the specific heat of frozen food is 1/2 of than for unfrozen. Considering the densities to be comparable, we can calculate the ratios for thermal diffusivities, and find

the ratio $\alpha(\text{frozen})/\alpha(\text{unfrozen})$ to be approximately 10; that is, the thawing process is inherently 10 times slower than the freezing process.

Various processing methodologies including microwave thawing may be used to accelerate thawing, and may minimize its damaging effects.

SYMBOLS

| | |
|---------------------|---|
| A | constant or area |
| Bi | Biot number |
| Cg' | maximum freeze concentration |
| G/n | free energy per mole |
| h | coefficient of heat transfer |
| J | rate of nucleation |
| k | thermal conductivity |
| k, K_1, K_2, τ | constants |
| r | radius |
| R | gas constant |
| r^* | critical radius for nucleation |
| $T'm$ | equilibrium melting point |
| Tm | melting point |
| T^* | critical nucleation temperature |
| $T'g$ | Tg at maximum freeze concentration |
| Tg | glass transition temperature |
| v | molar volume |
| x | distance |
| X | mole fraction |
| ΔG_v | free energy per cluster or free energy per mole |
| ΔH_F | latent heat of fusion |
| ΔV | volume change in freezing |
| γ | surface free energy |

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9

Concentration

I. INTRODUCTION

Removal of water and the consequent lowering of water activity constitutes an important principle of food preservation. When removal of water is carried to essential completion resulting in food materials with water contents between 0 and 15–20%, the methods involved are called *dehydration processes*. In other cases only part of the water is removed, which results in concentrated solutions or dispersions or in semisolid products with water contents in excess of 20%. The methods involved are called *concentration processes*. The purposes of concentration can vary. It may be used as an economical preparatory step for subsequent dehydration, as in the cases of spray-dried tea or freeze-dried coffee. It may be used to reduce the bulk of materials to be preserved by freezing or by sterilization, as in the cases of frozen orange juice or evaporated milk. It may also be used as a method of preservation in its own right, for such food products as maple syrup, which do not deteriorate readily at the water activities achievable by concentration.

Methods of concentration which are discussed in this chapter include evaporation, freeze concentration, and membrane separation. Osmotic dehydration and solvent extraction also achieve concentration but are usually carried out in conjunction with dehydration methods. Osmotic dehydration is discussed in Chapter 10.

II. EVAPORATION

A. Principles of Evaporator Operation

Evaporation is the removal by vaporization of part of the solvent from a solution or dispersion of essentially nonvolatile solutes. Evaporation is distinguished from crystallization and drying by the fact that the final product is a concentrated dispersion or solution rather than precipitated solids.

In practice, evaporation is conducted by boiling off the solvent; that is, vaporization is conducted at the boiling point of the solution or dispersion. Where heat sensitivity is a factor, as is often the case with foods, the boiling point may be lowered by lowering the pressure at which evaporation takes place. The process of vaporization involves simultaneous heat and mass transfer, since it depends on the supply of heat required to vaporize the solvent and on removal of vapor from the vicinity of the surface at which vaporization takes place.

Several rate processes are involved in evaporation, but the engineer concerned with the operation can usually consider the entire process in terms of transfer of heat from the heater to the boiling liquid. Heat-transfer analysis, combined with mass and energy balance, is usually adequate for evaporation, provided the boiling point of the liquid is known as a function of pertinent temperatures and concentrations.

An evaporator consists of a heat exchanger capable of maintaining the liquid at its boiling point and a device to separate the vapor phase from the liquid. The mass and energy balance may be developed as shown schematically in Fig. 9.1. Figure 9.1 represents an evaporator operating in steady state. The following symbols are used:

- L, L' is liquid streams (kg/s)
- G is vapor stream (kg/s)
- w is solid concentration (kg/kg)
- T is temperature ($^{\circ}\text{C}$)

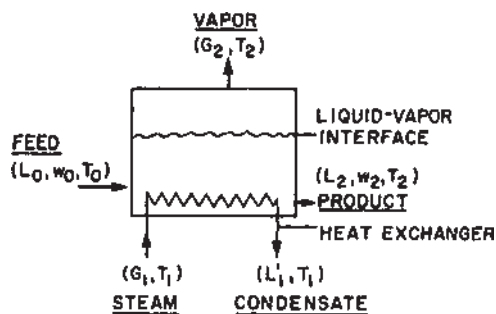


FIGURE 9.1 Schematic representation of an evaporator in steady-state operation.

The subscripts are

0 = feed stream

1 = steam of condensate in heat exchanger

2 = streams leaving evaporator

It is assumed that the entering feed is brought instantaneously to the boiling point T_2 and that the vapor G_2 and the product L_2 leave the evaporator at this temperature. It is further assumed that steam enters the heat exchanger as saturated vapor (G_1) at temperature T_1 and leaves as liquid condensate (L_1) at the same temperature.

Mass balance results in the following equations:

Overall material balance:

$$L_0 = L_2 + G_2 \quad (1)$$

Solute balance:

$$w_0 L_0 = w_2 L_2 = w_2 (L_0 - G_2) \quad (2)$$

Therefore,

$$G_2 = L_0 \left(1 - \frac{w_0}{w_2} \right) \quad (3)$$

An energy balance may be conducted on the assumption of negligible heat losses to the surroundings: Heat supplied by condensing steam is heat required to heat and vaporize.

$$G_1 \lambda_1 = L_0 c_{p0} (T_2 - T_0) + G_2 \lambda_2 \quad (4)$$

where λ_1 is latent heat of vaporization of water at T_1 (kJ/kg), λ_2 is latent heat of vaporization of water at T_2 (kJ/kg), and c_{p0} is specific heat of feed solution ($\text{kJ kg}^{-1} \text{ } ^\circ\text{C}^{-1}$).

Combination of Eqs. (3) and (4) allows calculation of the amount of steam required per pound of water removed for a given degree of concentration (w_2/w_0) and a given feed temperature (T_0).

An equally important consideration is the size of heat exchanger capable of supporting the necessary overall rate of heat transfer. The heat transfer rate is

$$q = UA(T_1 - T_2) \quad (5)$$

where U is overall heat transfer coefficient ($\text{W m}^{-2} \text{ } ^\circ\text{C}^{-1}$), A is heat transfer area (m^2), and q is overall heat transfer rate (kJ/s).

It should be noted that the coefficient U is a function of the sum of resistances to heat transfer:

$$U = 1/r_{\theta} \quad (6)$$

where r_{θ} is the total resistance:

$$r_{\theta} = 1/h_1 + r_{\text{wall}} + 1/h_2 \quad (7)$$

where

$1/h_1$ is the resistance in steam.

h_1 is heat transfer coefficient in steam phase ($\text{Wm}^{-2}\text{°C}^{-1}$).

r_{wall} is ($X_{\text{wall}}/k_{\text{wall}}$) is the resistance of heat exchanger wall.

X_{wall} is wall thickness (m).

k_{wall} is thermal conductivity of wall ($\text{Wm}^{-1}\text{°C}^{-1}$).

$1/h_2$ is resistance in liquid phase.

h_2 is heat transfer coefficient in liquid phase ($\text{Wm}^{-2}\text{°C}^{-1}$).

In well-designed and efficiently operated evaporators, the overall resistance r_{θ} is dominated by resistance in the boiling liquid, and U is often well approximated by h_2 . It must be noted here that h_2 depends strongly on the conditions in the liquid, in particular on viscosity, temperature, and type and magnitude of convection. Furthermore, the overall resistance is increased greatly by deposition of a solid or semisolid layer on heat-exchange surfaces (fouling).

B. Boiling Point Estimation

The driving force for heat transfer is the temperature difference ($T_1 - T_2$), which depends on the pressure of steam in the heat exchanger and on the boiling point of the liquid (T_2). The boiling point in turn depends on pressure at the evaporating surface and on concentration of solutes. Boiling point elevation is a colligative property which depends on the number of kinetic units in solution. Under ideal conditions, therefore, the boiling point depends only on the total number of particles, molecules, and ions present per unit weight of solvent. In practice, however, the situation in food materials is quite removed from ideality and the boiling point must be determined empirically. An aid to this determination is the use of the Dühring plot (Fig. 9.2), which is based on the often applicable rule that the boiling point of a solution is a linear function of the boiling point of the solvent. The Dühring plot allows approximation of boiling points of solutions on the basis of measurements of boiling points at only two pressures.

Another consideration in boiling point elevation is the contribution to pressure of the hydrostatic head due to depth of the liquid. It is often negligible, but where it is of importance it is common to base design calculations on a boiling

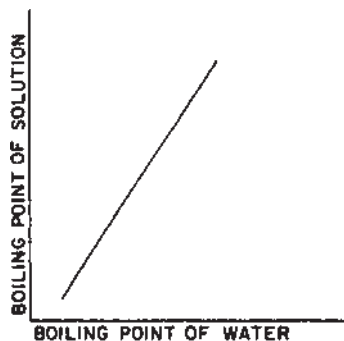


FIGURE 9.2 Duehring plot.

temperature determined from the pressure at half the depth of the liquid in the evaporator.

C. Food Properties and Evaporator Performance

A major consideration in engineering reviews of evaporation is the problem of steam economy, that is, the problem of maximizing evaporation per unit of energy supplied to the evaporator. In food applications, however, a number of considerations pertaining to properties of the foods assumes a dominant role. The following are of particular importance.

1. Viscosity and Consistency

Many of the food products subjected to evaporative concentration become quite viscous when concentrated. In some cases, non-Newtonian behavior is observed and peculiar temperature dependence is encountered due to such effects as denaturation of proteins. Viscosity affects not only the rate of heat transfer but also pumping requirements and other material handling considerations. In processing of very viscous fruit juices, special treatments may be necessary to reduce viscosity. Israeli scientists, Mizrahi (1968) for instance have developed an ultrasonic process for reduction of viscosity during concentration of orange juice.

2. Fouling

Fouling is often critical in food evaporation. Proteins and polysaccharides in particular are capable of forming deposits that are difficult to remove and which adversely affect efficiency of heat transfer. The interactions are often complex. In a study concerned with fouling during evaporation of tomato juice,

Morgan (1967) found that the presence of fiber, pectin, and protein was necessary for fouling, and that removal of any one of these components would greatly improve evaporating efficiency. Practical solutions to the problem involve design of evaporators which minimize development of stagnant layers along surfaces of heaters.

3. Foaming

The presence of various natural surface-active components, including proteins, is often the cause of extensive foaming, and this reduces heat transfer efficiency and may produce problems in removal of product and vapor from the evaporator. Use of antifoam agents can be of some value, but their choice is limited to those acceptable as food additives.

4. Corrosion

Some foods, especially fruit juices, contain components which are corrosive to heat-exchange surfaces. This damages the equipment and results in undesirable transfer of metals to the evaporated product.

5. Entrained Liquid

Separation of entrained liquid from the vapor stream is often difficult. Efficient separation is, however, important in order to avoid economically intolerable losses of solid matter.

6. Flavor

Desirability of food depends on various volatile flavor components which often are lost during vaporization of water. Design of evaporation processes is often directed either toward decreasing such losses or toward recovering volatile flavor components from the vapor phase.

7. Heat Sensitivity

Heat sensitivity is a problem of particular concern since it affects the quality of food. The operational factors, time and temperature, affect the degree of damage caused by heat. A "heat hazard index" has been discussed by Carter and Kraybill (1966). This index assumes the following relationship:

$$D_h = \log_{10}(P)(t) \quad (8)$$

where D_h is decomposition hazard index, P is absolute pressure (μm), and t is time of residence (s).

Carter and Kraybill (1966) showed that evaporators have operating conditions corresponding to a D_h range of about 1 for molecular stills, which operate in high vacuum, to 12 or more for equipment operating at atmospheric pressure. For reference purposes, these authors indicated that preservation of vitamin D would require a D_h value below 1 but that petroleum oils could tolerate D_h values above 12.

Unfortunately, heat sensitivity of food is too complicated to be predicted adequately by an index as simple as D_h . One of the complicating factors is the fact that time of residence is a mean value, and some liquid resides much longer than this mean. Mean residence times in various types of evaporators used for juice concentration are reported by Casimir and Kefford (1968) to range from 0.11 min in a centrifugal evaporator to 54 min in a recirculating tube-and-shell evaporator. They have found, however, that the time to replace 97% of a tracer (that is, the minimum time required to remove all but 3% of the original liquid) is three to four times greater than the mean residence time. Furthermore, that portion of the liquid immediately adjacent to heat exchanger surfaces may be at a temperature significantly higher than the mean temperature (boiling point) of the liquid. As should be obvious from the hypothetical temperature gradients shown in Fig. 9.3, heat damage at the wall (surface of the heat source) is more likely when the liquid heat-transfer coefficient is low. This condition arises when viscosity of the liquid is high or there is inadequate motion of the liquid.

When average changes in food properties are the primary consideration, deviations from mean conditions may not be too important. It may, for instance, be possible to predict average nutrient losses or average increase in optional density caused by browning from an index based on mean conditions. In other situations, however, including production of trace compounds with high potency (very strong off flavors, toxins), such oversimplification may be dangerous.

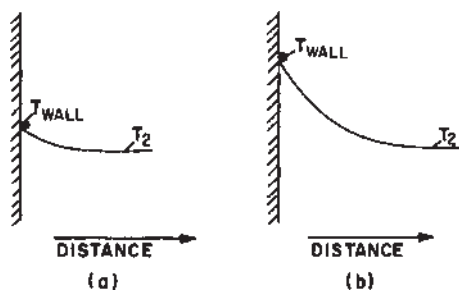


FIGURE 9.3 Temperature gradients in evaporating liquids: (a) high h_2 , (b) low h_2 . h_2 = liquid heat-transfer coefficient, T_{wall} = wall temperature, and T_2 = boiling temperature.

D. Types of Evaporators

Evaporators used in the food industry may be classified in different ways: by operating pressure; vacuum versus atmospheric; by number of effects; single effect versus multiple effect;* by type of convection; natural versus forced; and by continuity of operation; batch versus continuous.

Natural convection evaporators can be operated either at atmospheric or at reduced pressure and on either a batch or a continuous basis. Examples are discussed below.

1. Unstirred Open Pan or Kettle Operating At Atmospheric Pressure

These simple batch evaporators are either steam jacketed or heated with closed steam coils and are used for concentration of sauces, jams, and confections when product temperatures in excess of 100°C can be tolerated.

2. Short Tube Evaporator

A number of different designs using tubular heat exchangers can be used for continuous evaporation processes. Of these the standard evaporator shown in Fig. 9.4 is used quite extensively. In this evaporator the solution boils inside vertical tubes with the steam condensing in a chest through which the tubes pass. The steam chest is doughnut shaped, allowing easy downward flow through the large central opening.

Circulation past the heating surface is induced by boiling in the tubes, each of which is usually 5–7 cm in diameter and 1–2 m in length.

This standard evaporator is quite satisfactory for evaporation of relatively low-viscosity, noncorrosive liquids that are resistant to high temperatures. The overall heat transfer coefficient U can be quite high under some conditions (over $500 \text{ Wm}^{-2}\text{°C}^{-1}$).

3. Long-Tube Evaporators (Climbing Film Evaporators)

A very effective type of evaporator construction consists of a vertical shell and tube heat exchanger. The boiling liquid is inside vertical tubes (2–5 cm in diameter, 3–12 m in length), and steam condenses on the outside of the tubes.

*It is often possible to conserve total expenditure of energy by utilizing the vapor from an evaporator to heat and boil the liquid in another evaporator, operating at a lower pressure. In this situation, each evaporator is called an *effect* and the process is called *multiple-effect evaporation*.

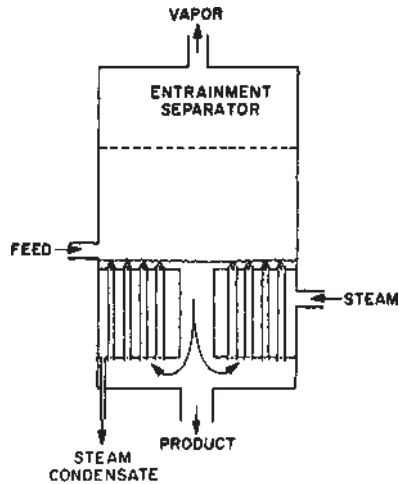


FIGURE 9.4 Standard evaporator.

Good heat transfer characteristics are imparted by formation of a thin liquid film on internal surfaces of the tubes, due to the lift provided by the vigorous upward flow of vapor through the center of the tube. Under proper operating conditions, high heat transfer coefficients can be attained and foaming is prevented. Major problems are

1. Potential for formation of bubbles and entrained liquid flow. (Fig. 9.5 shows proper and faulty flow conditions inside tubes.)

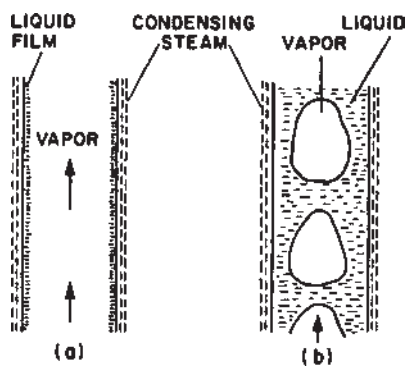


FIGURE 9.5 Correct film evaporator. (a) Correct operation and (b) incorrect operation because of bubble formation and liquid entrainment.

2. Susceptibility to formation of deposits on the internal tube surface (fouling)

In applications involving viscous liquids it is usually necessary to resort to forced convection. Typical examples of such evaporators include tube-and-shell evaporators similar to those discussed above but utilizing pumps for circulation of the fluid. Forced-convection evaporators can be operated at atmospheric or reduced pressure and on a continuous or on a batch basis.

Of particular importance in the food industry, which often deals with viscous, heat-sensitive fluids, are the vacuum evaporators utilizing forced convection.

4. Stirred Vacuum Kettle

A simple example of a forced-convection evaporator is the stirred vacuum kettle shown in Fig. 9.6. This evaporator is used extensively in various batch applications.

For evaporation of liquids with high viscosities a modification of the simple stirred vacuum kettle has been developed by Western Utilization Research Division of the USDA. In this evaporator, called the Wurling evaporator, the heat exchanger, in the form of a steam coil, is rotated through the liquid. Good heat transfer has been reported in concentration of tomato paste to 20–50% solids (Carlson et al., 1967).

5. Mechanically Aided Thin-Film Vacuum Evaporators

Continuous processes for heat-sensitive materials often necessitate mechanically aided thin-film evaporators. In these evaporators mechanical devices are used to

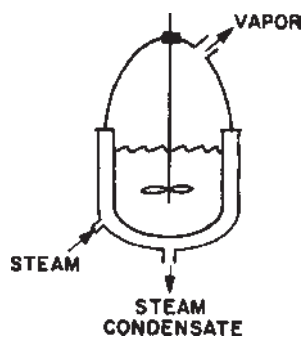


FIGURE 9.6 Vacuum kettle.

assure that the boiling liquid flows as a thin film at the heat exchanger surface. Equipment is usually operated at a much reduced pressure which allows high evaporation rates and low operating temperatures.

Evaporators of this type include several in which a thin film of liquid is spread by an internal rotor. Rotors often have a fixed clearance of less than 1 mm, fixed blades with adjustable clearance, or blades which are spring loaded and “wipe” the heat-exchange surface. An example of this type of evaporator is

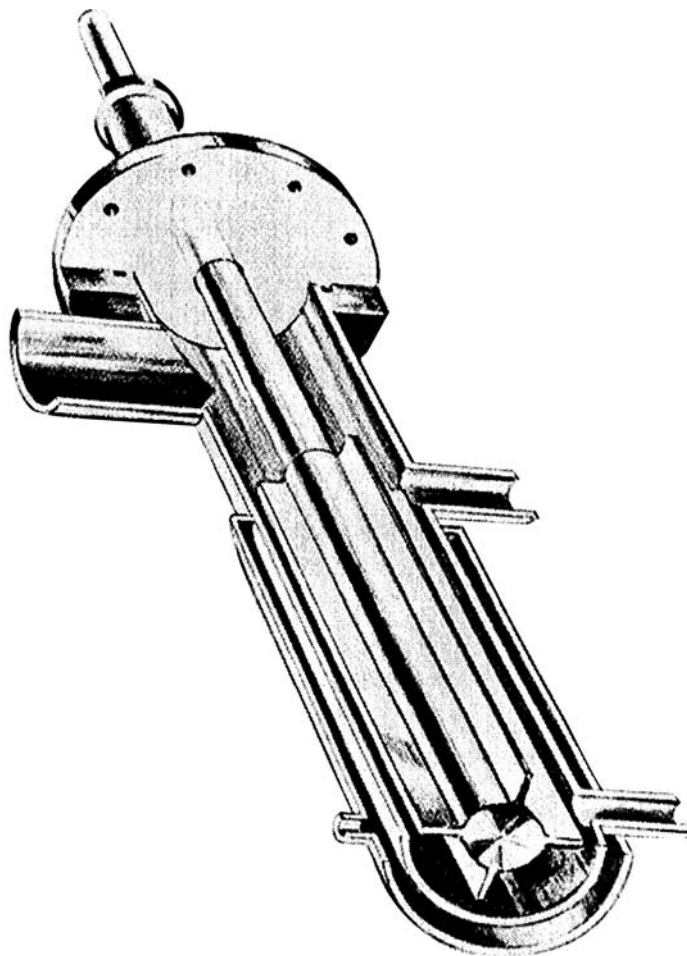


FIGURE 9.7 Horizontal thin-film evaporator. (Courtesy of Artisan Ind., Inc. Waltham, MA.)

the Rototherm E, shown in Fig. 9.7. This evaporator operates at very low pressure, has a residence time of as little as 10–15 sec, and can handle fluids of very high viscosities. Heat is applied to the jacket. Centrifugal force holds the liquid on the heated wall and produces a turbulent film between the wall and the rotor blade tips. Vapor flow can be either co-current with or counter-current to the liquid.

Another example is the centrifugal evaporator. In this evaporator a film is spread centrifugally on a moving heated surface. A film thickness of 0.1 mm and contact times of 0.5–2 s are possible for low-viscosity liquids. A diagrammatic representation of a centrifugal evaporator is shown in Fig. 9.8.

Mechanical thin-film evaporators are used for heat-sensitive liquids, especially if their viscosities are high (over 1–10 Pas) or if there is a tendency to foam. A comparison of performance factors for several types of evaporators is given in Table 9.1.

6. Plate Evaporators

Plate evaporators operate in a manner similar to that of plate heat exchangers. The fluid to be evaporated passes on one side, and the heat exchange medium (steam or hot water) flows on the other side. Evaporation may take place within the plate heat exchanger, or the heated fluid may evaporate in a flash chamber. Plate evaporators offer high heat exchange rates and can be used efficiently for viscous liquids. However, the capacity of these evaporators is lower than in tubular evaporators (Hartel, 1992).

A high-capacity three-effect plate evaporator with thermal vapor recompression was reported to be in use in California to concentrate lemon juice. It had a capacity of 5000 to 13,000 kg/h, and a steam economy approaching

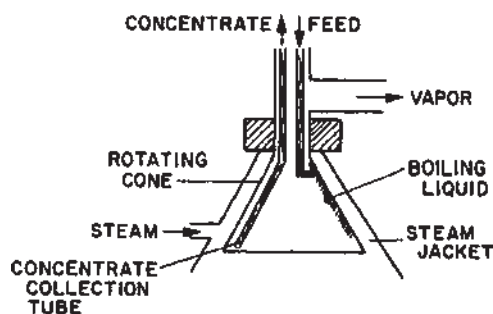


FIGURE 9.8 Centrifugal evaporator.

TABLE 9.1 Characteristics of Evaporators

| Evaporator type | U^a Low η | U^a High η | Relative cost | Heat damage factor |
|------------------|------------------|-------------------|---------------|--------------------|
| Short tube | 250 | Not suitable | 1 | Very high |
| Rising film | 2000 | < 500 | 3 | High |
| Plate evaporator | 2500 | 500 | 7 | High |
| Agitated film | 3000 | 1000 | 15 | Low |
| Molecular film | | | > 100 | Very low |

^a U is in (Wm^{-2}C).

4 kg/kg. The final concentration achieved was 41%, and the residence time was 135 s (Dinnage, 1970).

E. Evaporation with Feed Preheating

It has been mentioned previously that steam economy is a major engineering consideration in evaporation, albeit one which in food processing may have to be subordinated to considerations affecting product quality. Presented below are several types of evaporator designs allowing efficient steam consumption.

First consider the following example. A feed of 10% solids at a temperature of 45°C is to be concentrated in a single-stage evaporator (Fig. 9.1) to 20% solids by boiling at 50°C (For simplicity's sake, assume no significant rise in boiling point.) Using 100 kg of feed as a base, Eq. (3) yields:

$$G_2 = 100 \left(1 - \frac{0.1}{0.2} \right) = 50 \text{ kg of vapor}$$

The heat required to evaporate 50 kg of water is calculated from Eq. (4), assuming $c_{p0} = 4.2$ and noting that λ_2 is 2260,

Total heat required (Btu)

$$= L_0 c_{p0} (T_2 - T_0) + G_2 \lambda_2 = (100)(4.2)(5) + (50)(2260) = 115,000$$

It should be noted that of the 115,000 kJ supplied to the 100 kg of liquid, 113,000 kJ goes into raising the energy of the 50 kg of vapor above that of liquid at the same temperature. That energy cannot be used for evaporation of more liquid in a single-stage evaporator because the vapor is at the same temperature as the boiling liquid and heat transfer cannot be accomplished without a temperature difference. There are, however, several ways in which this energy can be recovered.

In a single-stage evaporator the vapor (G_2) can be used for preheating the entering feed, thus reducing the amount of steam required for evaporation. A schematic diagram of this arrangement is shown in Fig. 9.9.

F. Multiple-Effect Evaporators

The energy contained in the vapor discharged from an evaporator can be partially recovered by using the vapor as a heat source in another evaporator (effect), operating at a lower pressure (lower boiling point). This is the principle of multiple-effect systems. Three different arrangements are shown in Fig. 9.10. Consider the *forward feed* arrangement. Three effects are shown in which boiling occurs at pressures P_2 , P_3 , and P_4 (where $P_2 > P_3 > P_4$), corresponding to temperatures T_2 , T_3 , and T_4 (where $T_2 > T_3 > T_4$). Calculations are often greatly simplified by making the following assumptions, which allow a reasonable approximation of the overall operation of multiple-effect evaporators:

1. Feed (L_0) enters at temperature T_2 .
2. There are no heat losses to surroundings.
3. Latent heats are independent of temperature ($\lambda_1 \approx \lambda_2 \approx \lambda_3 \approx \lambda_4$).
4. Areas of heat exchangers are the same in all effects.
5. Overall heat transfer coefficients are the same in all effects.

Natural consequences of the above assumptions are (1) the total amount of heat transferred and amount of water vaporized is the same in each effect and (2) the number of pounds of water vaporized per pound of steam supplied at the first effect (G_1) is equal to the number of effects. In actual operation the above assumptions are not true and trial-and-error methods must be used to establish the actual operating conditions accurately. The steam economy achievable under real operating conditions is less than that calculated from the ideal assumptions, as shown in Table 9.2.

Different arrangements with respect to direction of feed are possible: co-current or forward feed, counter-current or backward feed, and parallel feed.

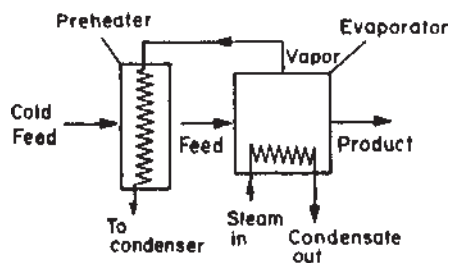


FIGURE 9.9 Schematic representation of an evaporating system with a preheater.

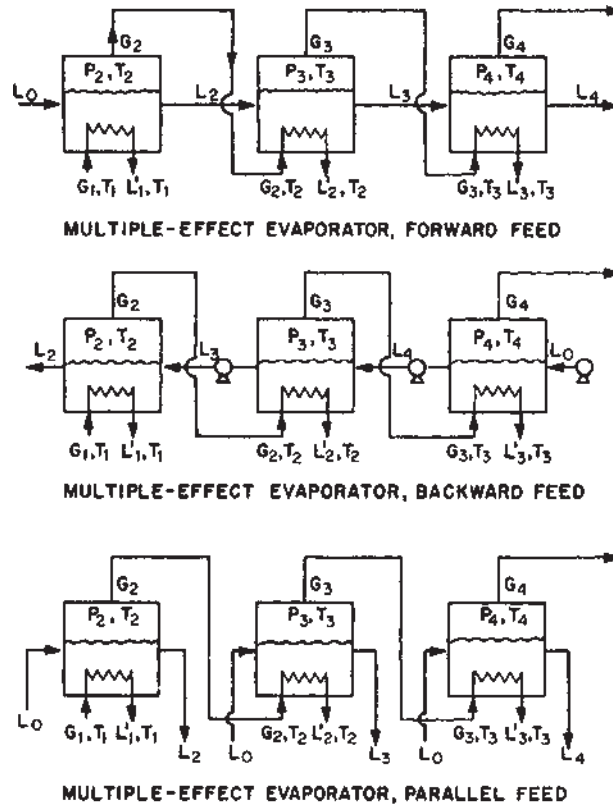


FIGURE 9.10 Multiple-effect evaporators with different flow arrangements.

Of these, parallel feed is not common in evaporators but is often used in crystallizers, where precipitation of solids makes continuous flow of feed from one effect to another impractical.

From an engineering point of view, forward feed has the advantage of having the liquid flow with the pressure gradient (the first effect is at the highest pressure). Costs of pumping equipment are minimized and control is less complicated than in backward feed evaporators. Backward feed has two important engineering advantages:

- (1) When the feed comes in relatively cold, steam consumption is more economical.
- (2) Viscosity of liquids decreases with increasing temperature but increases with concentration of solids.

TABLE 9.2 Steam Economy of Multiple-Effect Evaporators

| Number of effects | Theoretical: lb of water evaporated | Practical: lb of steam to primary effect |
|-------------------|-------------------------------------|--|
| One | 1.0 | 0.95 |
| Two | 2.0 | 1.7 |
| Four | 4.0 | 3.2 |

Source: From Slade (1967).

In backward feed, the tendency to high viscosity in the concentrated liquid is somewhat compensated for by its high temperature. Heat transfer and flow characteristics are thereby improved.

The two types of feed flow, however, are also different with respect to their effect on chemical changes in food quality. Many chemical reactions, notably nonenzymatic browning, proceed most rapidly in the range of water contents corresponding to those found in the product (outlet) stream. In backward feed, this stream is also at the highest temperature and chemical changes may be unacceptably high in this arrangement. Similarly, fouling due to precipitation of denatured proteins may be promoted by the coincidence of high concentration and high temperature in backward feed.

G. Evaporators with Vapor Recompression

Another way of obtaining improved steam economy is by vapor recompression. We may consider the rationale of this method with the following example. Consider an atmospheric single-stage evaporator (Fig. 9.1) with feed (L_0) entering at 100°C and boiling at the same temperature. (There is no boiling point rise.) Let the heat supply be provided by steam at a pressure of 1.6 atm. The steam (G_1) enters the heat exchanger as saturated vapor and leaves as saturated liquid (L'_1), both at 114°C. The process of vaporization of L_0 to G_2 , and of G_1 to L'_1 , are shown on a temperature-entropy diagram in Fig. 9.11. By consulting the steam table we find that the steam, condensing at 114°C, gives up 2232 kJ/kg. The amount of heat required per pound of vaporized liquid at 100°C is 2260 kJ/kg. Thus 1 kg of condensing steam vaporizes 0.985 kg of liquid.

In order to obtain 1 kg of steam at 114°C, the distillate L'_1 can be returned to the boiler, in which case 2220 kJ/kg must be supplied, (Fig. 9.12a). Another possibility is to obtain 0.985 kg by compressing G_2 from (atmospheric pressure) to 1.6 atm and 114°C and then to obtain the remaining 0.015 kg by boiling makeup water (Fig. 9.12b). Heat required is then only 65 kJ. A representation of the system in the form of a process path line on a temperature-entropy diagram is given in Fig. 9.11.

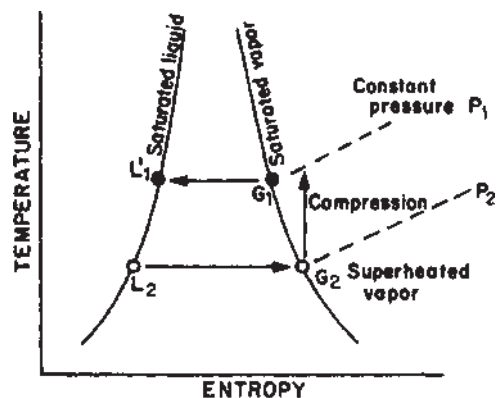


FIGURE 9.11 Temperature-entropy diagram representing processes in evaporation and vapor compression.

From the point of view of the thermodynamic cost of vaporization, therefore, it appears that recompression is quite attractive, even compared to multi-effect evaporation. Unfortunately, there are major drawbacks and, in particular, the volume of vapor to be compressed presents difficulties. If the operation is conducted at atmospheric pressure, each kilogram of vapor (at 100°C) to be compressed occupies 1.67 m^3 . The volume to be compressed is, of course, even larger when heat sensitivity of the product requires operation under vacuum. If, for instance, evaporation is carried out at 0.1 atm , corresponding to a boiling point of water of 46°C , then 1 kg of vapor occupies 13.9 m^3 . If constant displacement compression equipment is to be used under these conditions, the cost becomes prohibitive.

It is feasible, at least in the case of a reasonably high evaporation temperature, to use very high-pressure steam and combine it with part of the vapor to produce the steam required for the heat transfer. For instance, in the example shown in Fig. 9.13, 1 kg of steam at 9.5 atm is mixed with 0.75 kg of vapor at 1 atm to produce 1.75 kg of steam at 1.7 atm . In this example, over 40% of the energy potentially lost in the vapor is recovered. This method for improving steam economy requires very high-pressure steam and becomes feasible only in special circumstances.

The volume of gas to be compressed can be greatly reduced by transferring the energy in the water vapor to another gas. This can be done by using a heat pump cycle with a fluid, such as ammonia.

The operation of such a cycle is shown schematically in Fig. 9.14. Feed (L_0) enters the evaporator and is partially vaporized at temperature T_2 , the heat of

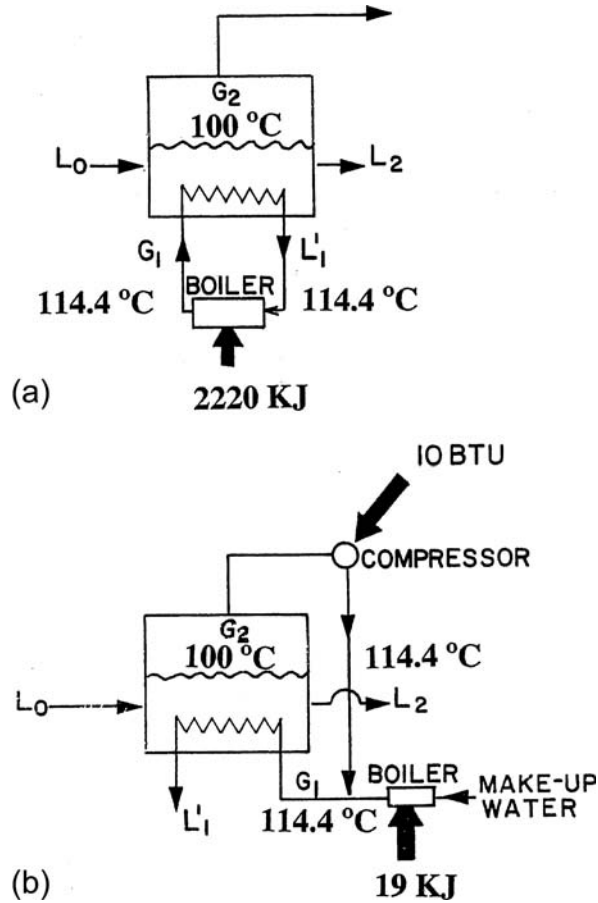


FIGURE 9.12 Schematic diagram of two arrangements for regeneration of high-pressure steam needed for evaporator operation: (a) steam condensate re-evaporated in boiler; (b) vapor compression system.

vaporization being supplied by ammonia condensing in a heat exchanger in contact with the evaporator surface. The resultant water vapor (G_2) condenses in a heat exchanger supplying the heat for boiling ammonia. Ammonia gas is compressed (E) to a temperature high enough for heat transfer to the boiling aqueous liquid, and the hot ammonia liquid is cooled by expansion at F .

The advantages of this system may be noted from the following typical operating conditions. Feed enters at 27°C and is evaporated at this temperature

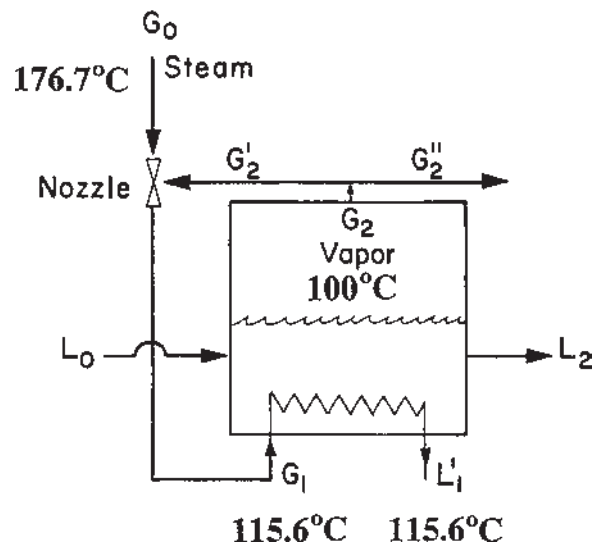


FIGURE 9.13 Vapor compression using a nozzle to compress low-pressure vapor with high-pressure steam.

in a vacuum at 0.1 atm. The resultant vapor (G_2), in order to provide adequate heat transfer, must be heated to a higher temperature. Assuming that 37°C is a suitable temperature, this requires compression of $39\text{ m}^3/\text{kg}$ to a volume of $22\text{ m}^3/\text{kg}$; if the latent heat carried per pound of vapor is considered, the volume involved is

$$\frac{39\text{ m}^3\text{ kg}^{-1}}{2446\text{ kJ kg}^{-1}} = 0.016\text{ m}^3/\text{kJ}$$

If, on the other hand, ammonia is used as shown in Fig. 9.14, the following operating conditions can be used:

1. Evaporator (A): temperature, 27°C ; pressure, 0.034 atm
2. Ammonia condenser (B): temperature, 37°C ; pressure, 14.35 atm
3. Vapor condenser (C): temperature, 37°C , pressure, 0.034 atm
4. Ammonia evaporator (D): temperature, 27°C ; pressure, 10.4 atm

Ammonia gas at 27°C and 10.4 atm occupies only $0.74\text{ m}^3/\text{kg}$ and even though it carries less latent energy per kg than water the volume reduction of this

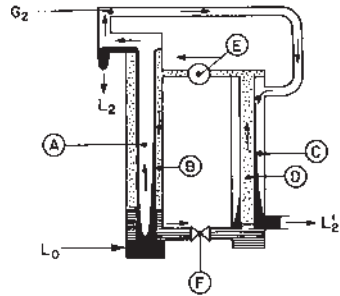


FIGURE 9.14 Heat pump cycle using ammonia for vapor recompression. L_o , Feed; L_2 , Concentrate; G_2 , Vapor; D_2 , Condensing vapor; A, Evaporator at T_2, P_2 ; B, Ammonia condensing at T_B, P_B ; C, Water vapor condenser at T_C, P_2 ; D, Ammonia boiling at T_D, P_D ; E, Ammonia compressor (vapor compressed from P_D to P_B); F, Ammonia expansion valve (liquid cooled from T_B to T_D); T, Temperature; P, Pressure. Subscripts B, C, D, and 2 refer to locations specified in the figure.

system is still enormous. The volume per unit energy content is

$$\frac{0.74 \text{ m}^3/\text{kg}}{1165 \text{ kJ/kg}} = 0.00064 \text{ m}^3/\text{kg}$$

The disadvantage of the system lies mainly in the capital cost of an ammonia compression system. In the food industry, these systems have been used in citrus juice evaporation and in some other applications in which refrigeration systems involving ammonia are needed in addition to vapor recompression.

H. Principles of Operation of Equipment Used in Evaporators

From an operational point of view the equipment used in evaporators performs the following operations: (1) flow of liquids (pumping of feed and concentrate streams, steam condensate, makeup water), (2) heat transfer (heat exchangers in evaporators, condensers, preheaters), (3) gas and vapor removal (pumps for maintenance of vacuum in evaporators), and (4) gas-liquid separation by mechanical means (entrainment separators for removal of droplets in vapor phase). Of these, vacuum pumps and entrainment separators deserve further discussion.

1. Vacuum Pumps

Removal of vapor and noncondensables (air) from evaporators can be accomplished by one of the following types of pumps:

1. Positive displacement, oil-sealed mechanical pumps for air removal used in conjunction with condensers for removal of water vapor. This type of equipment is suitable for pressures between 1 and 50 torr absolute.
2. Water-sealed mechanical pumps. The degree of vacuum which can be attained with these pumps depends on water temperature. Vacuum attainable in this type of equipment, represented by the *Nash pump*, 75 torr.
3. Steam ejectors. These are most useful in applications requiring removal of large quantities of vapor at absolute pressures of 20–100 torr.

Diffusion pumps backed by condensers and by mechanical pumps are used in applications requiring extremely low absolute pressures (1–100 $\mu\text{m Hg}$ or lower). Evaporators operating at these high vacuums are called *molecular stills*.

Steam ejectors are very common in the food industry and they can be used not only for producing a vacuum, but also for heating, cooking, mixing, and compressing various fluids. The operational principle is shown schematically in Fig. 9.15. A quantity of high-pressure steam (G_1 , kg/s) at pressure P_1 is injected into a convergent-divergent nozzle. It draws into the nozzle a quantity (G_2) of low-pressure vapor at pressure P_2 . It is usually assumed that mixing of the two streams results in pressure P_2 being attained by the combined stream of fluids ($G_1 + G_2$) at the throat of the nozzle, where the fluids attain a high velocity. In the divergent portion of the nozzle, the kinetic energy is converted in part to energy needed to increase the pressure of the stream from P_2 to P_3 . Thus high-energy steam is used to pump and compress low-pressure vapor to higher pressures. Ejectors have in common with Nash pumps the capability of operating without water-vapor condensers.

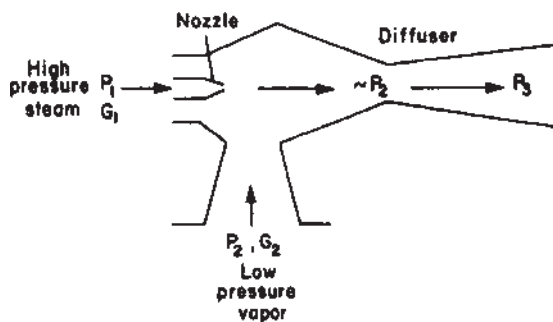


FIGURE 9.15 Steam ejector.

Mechanical pumps sealed with oil, on the other hand, are generally incapable of handling significant water vapor loads and require the use of water-cooled or refrigerated condensers.

Mechanical pumps operate at essentially constant volumetric speed over a range of pressures. Their pumping speed begins to fall off as the pressure in the system being pumped approaches the minimum or "blank-off" pressure which can be attained by the pump. Typical performance curves for single-stage and two-stage pumps are shown in Fig. 9.16.

Most pumps are available with a device designed to minimize condensation of vapors in the pump. This device, called a *gas ballast*, consists of a valve admitting atmospheric air during the compression stroke to assist in removal of water vapor. Use of gas ballast, however, carries with it the penalty of decreasing the ultimate vacuum which can be attained by the pump. Figure 9.16 shows schematic curves for a single-stage pump operating with the gas ballast valve open or closed.

It should be noted that in the range of pressures at which the volumetric speed of the pump remains essentially constant, the gravimetric speed decreases linearly with decreasing pressure. This is, of course, a direct consequence of

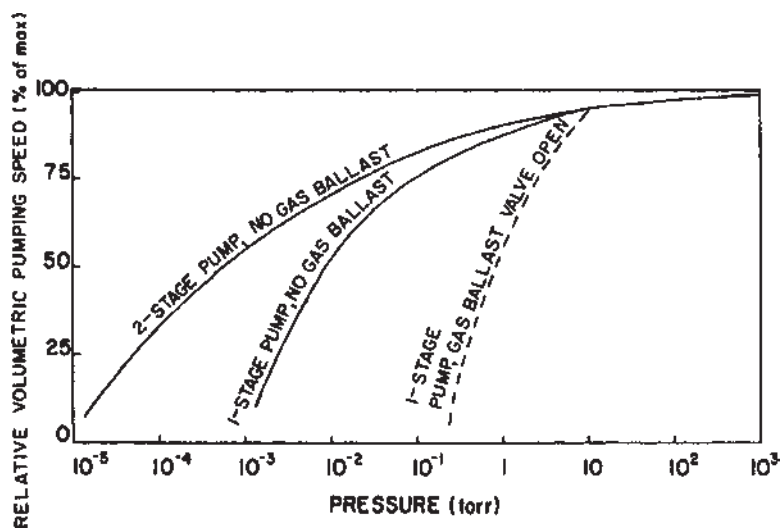


FIGURE 9.16 Dependence of volumetric pumping capacity of mechanical vacuum pumps on pressure.

the ideal gas law:

$$PV = nRT \quad (9)$$

where

P is pressure.

V is volume.

n is number of moles.

R is the gas constant.

T is absolute temperature.

Therefore, if the volumetric speed is constant,

$$\frac{dV}{dt} = S_p \quad (10)$$

then the molar pumping speed (dn/dt) is:

$$\frac{dn}{dt} = S_p \frac{RT}{P} \quad (11)$$

where S_p is the volumetric pump speed, and the gravimetric pumping speed is:

$$G = S_p \frac{RT}{P} \text{MW} \quad (12)$$

where G is the gravimetric flow of gas and MW is the molecular weight of gas.

As a consequence, the time to reduce pressure in a closed system from P_1 to P_2 , given a constant pump speed S_p , may be calculated from

$$\Delta t = \frac{V_s}{S_p} \ln \frac{P_1}{P_2} \quad (13)$$

where V_s is the volume of the closed system.

In practice, however, the time is often longer because S_p drops as the pressure drops and because there is often additional load on the pump due to outgassing of walls, water vapor infiltration from condensers, and system leaks. An empirical equation using a correction factor K_{corr} is often applied:

$$\Delta t = (K_{\text{corr}}) \frac{V_s}{S_p} \ln \frac{P_1}{P_2} \quad (14)$$

K_{corr} is close to unity at pressures above 10 torr, but increases to 4 or more at pressures between 0.1 and 10 torr. Of course, very much greater corrections are required when condensers do not function properly or in the presence of major leaks.

2. Entrainment Separators

Entrainment separators are devices used in evaporators to avoid incorporation of liquid droplets in the discharging vapor stream. They involve the principle of *momentum separation*: a sudden change of velocity of the stream, produced by impingement on some obstacle to flow, causes denser droplets to settle out. Some types of entrainment separators are shown in Fig. 9.17.

The food industry often uses combinations of the types of equipment discussed previously. For a more detailed discussion of equipment and practices in evaporation of food products, the reader is referred to Slade (1967), Farrall (1963), and Armerding (1966), and Hartel (1992). Engineering calculations involved in evaporation are well discussed by Loncin (1969) and Coulson and Richardson (1960).

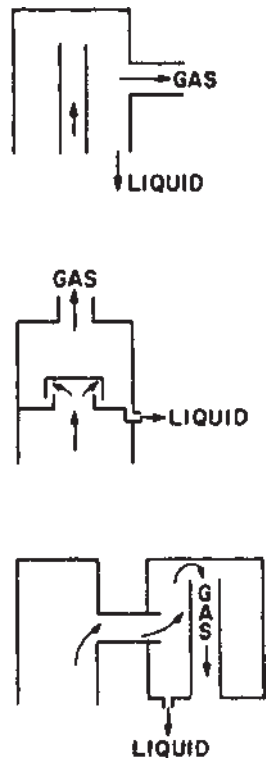


FIGURE 9.17 Entrainment separators.

I. Examples of Evaporator Systems in Industry

Capacities of evaporator system vary greatly with their application and can be readily tailored to individual needs. In applications involving low concentrations of solids, which involve liquids with relatively low viscosities, high capacities may be attained with relatively small equipment. An example of a low temperature evaporator for low-viscosity feeds is an evaporator for water desalination. This multieffect plus thermocompression system for desalination of water supplies is described by the French company (Entropie S.A., St. Germain en Laye, France). The low temperature of operation minimizes scale buildup problems. The system is readily transportable, requiring no permanent site erection. It may be installed at remote site or on board of ships. The standard unit can desalinate of 500 m³ of water per day. (Corresponding to a capacity of 20 tons of water/h) Smaller, readily portable units have capacities of 36 m³/day. The evaporator includes four cells at decreasing temperatures. The pressures and temperatures of evaporation in the four cells are

Cell 1: 0.26 atm, 66°C
Cell 2: 0.22 atm, 62°C
Cells 3 and 4: 0.15 atm, 54°C

The vapor from cell 4 is compressed by high pressure steam to 0.32 atm, and 70°C and is fed into a bundle of heat exchange tubes. Raw water is sprayed onto these tubes and is supplied with the energy for evaporation. The vacuum in the system is supplied by a hydroejector.

Typical food application of evaporation is the concentration of citrus juices. A detailed analysis of this industrial application in Florida was provided by Chen (1982). According to him approximately 80% of the 8 million ton annual crop of orange is processed into frozen concentrate. Most of the concentrate is produced in high-temperature short-time, multieffect vacuum tubular evaporators, so-called TASTE evaporators. In 1980, 91% of evaporating capacity was located in these evaporators, compared to approximately 8% in low temperature evaporators. The low-temperature evaporators are primarily used for concentration to lower levels than 65% solids desired for frozen orange juice concentrate.

The TASTE evaporators vary in number of effects, number of stages for each effect and in presence and location of preheaters which boost the energy efficiency of the system. A typical system was analyzed by Chen (1982). It consists of four effects, with the fourth effect consisting of three stages. In addition, it includes a preheater, which brings the feed temperature from 21 to 96°C, by heating it with steam at 100°C. This steam is also used in the first effect, in which the juice evaporates at 81°C to bring the concentration of the juice from 12 to

14.7%. In the three subsequent effects the evaporation occurs at 67.8, 53.6, and 37.8°C, respectively. The vapor from each effect is used to supply the heat of evaporation in the subsequent effect, as is usual in multieffect evaporators. The evaporation capacity of the system is 18,000 kg/h, and its evaporation area is 635 m². The overall heat transfer coefficient is 3400 (Wm⁻²°C⁻¹) in the preheater. In the evaporators it ranges from 1930 in the first effect to 1420 in the third, and 420–710 in the three stages of the fourth effect. The steam economy of the system is outstanding with 3.5 kg water evaporated per kg of steam. The total residence time is 430 s.

III. FREEZE CONCENTRATION

A. Introduction

Evaporation is the most economical and most widely used method of concentration. It has, however, two important limitations: (1) loss of volatile components other than water (flavors) and (2) potential for heat damage to product quality. Freeze concentration is a process which can sometimes be used to overcome these limitations. This process involves partial freezing of the product and removal of the pure ice crystals, thus leaving behind all of the nonaqueous constituents in a diminished quantity of water. The major limitations of the process include relatively high cost, difficulties in effective separation of ice crystals without loss of food solids, and a relatively low upper limit on the total solid concentration in the product.

Freeze concentration has been applied primarily where quality considerations and, in particular, the need for retention of organic volatiles are the dominant considerations, as in concentration of wines and beer (where alcohol and flavors are to be preserved) and concentration of coffee prior to freeze drying (where flavor retention is an important goal).

This chapter presents fundamentals of freeze concentration and some of the general aspects of procedures involved in current freeze concentration processes. More detailed discussion of the theoretical and engineering aspects of this process has been the subject of two recent reviews, and the interested reader is referred to them for further study. The pertinent references are: Hartel, (1992) and Schwartzberg, (1990). The freezing process itself was discussed in Chapter 8.

B. Principle of the Process

1. Equilibrium Considerations

Separation by freezing is based on solid–liquid phase equilibrium. The solution to be concentrated contains the solvent, water, and a large number of soluble components. It is, however, less complicated and usually adequate to consider

the system as pseudo-binary, that is, considering all substances dissolved in the water as one component.

The simplest phase diagram of a binary mixture is shown in Fig. 9.18. If a binary mixture is cooled under conditions allowing equilibrium to be attained, then pure ice crystals separate out at a point which corresponds to composition w_A and the freezing point of this solution (T_A'). Further cooling results in more of the ice crystals separating out, while liquid composition follows the line $[(w_A, T_A'), (w_B, T_B)']$. At w_E the crystallizing solid has the same composition as the supernatant liquid.

It is obvious that the concentration process can only be applied up to concentrations below that of the eutectic; and in most cases, because of problems connected with separating ice from a very viscous liquid (both because of concentration and of low temperature), it must stop well below the eutectic. In the example shown in Fig. 9.18, the final concentration is w_B . The quantity of water to be removed by freeze concentration can be obtained by a simple mass balance, shown in Fig. 9.19.

$$L_A = L_B + L_I \quad (15)$$

$$L_A w_A = L_B w_B + L_I w_I \quad (16)$$

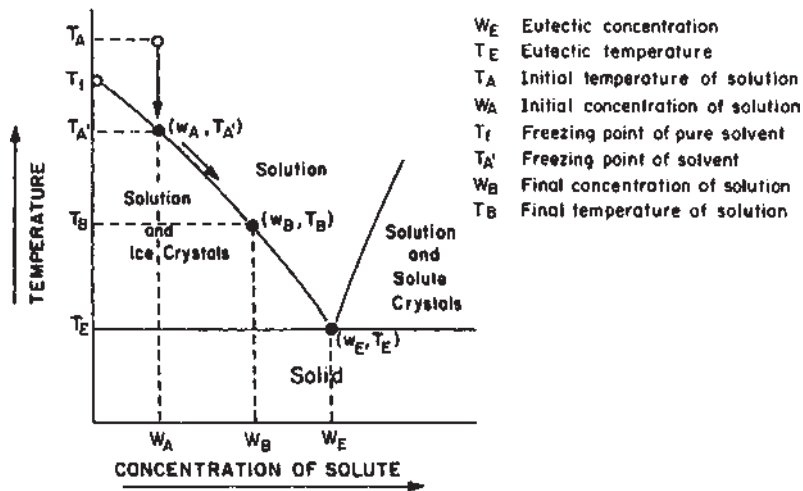


FIGURE 9.18 Phase diagram for a simple binary system.

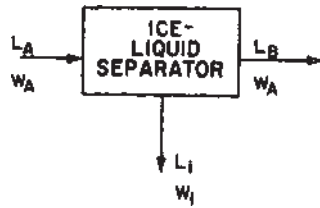


FIGURE 9.19 Schematic representation of an ice–liquid separator. L , gravimetric flow (kg/h); w , kg solute/kg water. Subscripts: A, feed; B, concentrate; i, ice.

If we assume that the separation is perfect and no solute is entrapped with the ice stream L_I . Then the water removed from the product stream is

$$L_A w_A - L_B w_B = L_I \quad (17)$$

and per pound of feed, the amount of water removed is

$$w_e \equiv \left(\frac{L_I}{L_A} \right) = 1 - \frac{w_A}{w_B} \quad (18)$$

When the amount of solute entrapped in ice is significant, the following equation applies:

$$w_e = \frac{w_B - w_A}{w_B - w_I} \quad (19)$$

The above discussion was based on a binary system. In real foods, of course, there are many components. If they all remain in solution, the considerations are identical to the binary process since, from equilibrium considerations, only freezing point depressions need to be considered and eutectic concentrations are never reached.

Initial solid concentrations of food liquids typically range from 5 to 20%, and final concentrations of 35–50% solids are achievable by freeze concentration. The equilibrium freezing temperatures [T_B when referring to the schematic diagram Fig. 9.18] corresponding to 40% solids are -5°C for coffee extract, -7°C for orange juice, and -10°C for apple juice. When high concentrations of low molecular weight solutes are present, T_B drops more rapidly with concentration. For instance, at -10°C the unfrozen phase of an alcohol solution contains 22% alcohol.

2. Rate Considerations

The rate of crystal growth and the average crystal size depend on a number of operational factors, including in particular (a) the rate of nucleation, which in turn

is strongly dependent on temperature and composition, (b) the rate of diffusion of water molecules to the surfaces of growing crystals, and (c) the rate of removal of the heat of fusion from the crystal surfaces.

In freeze concentration it is desirable to grow large, symmetrical crystals at a relatively slow rate. Large crystals are easier to separate by mechanical means, and large crystals have fewer points of contact per unit volume, thus minimizing the potential for entrapping liquid and solute. Symmetry of crystals also minimizes entrainment. Good mass transfer conditions, usually due to turbulent flow in the crystallizers, combined with large heat transfer areas at relatively high temperatures are most conducive to the type of crystal growth which is desired. Equipment design follows these principles, within limits imposed by economic factors.

Symmetry of crystals is also improved by partial melting and refreezing prior to separation, which is occasionally practiced in freeze-concentration systems.

C. Freeze Concentration and Freeze Desalination

One of the widely discussed applications of freeze separation is desalination. Freeze concentration and desalination are based on the same general principles but differ primarily in their products. In desalination the product is the pure ice crystal stream; in freeze concentration, it is the liquid from which the ice crystals are separated. Entrainment of solute in the ice stream is undesirable in either case. In desalination, however, it is feasible, at least in principle, to obtain high purity of the ice stream by maintaining the degree of concentration at a low level. Since a high degree of concentration is needed in the freeze concentration of foods, this course of action is not feasible in food applications. An additional difference lies in the high viscosity at moderate concentration due to polymers and dispersed particles present in food liquids such as juices. Finally, freezing by direct injection of refrigerant is often more feasible in desalination than in food concentration, because refrigerant removal from the product stream is difficult in the case of foods.

D. Principles of Equipment Used in Freeze Concentration

A freeze-concentration system contains as a minimum the following components: (1) a crystallizer or freezer in which the crystals are produced and (2) a separator for separation of the crystals and the liquid concentrate. Various additional components may be added to improve operational efficiency. Examples are shown in Fig. 9.20, which shows a hypothetical two-stage process utilizing centrifuges for ice separation, and in Fig. 9.21, which represents a pulsating unit developed by Phillips Petroleum Company for concentrating beer.

1. Crystallizer

It has been mentioned previously that the rate of growth of crystals and the size and uniformity of ice crystals depend on heat and mass transfer conditions existing during crystallization. Very large uniform crystals require a very large exchange surface and a high degree of turbulence. When these are provided, crystals as large as 3 mm in diameter can be grown continuously under laboratory conditions. In commercial equipment, cost considerations preclude growing crystals larger than 1/4 to 1/2 mm. This size, however, is usually adequate to achieve separation.

2. Separators

Centrifuges are commonly used for separation. They provide forces up to $1000 \times g$, which forces even viscous liquid off crystal surfaces. There remains a layer held by surface forces, however, and this layer may represent a substantial loss of valuable solids or alcohol. One approach to minimizing this loss is the washing of ice crystals prior to their discharge to the melter. The spent wash water is of course returned to the crystallizer if solids are to be recovered (Fig. 9.20).

Filter beds may be used instead of centrifuges and this method is utilized in a design developed by Phillips Petroleum Company (Fig. 9.21).

Recently freeze concentration of food materials has utilized as separators wash column of the type developed by Thijssen and his colleagues (Thijssen, 1974) and developed further by the company Gresco (Van Pelt and Swinkels, 1986). In a wash column a countercurrent flow is achieved between ice and concentrate. Ice crystals are transported in a vertical column to the top of the column and are separated by scraping

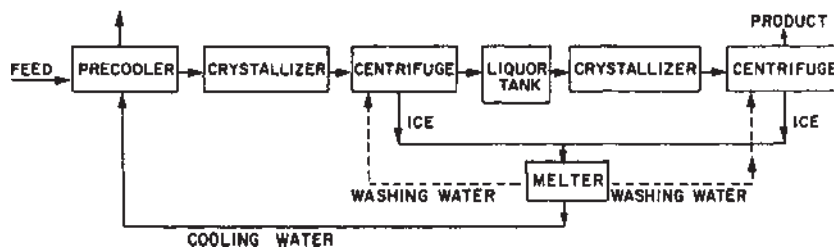


FIGURE 9.20 Two-stage freeze-concentration system.

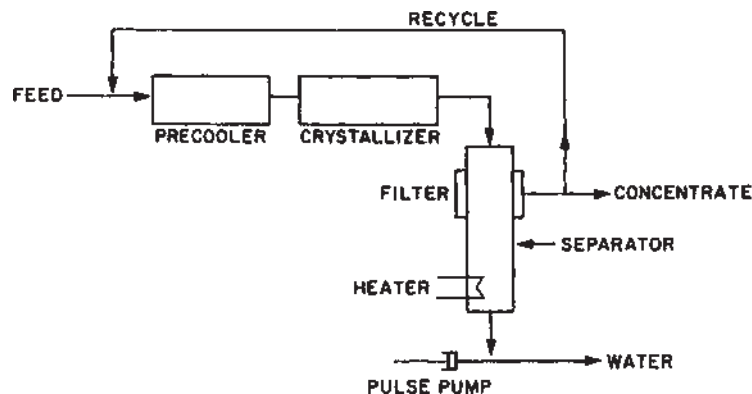


FIGURE 9.21 Freeze-concentration system using a filter bed.

device. A small amount of the ice is remelted and the water provides the washing effect. The concentrate flows downward and is removed at the bottom of the column after passing through a filter. Under the right conditions a sharp “wash front” is achieved between the ice crystals in the melt, and ice crystal containing concentrate. Figure 9.22 shows a schematic representation of the wash column.

In the original Gresco design the ice crystals were forced to the top, and the concentrate down by the action of porous reciprocating piston. The porous piston also acted as a filter (Hartel, 1992).

An important more recent development was the Gresco continuous packed bed wash column, the first fully continuous flooded wash column with a flat wash front (Van Pelt and Swinkels, 1986). In this system the ice slurry is injected in the bottom of a cylinder. The bottom of the cylinder contains a set of rotating vanes, which scrape the bottom filter, and also transport the ice slurry. Above the vanes a homogeneous bed of ice crystals is packed, and the concentrate is pushed down by the flow of wash water obtained from the melting of a portion of the separated crystals. The displacement of the concentrate by the less viscous wash water is stable, and is promoted by the dendritic re-crystallization of washwater on the colder ice crystals. The continuous column has a capacity of $10\text{--}20\text{ ton m}^{-2}\text{ h}^{-1}$. Further improvements include multistage equipment.

E. Normal Freezing

The freeze-concentration methods referred to previously involved the pumping of a liquid–ice crystal mixture in the form of a slush from a crystallizer to a

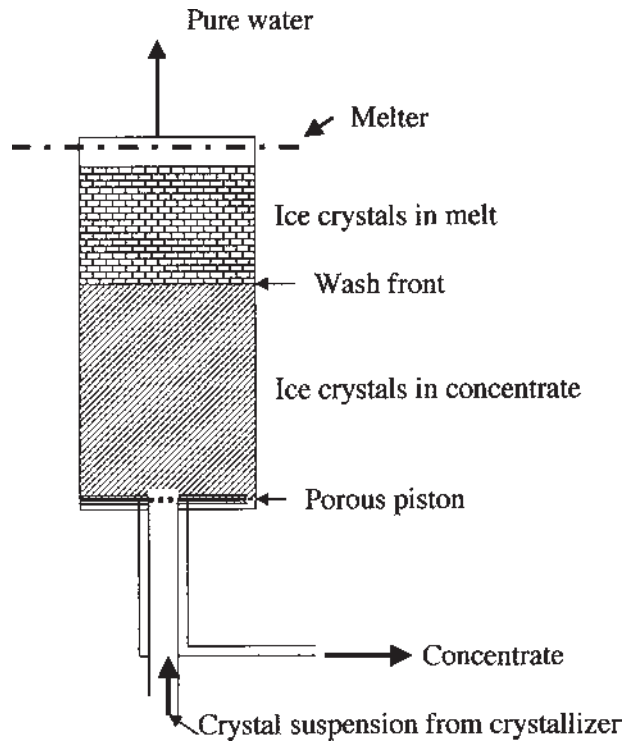


FIGURE 9.22 Schematic representation of a wash column.

separator where the crystals are removed. The separation often presents difficulties and in small-scale applications where batch operation is feasible these difficulties can be overcome by the use of normal freezing. In this method, a solid ice front is produced at the wall of crystallizing vessel; this wall progresses slowly, thus directing the flow of concentrated liquid away from the wall toward a location where it is drawn off. Three possible arrangements are shown in Fig. 9.23. In Fig. 9.23a is shown a tube with stirred liquid which is being immersed gradually into a freezing bath. The ice layer grows from the bottom toward the top of the tube. Concentrated solution may be withdrawn from the top. In Fig. 23b, a “cold finger” condenser is inserted into a stirred bath containing the solution which is to be concentrated. The ice layer progresses from the outside wall of the condenser. In Fig. 9.23c, a stirred bath of liquid is surrounded by

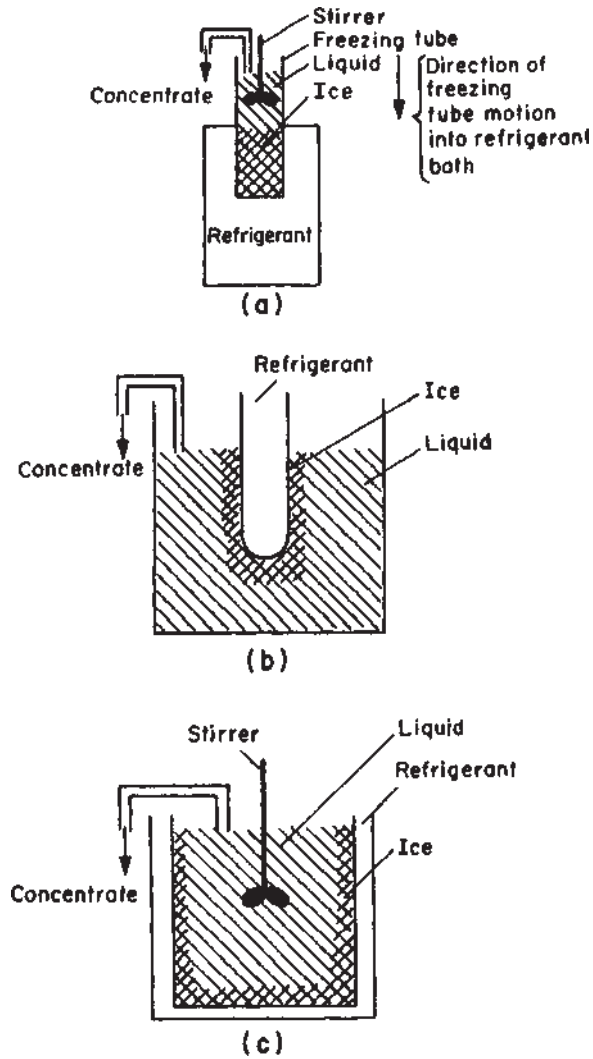


FIGURE 9.23 Schematic representation of systems for normal freezing.

a cooling jacket, with the ice growing from the walls toward the center of the bath; concentrate is eventually removed from the center.

Applications of normal freezing are quite limited. For reviews of this method the reader is referred to Kepner et al. (1959) and Gouw (1968).

F. Problems Caused by Precipitation of Solids Other than Ice

In some food liquids, including tea infusions, the solids are only sparsely soluble at freezing temperatures. As a consequence, some soluble compounds, including polymers, precipitate in the crystallizer and are lost with the ice phase. This precipitate can also interfere with efficient operation of crystallizers and separators. To overcome this problem in freeze concentration of tea, a design has been patented by Struthers Scientific and International Corporation (1968). In this design, the tea extract is cooled and then passed through a setting tank, where some of the solutes precipitate. The extract continues on to the crystallizer and separator, where some of the water is removed as ice. The precipitate is redissolved in a small quantity of water and is then returned to the concentrate. The particular patent referred to here pertains to pre-concentration of tea for subsequent freeze drying but can be applied to coffee as well.

A patent issued to Ganiaris (1969) of the same company refers to problems with precipitation of coffee solids. The patented design overcomes the problem of solute precipitation by minimizing residence time in the crystallizer.

G. Concentration by Gas Hydrate Formation

Gas hydrates are icelike compounds, consisting of small “guest” molecules which are physically entrapped in hydrogen-bonded cages of water molecules (the *host*). Many of the fluids of consequence in food applications are capable of hydrate formation in the presence of various gases, such as halogenated, short-chain hydrocarbons. Many such hydrates are capable of existing at temperatures well above 0°C provided pressures are maintained at an elevated level.

Application of the above principle to freeze concentration (or more appropriately concentration by gas hydrate formation) was reported by Huang et al. (1966). They showed that fruit and vegetable juices could be concentrated by formation of CH₃Br and CCl₃F hydrates.

Werezak (1969) removed water from various substances, including coffee extract and solutions of sucrose and sodium chloride, by forming hydrates of fluorocarbons, ethylene oxide, methyl chloride, and sulfur dioxide. The author described a process for concentrating coffee using ethylene oxide as the hydrate former. Much more research is needed to determine whether this process can be made mechanically and economically feasible.

H. Applications in the Food Industry

Food applications of freeze concentration are still limited. The following applications have been reported, but their extent of their use is not extensive (Van Pelt and Swinkels, 1986).

1. Concentration of wine in order to increase alcohol content without adding pure alcohol, a procedure which is illegal in many countries.
2. Concentration of beer to improve stability, reduce distribution costs, and develop new higher alcohol beverages.
3. Production of high quality fruit juice concentrates.
4. Concentration of cider and production of vinegar with up to 40% acetic acid.
5. Coffee has been concentrated prior to freeze drying, and its concentration prior to spray drying was reported. The concentrations achieved were up to 45 wt% solids.

The Electric Power Research Institute (EPRI) of Palo Alto, CA has been promoting research aimed at industrial applications. In addition to the applications discussed above, EPRI has been suggesting the use of freeze concentration in concentration of dairy products, in sugar production, and in waste processing (Douglas, 1989).

IV. MEMBRANE PROCESSES FOR CONCENTRATION

A. Introduction

Evaporation is the most economical and most common concentration process. Its limitations are due to undesirable effects of high temperature or to losses of volatile components when operating temperatures are lowered through use of vacuum. Freeze concentration is conducted at low temperature and is thus more likely to result in high-quality products. The mechanical separation of the ice, however, is a difficult and expensive process if losses of solids are to be avoided.

Another approach to production of high-quality products is the use of membrane processes. The principle involved is the interposition of a membrane between the feed stream and a waste or transfer stream, and the establishment of conditions providing a driving force for transport of water across the membrane from the feed to the transfer stream. The rate of transport, of course, is dependent on the driving force as well as on resistance, which depends on membrane properties and on conditions in the fluid streams on each side of the membrane. The possibility of obtaining high-quality products depends on the use of semipermeable membranes, which means membranes with much less resistance to water transport than to transport of components which are to be retained.

B. Driving Forces for Membrane Processes

When a membrane separates two regions, the following driving forces can be used to cause flow of a molecular or ionic species:

1. Concentration difference
2. Pressure difference
3. Difference in electric potential
4. Temperature difference

The different membrane processes resulting from the application of these driving forces are listed in Table 9.3. Figure 9.24 shows schematically the principles involved in dialysis, osmosis, thermoosmosis, and reverse osmosis. Osmosis and dialysis are based on concentration differences. In thermoosmosis high temperature is used to increase the partial pressure of solvent in the feed stream to create a driving force for transport. In reverse osmosis, hydraulic

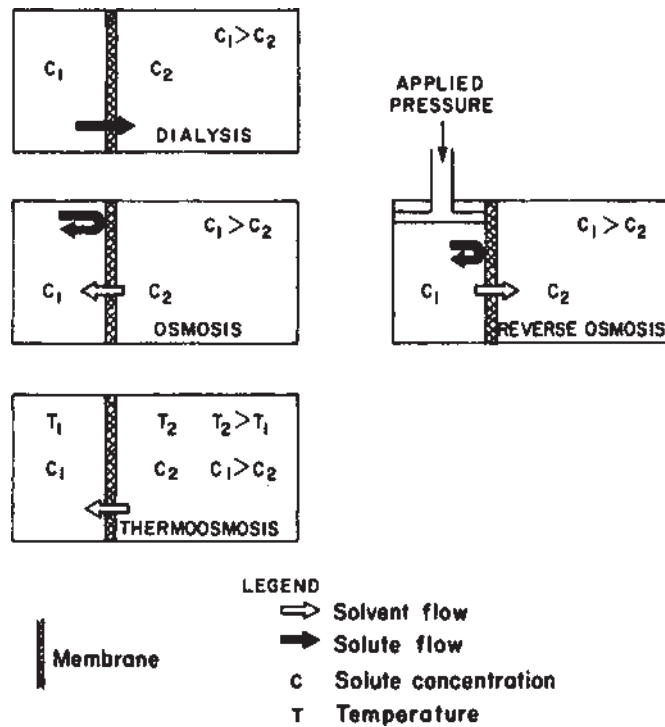


FIGURE 9.24 Schematic representation of some membrane processes.

TABLE 9.3 Membrane Processes in Separation of Food Components

| Driving force | Component separated | Name of process |
|--------------------------|---------------------|-------------------------------------|
| Concentration difference | Solvent | Permeation, osmosis |
| | Solute | Dialysis |
| Temperature difference | Solvent | Thermosmosis, pervaporation |
| Pressure difference | Solvent | Reverse osmosis, ultrafiltration |
| Electrical potential | Solute | Electrodialysis |
| | Solvent | Electroosmosis |

pressure is applied to the feed stream to counteract and overcome the osmotic driving force, hence reverse osmosis.

Ionized species, such as salts, can be used in separations utilizing electric current. The processes utilize membranes permeable only to ions which are positively charged (cation membranes) or only to ions negatively charged (anion membranes). When electric potential exists across the membrane, ionic flow occurs. This process can be used to reduce the ion content of solutions and is called *electrodialysis*. In concentration, use is made of the fact that ions transported across membranes carry water of hydration. The process may therefore be used for removal of water, that is, for concentration. It is then called *electroosmosis*.

In Fig. 9.25 are shown two arrangements of membranes for electroosmotic concentration of fluid foods containing electrolytes. In the arrangement of membranes in Fig. 9.25(a), a stack of membranes alternating with flow channels is located between the anode and the cathode of the completed electric circuit. Each flow channel containing the feed stream is sandwiched between two transfer stream channels from which it is separated by membranes, a cation membrane on the cathode side and an anion membrane on the anode side. Ions and associated water can thus flow out of the feed stream channels via the membranes, but flow of ions into the feed channel is prevented because the electric gradient causes the ions to move toward a membrane through which they cannot pass. In order to provide an ionic flow sufficient to remove the desired amount of water, salt can be added to the feed stream.

In Fig. 25(b), only cation membranes are used but there is an alteration between highly permeable (loose) membranes, and relatively impermeable

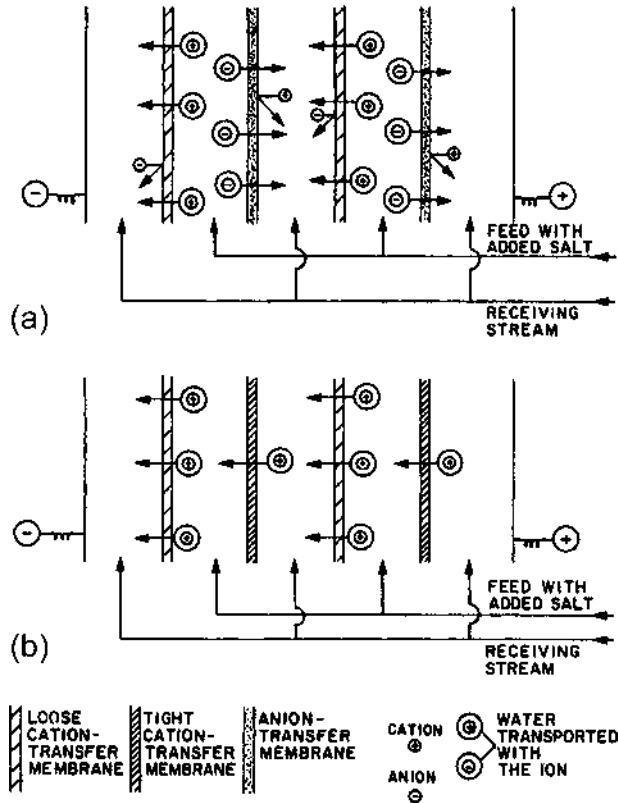


FIGURE 9.25 Schematic representation of two types of electroosmosis systems: (a) using cation and anion membranes; (b) using only cation membranes.

(tight) membranes. The flux of ions and water into the feed stream is less than the flow out of it, resulting in net water removal.

C. Membranes

Membranes used for the separation processes described above are composed of natural or synthetic polymers. They may be classified in a variety of ways but the following categories are particularly descriptive of their functional transport process properties.

1. Porous Membranes

When pores of the membranes are very much larger than the molecular size of the permeating substances, the membranes are referred to as *porous*. Other essentially synonymous terms are *microporous*, *Millipore membrane*, and *ultrafiltration membranes*. In this type of membrane, pore size ranges from 10^{-2} to 10^2 μm . Hydraulic flow of solvent and low-molecular weight solutes occurs through these membranes, whereas solutes of high molecular weight cannot pass.

2. "Solution" Membranes

When the holes within the membrane are small, that is, of the order of magnitude of the diffusing molecules, it is usually accepted that transport occurs by "solution" or "activated" diffusion. This type of diffusion is best described by a model in which the permeating molecules are assumed to condense or dissolve at one face of the membrane, are transported in the membrane as a dissolved species, and are then re-evaporated or re-extracted at the other face. Transport rates and separation factors are determined by solubility and diffusivity of the permeants in the membrane material.

3. Membranes Intermediate Between Porous and Solution Membranes

It is often difficult to establish a sharp distinction between microporous membranes with very narrow pores and solution membranes of high permeability, both of which may be used in ultrafiltration.

An intermediate type is the heterogeneous membrane, such as the *Loeb-type* cellulose acetate membrane, which consists of a thin layer of dense, "solution" membrane upon a much thicker substrate of a loose, porous membrane. A representation of resistance to flow with this type of membrane is shown in Fig. 9.26.

The cellulose acetate membrane of the Loeb type is prepared by converting a solution membrane into a porous membrane, except for a thin dense "skin." This is achieved by chemical treatment. Other means of preparation of heterogeneous membranes, including coating and graft polymerization, are possible.

It can be noted in Fig. 9.26 that in addition to resistance due to the membrane itself, flow is also impeded by resistance of stagnant fluid films on each side of the membrane, and especially by the deposition at the membrane-fluid interface of a film of condensed hydrocolloidal solutes, usually polymers or proteins.

This "fouling" of the membrane is similar to the fouling which occurs in evaporators and is sometimes called *concentration polarization*.

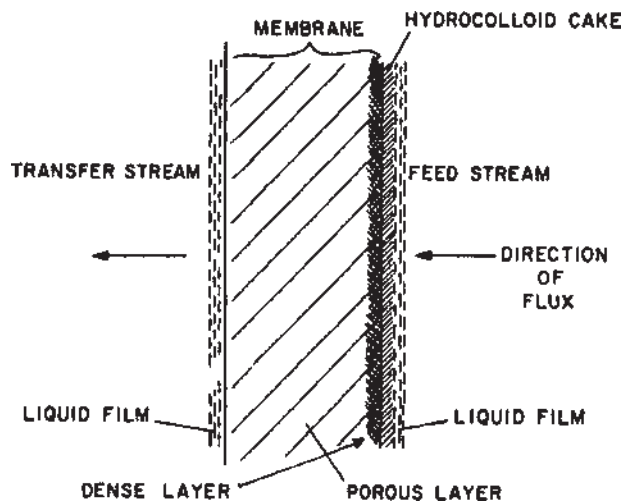


FIGURE 9.26 Schematic representation of resistances to solvent flow across a heterogeneous cellulose acetate membrane separating two liquid streams.

The resistance of this fouling layer often critically decreases the flux across the membrane.

Another consideration of importance in the properties of solution membranes is the mobility of the polymeric chains of which the membranes are composed. In the case of noncrystalline (amorphous) membranes, the mobility is relatively high at high temperatures, especially in the presence of solvents having an affinity for the membrane. Consequently, the material is considered to be in the rubbery state as opposed to the glassy state, which occurs at lower temperatures and in which mobility is greatly restricted. The permeability of a membrane increases and its selectivity decreases as the transition from glassy to rubbery state occurs due to a rise in temperature. In partial crystalline (microcrystalline) polymers, the permeability is further reduced by the presence of the crystalline regions, which are not permeable and which may, in addition, restrict polymeric chain mobility in adjacent amorphous regions.

4. Ion-Exchange Membranes

Ion-exchange membranes contain fixed charges in the matrix of the membranes. As a consequence, they tend to attract oppositely charged ions (counter-ions) and allow their transport. Co-ions (ions of the same sign as the fixed charges) are excluded from the membrane.

Cation membranes usually contain fixed negatively charged sulfonate ions; anion membranes usually contain fixed quaternary ammonium ions. The degree to which these membranes are hydrated is dependent on pH.

D. Reverse Osmosis

The flux of water across a membrane is given by

$$J_w = \frac{\bar{D}_w \bar{C}_w (\Delta\mu)_w}{RT \Delta X} \quad (20)$$

where

J is flux (mol/cm² s).

\bar{D} is average diffusion coefficient in membrane (cm²/s).

R is the gas constant (erg/mol K).

T is absolute temperature (K).

\bar{C}_w is average concentration of water in membrane (mol/cm³).

ΔX is membrane thickness (cm).

$\Delta\mu$ is the chemical potential difference across membrane (erg/mol).

The subscript w refers to water.

For the case of reverse osmosis, shown in Fig. 9.24, the difference in chemical potential may be related to applied pressure and to osmotic pressure by

$$\Delta\mu_w = \bar{V}_w (\Delta P - \Delta\Pi) \quad (21)$$

where \bar{V}_w is molar volume of water (cm³/mol), ΔP is applied pressure (Pa/cm²), $\Delta\Pi$ is osmotic pressure (Pa/cm²).

In practical units, therefore, it is possible to relate flux of water to applied and to osmotic pressure as shown in

$$J_w = K_w (\Delta P - \Delta\Pi) \quad (22)$$

where J_w is water flux in convenient units, K_w is a permeance constant incorporating membrane properties and various constants shown in Eq. (21), and ΔP and $\Delta\Pi$ are pressures expressed in units consistent with the units of J_w . When the transfer stream is relatively dilute, the calculations may be simplified and approximations to membrane performance obtained by assuming that osmotic pressure is proportional to solute concentration in the feed stream.

The flux of solute across the membrane is then given by

$$J_s = K_s C_{s(\text{feed})} \quad (23)$$

where J_s is flux of solute, K_s is a permeance constant for solute, and $C_{s(\text{feed})}$ is

solute concentration in the feed stream. If a rejection factor is defined, as given in

$$\text{Rejection} \equiv 1 - \frac{C_{s(\text{transfer})}}{C_{s(\text{feed})}} \quad (24)$$

where $C_{s(\text{transfer})}$ is solute concentration in transfer stream, then the rejection factor can be related to operating variables by

$$\text{Rejection} \equiv 1 - \frac{K_s \rho}{K_w (\Delta P - \Delta \Pi)} \quad (25)$$

where ρ = density.

It is evident from Eqs. (22) and (25) that the flux of water increases with increasing applied pressure (ΔP), with increasing K_w , and with decreasing solute concentration in the feed stream. The selectivity of the process, that is, its ability to remove water while retaining solute, improves with increasing ratio K_w/K_s but decreases with increasing ΔP .

At the same operating pressure and given the same type of membrane the selectivity of the process decreases with increasing membrane permeability (increasing porosity). For instance, Merson and Morgan (1968), working with the Loeb membrane at a pressure of 1000 psi, found that when the flux of water was 30 gal/ft² day there was almost no transport of dextrose (the solute in the feed stream). At fluxes higher than 50 gal/ft² day, however, substantial loss of the ester was observed.

E. Applications of Reverse Osmosis

The Loeb cellulose acetate membrane has been applied in several different types of pilot plant equipment to evaluate various proposed food applications. Among the initial applications proposed by USDA researchers were (1) concentration of various fluid foods, including juices, egg white, coffee, and syrups and (2) water recovery from waste streams (Morgan et al., 1965). Modern membrane systems utilize a variety of polymeric membranes. Among the polymeric films used most frequently are cellulose derivatives, polyamides, polyacrylates, and polybenzimidazoles. They are different designs of the membrane modules, which may be tubular, hollow fiber, spiral, or in plate configurations (Cheryan, 1992).

Cheryan (1992) reports that current applications of reverse osmosis (RO) include preconcentration of egg whites, of coffee and often before drying, as well as concentration of maple sap, tomato juice, and of sugar solutions. Major applications of RO exist in the dairy industry. They include concentration of milk and of whey, often in combination with a preceding ultrafiltration (Ostergaard, 1986).

Desalination of seawater and of brackish water is a prominent application. An early report on this subject was presented by Merten, 1966. Since then the applications have grown rapidly. In 1986 24% of the global desalination capacity was based on reverse osmosis. An inventory by the consulting firm Wangnick Consulting GmbH, Guarrenburg, Germany reports 1988 global capacity for desalination of $22.6 \times 10^6 \text{ m}^3/\text{day}$ in 12433 plants; 44% of this capacity is in membrane processes (39% RO and 5.6% electro dialysis). Evaporators account for 49% percent of the capacity.

The Gulf States are major users of desalination accounting for almost half of the global capacity. These states using predominantly thermal evaporators consistent with the relatively low local energy cost. However even there RO represents approximately 20% of capacity.

Recent droughts in the Middle East have produced a water supply crisis in Israel, Jordan, and Syria. In the next 2–3 years Israel is expected to increase its desalination capacity by two reverse osmosis installations with a capacity of $50 \times 10^6 \text{ m}^3$ of water per year. (Jerusalem Post of March 6 2001). In June of 2001 the Israeli Finance Ministry has published requests for proposals for additional capacity of $115 \times 10^6 \text{ m}^3$ per year.

F. Ultrafiltration

Ultrafiltration can be differentiated from reverse osmosis by the relative porosity of the membranes. In the case of ultrafiltration only large molecules are retained and most of the small solute molecules, including salts, sugars, and most flavor compounds, are transported with the water. Since osmotic pressure depends on the number of molecules in solution and since the number of large molecules is small, the osmotic pressure across the membrane is negligible.

The water flux is caused by hydraulic flow and is proportional to applied pressure.

$$J_w = K'_w \Delta P \quad (26)$$

where K'_w is a constant,

Rejection factors depend almost entirely on the size of the solute molecule, whereas in reverse osmosis membrane polarity and affinity for membrane material are equally important.

According to published data, ultrafiltration is highly suitable for purification of biological materials, as well as for dewatering and desalting of protein solutions. Typical operating pressures are in the range of 1 to 8 atm, and flux rates of $10\text{--}30 \text{ l(m}^2\text{h)}$ are reportedly attainable with membranes retaining essentially all of the protein.

Ultrafiltration (UF) has been found to give significant advantages in dairy industry. A review of this application was presented by Ostergaard (1986). Major applications of ultrafiltration in the dairy industry include

1. Preconcentration of whey obtained as a waste stream in cheese making
2. Production of whey protein concentrates
3. Concentration of milk as an aid in cheese making.

Depending on the application with cut-off molecular weights (mW) of 5000 to 50,000 daltons are utilized. According to Ostergaard (1986) the specific applications of these membranes include

Membranes with cut-off MW of 50,000: UF of acidified skim milk to produce quark and other specialized fresh cheeses.

Membranes with cutoff of 25,000 daltons: Production of whey protein concentrate and UF of acidified whole milk for production of cream cheese.

Ostergaard notes that membranes with cutoff of 5000 daltons are not usually used in the dairy industry. These membrane are however used in production of protein concentrates from other protein sources.

Units with capacities of several thousand liters per hour are readily available and utilized commercially.

G. Electroosmosis

As discussed above, electrically driven processes can be used either for desalting, for ion exchange, or for concentration. The process of water removal, that is, concentration, is called *electroosmosis* and is represented schematically in Fig. 9.25.

The flux of ions of a given sign across a membrane is given by

$$J_i = K_i \frac{\Delta C_i}{\Delta X} + K'_i \frac{\Delta \psi}{\Delta X} \quad (27)$$

where

ΔC_i is the difference in concentration of ions.

K_i is the permeance of the membrane caused by the concentration gradient.

K'_i is a constant relating ion flux to electric potential gradient.

ΔX is membrane thickness.

J_i is ion flux (mole equivalent per unit area and time).

$\Delta \psi$ is electric potential difference.

The associated flux of water depends on the type and concentration of ions, type of membrane, and other factors. Typical values are 100–1000 cm³ of water per mole equivalent of ions.

The rate of removal which may be attained depends on current density. For example, if the arrangement shown in Fig. 9.25a is assumed and if a current density of 1 farad/ft² h is assumed, then 1 mole equivalent of cations per square foot of cation membranes and 1 mole equivalent of anions per square foot of anion membranes are transported. If we assume that each mole equivalent transports 0.5 l of water, then we obtain a flux of 1 l/ft² of membrane pair each hour. It should be noted that in order to accomplish the separation, salt must be added to the feed stream, since the natural electrolyte content is usually much lower than the amount needed for electroosmotic transport.

Electroosmotic concentration has been proposed for concentration of whey, of “stickwater” (residue of manufacture of fishmeal), and of various biological preparations. Problems in operation of electroosmosis equipment are similar to those in reverse osmosis(RO): membrane fouling, sanitation problems, and cost.

H. Thermoosmosis and Pervaporation

In a system proposed by Thijssen and Paardekooper (1964), an evaporator and a condenser are separated by a membrane permeable to water but impermeable to flavor compounds, and the liquid is evaporated at a temperature above that in the condenser. The major advantage of such an arrangement is the retention of valuable organic compounds that otherwise would be steam distilled with the water. The major difficulty lies in the lack of membranes which allow a high flux of water and retention of food flavors.

V. COST OF FOOD CONCENTRATION

The cost of food concentration is obviously a major consideration in process selection. In spite of its overall importance, however, it is difficult to obtain authoritative data on the subject. Among the difficulties involved is the dependence of cost on a large number of variables, feed concentration, product concentration and maximum tolerable temperature, and the specific requirements of each process for sanitation, quality, and inspection. Evaporation processes, for instance, are relatively inexpensive when conducted at high temperatures and when flavor recovery is not required.

Thijssen (1970) compared the cost of concentration of a liquid food from 10% to 35% solids for several processes. He arrived at the following cost per pound of water removed, using a typical set of assumptions.

| Process | Cost (cents) |
|--|--------------|
| Two-stage evaporator with flavor recovery tower | 0.3 |
| Thin-film evaporator with flavor recovery tower | 0.4 |
| Reverse osmosis | 0.2 |
| Freeze concentration | 0.2 |

More recently estimates of energy requirements, and costs for different methods of concentration were presented by Cheryan (1992). Comparing operating costs in concentration of cheese whey in an operation involving removal of 8500 kg/h, he reports an annual saving of \$250,000, which exceeds the cost of investing in an RO plant. Comparing evaporator and RO costs of dewatering corn steep liquor he also reports advantages for the membrane process.

The cost comparisons are highly dependent on relative costs of capital equipment, labor, and energy. Membrane processes are certainly less energy consuming than evaporation. Cheryan (1992) analyzed the energy consumed in concentrating whole milk from 15% to 31% solids. The most energy-efficient evaporation systems using mechanical vapor recompression require 135 kcal/kg of milk, compared with less than 10 kcal/kg for the most efficient, three-stage membrane process.

The selection of a specific concentration process must necessarily involve analysis of cost, quality, reliability and stability and is likely to result in different methods being chosen depending on product, location, size of operation, and other factors.

SYMBOLS

| | |
|-------------|---|
| A | area (m^2) |
| C | concentration (mol/cm^3 or lb/ft^3) |
| D | diffusion coefficient (cm^2/s) |
| D_h | decomposition hazard index |
| G | vapor flow rate (kg/s) |
| J | flux through a membrane ($mol\ cm^2\ s/or\ lb/ft^2\ hr$ or $gal/ft^2\ day$) |
| K_{corr} | constant in Eq. (4). |
| K_i, K'_i | ionic permeance constants defined in Eq. (27). |
| K_S | permeance constant defined in Eq. (23). |
| K_w | permeance constant defined in Eq. (22). |
| K'_w | permeance constant defined in Eq. (26). |

| | |
|-------------------|--|
| L, L' | liquid flow rate (kg/s) |
| MW | molecular weight |
| P | pressure |
| R | gas constant |
| S_p | volumetric pumping speed |
| T | temperature |
| U | overall heat transfer coefficient ($\text{Wm}^{-2}\text{°C}^{-1}$) |
| V | volume |
| V_S | volume of a closed system to be evacuated |
| V_w | molar volume of water (cm^3/mol) |
| X | distance |
| ΔX | membrane thickness (cm) |
| X_{wall} | wall thickness (ft) |
| c_p | specific heat ($\text{kJ kg}^{-1}\text{°C}^{-1}$) |
| h | film coefficient of heat transfer ($\text{Wm}^{-2}\text{°C}^{-1}$) |
| k_{wall} | thermal conductivity of wall material ($\text{Wm}^{-1}\text{°C}^{-1}$) |
| \ln | natural logarithm |
| n | number of moles |
| g | heat transfer rate (Btu/hr) |
| r_θ | total resistance to heat flow ($\text{hr ft}^2\text{°F Btu}^{-1}$) |
| r_{wall} | wall resistance to heat flow ($\text{hr ft}^2\text{°F Btu}^{-1}$) |
| t | time |
| Δt | time interval |
| w | solids concentration (kg/kg) |
| λ | latent heat of vaporization (kJ/kg) |
| $\Delta\Pi$ | osmotic pressure |
| $\Delta\mu$ | chemical potential difference (ergs/mole) |
| ρ | density |
| $\Delta\psi$ | electric potential difference |

Subscripts

| | |
|-----------------|--|
| 0,1,2,3,... | subscripts referring to specific flow streams or regions as shown in pertinent figures |
| $A, B, C, D...$ | referring to specific components of a phase as defined in text |
| feed | refers to feed stream |
| I | ice |
| i | ions |
| transfer | refers to transfer stream |
| e | component removed from the system |
| s | solute |
| w | water |

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10

Dehydration

I. INTRODUCTION

Dehydration is one the oldest food preservation techniques known to man. The primary objective of dehydration is the prevention of occurrence of dangerous or undesirable changes due to activity of microorganisms. This objective is attained by reducing the water activity below the threshold of relevant microbial activity. The reduction of water content and water activity may also have the beneficial effect of reducing the probability of nonmicrobial changes in quality, in particular those due to enzyme action, to nonenzymatic browning, and to hydrolytic reactions. The effect of water activity on these deteriorative changes were discussed in some detail in Chapter 6.

Secondary objectives of dehydration may include

- Reduction of weight, which facilitates shipment
- Potential reduction in volume
- Engineering of desirable textures
- Generation of a food structure useful as a preparation for subsequent processing, such as frying and impregnation with desirable ingredients
- Encapsulation of desirable components

II. PRINCIPLES OF DEHYDRATION PROCESSES

A. Introduction

Dehydration is perhaps the most multifaceted method of preservation in terms of methodology, applicability and versatility, and yet the principle underlying dehydration is extremely simple: a material is placed in a medium in which the partial pressure of water is low until the water content drops to the desirable level. The medium used is usually air (at pressures ranging from high vacuum to atmospheric or higher), but superheated steam, hot oil, solvents, and solutions may be used for this purpose as well. Solid dehydrating agents (e.g., salts) are also used, but in these cases the contacting medium is either a solution (in the case of soluble salts) or air in the case of desiccants. Water to be removed may be in the liquid state, sorbed by food component, or present as ice (sublimation).

Design and operation of dehydration processes depends therefore first of all on understanding the equilibrium relations between water in food and water in the dehydrating medium. These determine the driving force for the process of dehydration.

The resistances to dehydration depend on two aspects:

1. Resistance to the transport of water in the liquid or vapor phase. Mass transfer is the focus of this aspect.
2. In addition, as discussed in detail in Chapter 5, the transfer of water from the liquid state or from the state of being sorbed by the food requires the supply of energy due to the latent heats of vaporization, sorption, or sublimation. Heat transfer is therefore a key aspect of dehydration processes.

Depending on the specific process the water removal may be limited by either heat or mass transfer, or the resistances to the two transport phenomena may be coupled, that is, depend on each other.

B. Equilibrium Relations in Air–Water Mixtures

Dehydration involves transfer of water from food to another medium, most importantly to air. The equilibrium relations between food and water vapor were discussed in Chapter 6, and the reader is encouraged to review that chapter. Air–water relations are the subject of the discussion in this section. These relations frequently referred to as *properties of humid air* are critical to understanding of dehydration processes, as well as to the processes of humidification and dehumidification of air.

It is convenient to express the properties of air–water mixtures on the basis of unit amount of dry air, usually 1 kg. In the range of temperatures and pressures used in dehydration these mixtures behave as ideal gases. Dry air with an

approximate composition of 78% nitrogen, 21% oxygen, and 1% of other gases (principally argon) has an average molecular weight of 29 Da. The following variables are important in processes involving humid air:

$$Y = \left\{ \frac{p}{P-p} \right\} \left(\frac{18}{29} \right) \quad (1)$$

where Y is absolute humidity (kg water /kg dry air), p is partial pressure of water (Pa), and P is total pressure (Pa).

We can further define or restate the following:

p° = vapor pressure of water (Pa).

Y_s = absolute humidity at saturation (that is, when $p = p^\circ$).

RH = $100(p/p^\circ)$ = percent relative humidity.

Note that Y and RH are related by

$$\frac{Y}{Y_s} = \text{RH}(0.01) \frac{P-p^\circ}{P-p} \quad (2)$$

When P is very much greater than p° (at relatively low temperatures) the following relation is gives a good approximation:

$$\frac{Y}{Y_s} = 0.01\text{RH}$$

The coupled heat and mass transfer and the relationships governing equilibria in humid air are traditionally and conveniently introduced by considering two processes, namely the adiabatic saturation of air and the evaporation of water into a stream of air maintained at constant temperature and humidity.

Figure 10.1 shows schematically the adiabatic saturation process. Air is passed over a water reservoir maintained at constant level under conditions resulting in transfer of sufficient water to achieve saturation of the air. All the heat required for the evaporation of the water is supplied by cooling of the air. The water in the reservoir is assumed to remain at a constant temperature

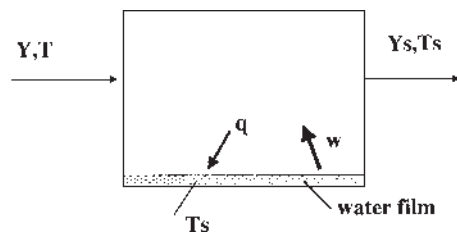


FIGURE 10.1 Schematic representation of adiabatic drying.

corresponding to the exit air temperature, and therefore does not influence the energy balance shown in

$$(Y_S - Y)(\Delta H_V) = (T - T_S)(c_{pA} + c_{pV}Y) \quad (3)$$

where

Y is absolute humidity of air (kg water vapor/kg of dry air)

$Y_S = Y$ saturation humidity at temperature T_S .

ΔH_V = Latent heat of vaporization kJ/kg

c_{pA} = specific heat of dry air $\text{kJ kg}^{-1}\text{C}^{-1}$

c_{pV} = specific heat of water vapor $\text{kJ kg}^{-1}\text{C}^{-1}$

The quantity $c_{pA} + c_{pV}Y$ is called *humid heat* (c_h) and is the specific heat of an air–water vapor mixture in units of $\text{kJ}^\circ\text{C}^{-1}/\text{kg}$ of dry air. It is useful to note that Eq. (3) may be written as

$$Y_S - Y = \frac{C_H}{\Delta H_V}(T - T_S) \quad (4)$$

Figure 10.2 shows schematically the process of evaporation of water from a thin film under conditions in which the heat of vaporization is supplied by the air, but the air is in very large excess so that its temperature and humidity may be considered constant. The temperature of the thin film reaches a constant temperature, the so-called wet bulb temperature (T_w).

The origin of the name is derived from a device used to measure relative humidity of air by exposing a wetted thermometer bulb to moving air.

T_w depends of air temperature T , its humidity Y , the latent heat of vaporization ΔH_V , and the heat and mass transfer coefficients of air (h and k_g'). The relations between the variables result from the coupled heat and mass transfer as shown in the following equations.

$$dw/dt = k_g A(p^\circ - p) = k_g' A(Y_S - Y) \quad (5)$$

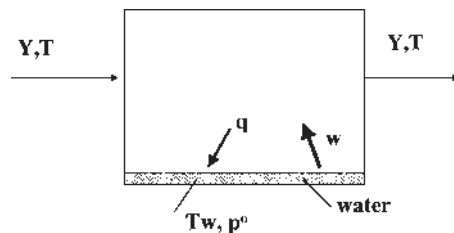


FIGURE 10.2 Schematic representation of evaporation in excess air.

where

w = mass of water (kg).

t = time (s).

k_g = coefficient of mass transfer for air ($\text{kg m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$).

k_g' = coefficient of mass transfer based on humidity difference ($\text{kg m}^{-2} \text{s}^{-1} Y^{-1}$).

A = evaporation area of the water film (m^2).

It should be noted that for low temperatures $Y = (p/P)(18/29)$, where p is partial pressure of water in the air, and P is the total pressure, and 18 and 29 are the molecular weights of water and air, respectively. As a consequence we obtain: $k_g' = k_g P(29/18)$.

The evaporation of water requires the supply of heat, and since in the system shown in Figure 10.2 all the heat is transferred from the air, heat and mass transfer are coupled as shown in

$$k_g' A (Y_S - Y) \Delta H_V = h A (T - T_w) \quad (6)$$

where h = coefficient of heat transfer of air ($\text{kJ m}^{-2} \text{s}^{-1} \text{C}^{-1}$). We write Eq. (7) in a form similar to that of Eq. (4),

$$Y_S - Y = \frac{h}{k_g' \Delta H_V} (T - T_w) \quad (7)$$

If we combine the Eqs. (4) and (7), we obtain the relation between T_S (temperature of adiabatic saturation) and T_w (wet bulb temperature): For the system air–water vapor at atmospheric pressure the following relations apply:

$$\frac{T - T_w}{T - T_S} = \frac{h}{c_h k_g'} \quad (8)$$

$$\frac{h}{c_h k_g'} = 1 \quad (9)$$

As a consequence for this system $T_w = T_S$. It should be kept in mind however that this equality is unique to this system, and T_S and T_w for other evaporating liquids and for different pressures may not be equal.

C. Humidity Charts

Heat and mass balance calculations involving air–water mixtures are facilitated through the use of graphical representation of relations between the previously defined variables: T , T_w , Y , Y_S , RH as well as the variables T_{dp} and H_{hg} , where T_{dp} is the dew point temperature, and H_{hg} is the enthalpy of humid air per kg of dry air. The dew point temperature is the temperature at which a given air water

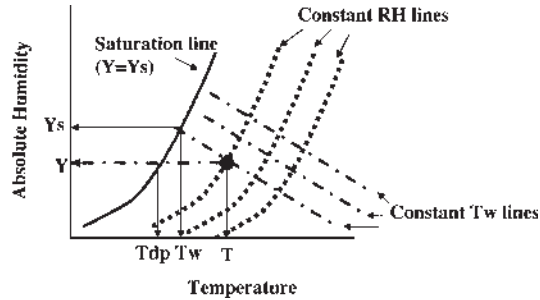


FIGURE 10.3 Parameters of the psychrometric chart.

mixture reaches saturation. If, for convenience we set the enthalpy equal to zero at the freezing point:

$$H_{hg} = c_{pA}T + Y(\Delta H_V) + c_{pV}TY \tag{10}$$

The most widely used representations are the psychrometric chart and the Molier enthalpy–humidity chart.

Figure 10.3 shows a schematic representation of the psychrometric chart. It is a plot of absolute humidity Y vs the air temperature T . The variable T_w , Y_s , RH , and T_{dp} are shown as parameters. As shown in Fig. 10.3 for a point (T, Y) the knowledge of any two of the above variable allows the immediate estimation of all the others.

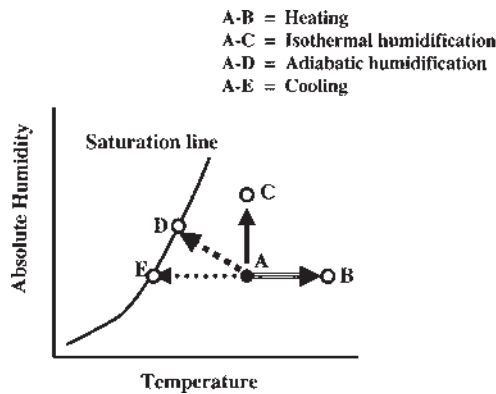


FIGURE 10.4 Representation of processes in the psychrometric chart.

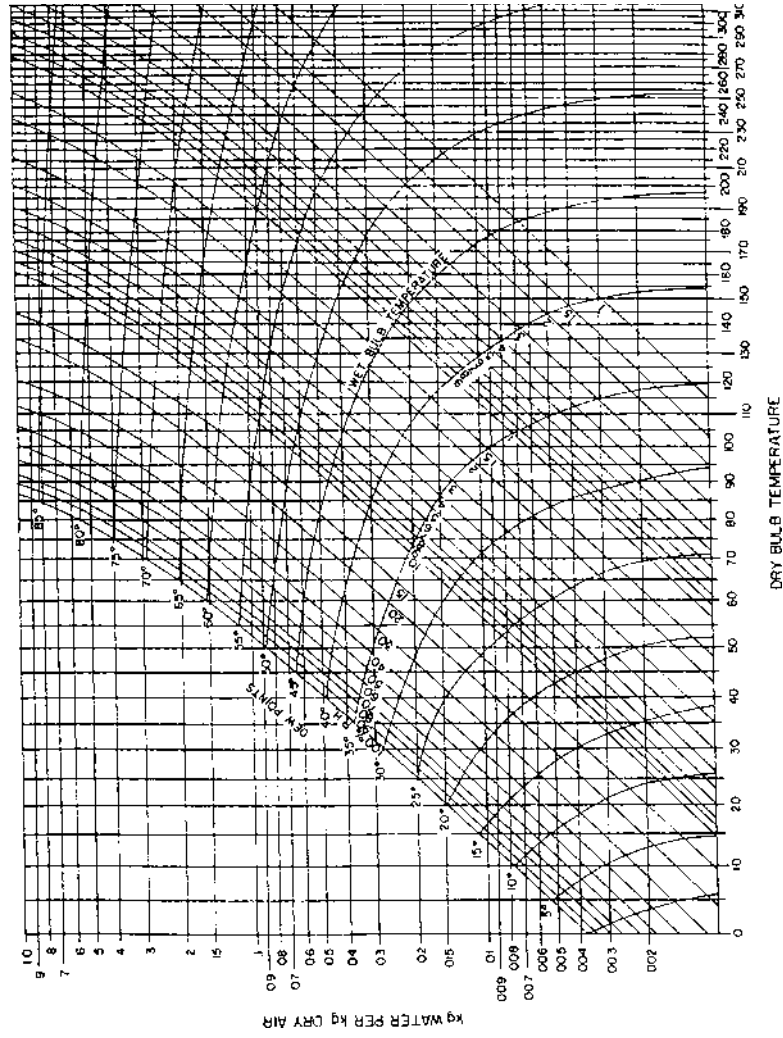


FIGURE 10.5 Psychrometric chart.

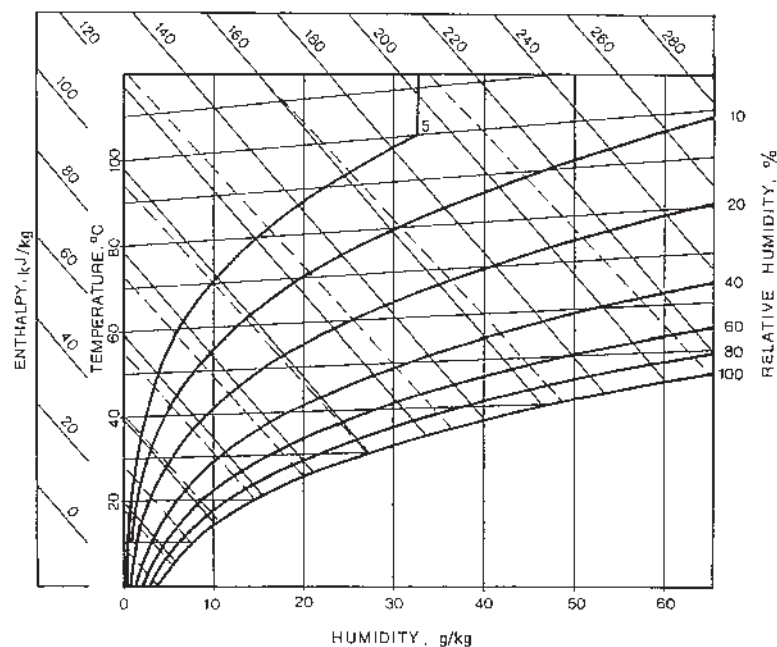


FIGURE 10.6 Enthalpy diagram for humid air.

The psychrometric chart is also useful in visualizing various process paths and obtaining the parameters resulting from these processes. Figure 10.4 shows the representation of several processes in an air–water mixture.

Figure 10.5 shows a psychrometric chart in more detail allowing the estimation of air–water mixture parameters. Another useful humidity chart is the enthalpy–humidity chart, which allows the direct estimation of enthalpy for any combination of Y and T , or Y and RH. It is shown in Fig. 10.6.

D. Energy and Material Balance on an Air Dryer

Consider a steady-state operation of a continuous dryer operating in a counter-current mode as shown in Fig. 10.7. (The heat and mass balances would be identical if we chose a co-current operation.) The basis for our balance will be a unit of time. During that unit time the amount of food solids entering and leaving the dryer is s (kg), the corresponding amount of dry air entering and leaving the dryer is G (kg). In addition to energy entering and leaving as a result of the food and gas streams, we consider additional heat Q (kJ) (e.g., supplied by an electric heater during the unit time) and heat loss Q' (e.g., loss to dryer walls).

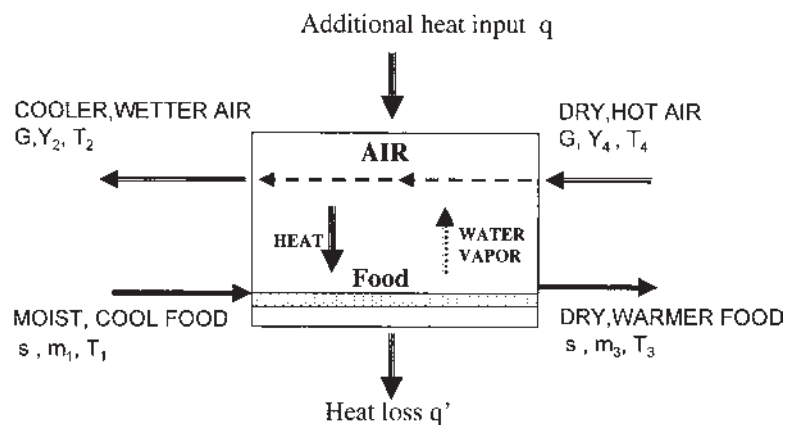


FIGURE 10.7 Schematic representation of material flows in a dryer.

The mass balance on the dryer is then given by

$$sm_1 + GY_4 = sm_3 + GY_2 \quad (11)$$

where m = moisture content (kg water/kg solids). In doing the energy balance we assume that vaporization takes place at the food exit temperature T_3 and that the latent heat of vaporization of the water in the food is the latent heat of pure water at that temperature. The balance is given by

$$\begin{aligned} Q + G\{c_{pA}(T_2 - T_4) + c_{pV}Y_2(T_2 - T_4)\} \\ = Q' + s(m_1 - m_3)[c_{pV}(T_4 - T_3) + \Delta H_V] + sc_{ps}(T_3 - T_1) \\ + sm_1(c_{pL})(T_3 - T_1). \end{aligned} \quad (12)$$

where c_{pL} is the specific heat of liquid water ($\text{kJ kg}^{-1}\text{C}^{-1}$) and c_{ps} is the specific heat of solids ($\text{kJ kg}^{-1}\text{C}^{-1}$).

E. Transport of Water in Foods

Dehydration is combined heat and mass transfer process the principles of these processes were discussed in previous chapters. It may worthwhile, however, to review the mechanisms by which water in foods moves within the food during dehydration. Three important modes of transport are usually of consequence: diffusion of liquid water, capillary transport, and diffusion of water vapor.

Diffusion of liquid water is driven by concentration differences, and its rate is given by

$$\frac{dw}{dt} = -DA \frac{dc}{dx} = -DA\rho_s \frac{dm}{dx} \quad (13)$$

where

- D = diffusivity of liquid water in the food (m^2/s).
- dw/dt = diffusional flux of liquid water (kg/s).
- A = cross-sectional area for diffusion (m^2).
- c = concentration of liquid water (kg/m^3).
- ρ_s = density of solids (kg/m^3).
- m = water content ($\text{kg water}/\text{kg solids}$).
- x = distance in direction of diffusion.

Water flow due to capillarity depends on capillary radius. For a single capillary the pressure difference due to capillary suction is given by Eq. (14) and is represented schematically in Fig. 10.8.

$$l = \frac{2\gamma}{rg\rho_L} \quad (14)$$

where

- l = pressure difference as height of water (m).
- r = capillary radius (m).
- g = acceleration due to gravity (m/s^2).
- ρ_L = density of liquid (kg/m^3).
- γ = surface free energy.

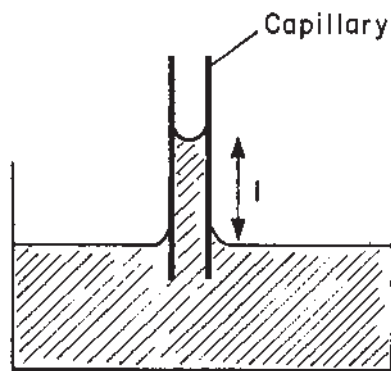


FIGURE 10.8 Schematic representation of capillary rise.

The pressure difference in Fig. 10.8 and Eq. (14) is expressed as the height of a water column supported by capillarity (l).

Flow due capillarity is complex because of the complex system of capillaries existing in food, and for this reason it is preferable to express the transport of liquid water in terms of a *overall liquid diffusivity* D_L , which includes both capillary and diffusional flow:

$$\frac{dw}{dt} = -D_L A \frac{dc}{dx} = -D_L A \rho_s \frac{dm}{dx} \quad (15)$$

The magnitude of D_L depends on water content. Typical pattern of this dependence is shown in Fig. 10.9.

As the water content of food decreases the transport through the system of pores and capillaries is primarily due to flow of water vapor. The rate of this flow may be expressed in terms of a permeability constant B or an effective diffusion coefficient D_{EF} .

$$\frac{dw}{dt} = -Ab \frac{dp}{dx} \quad (16)$$

where b = permeability ($\text{kg m}^{-1} \text{Pa}^{-1} \text{s}^{-1}$), p = partial pressure of water (Pa),

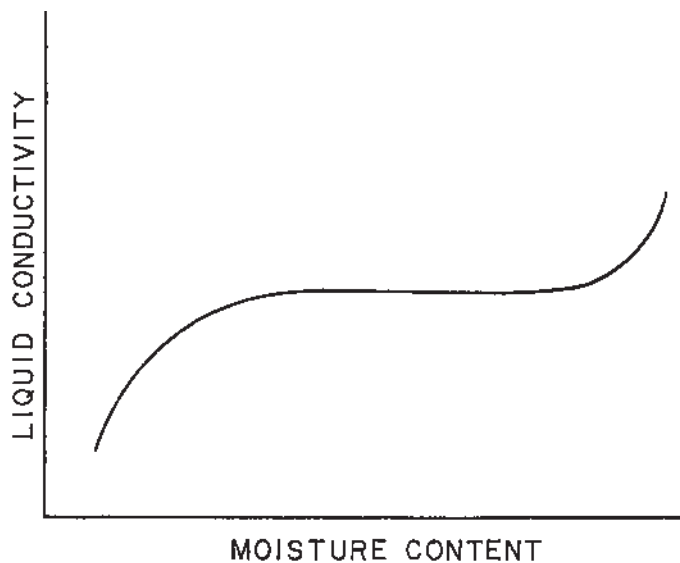


FIGURE 10.9 Dependence of liquid conductivity on moisture content.

and

$$\frac{dw}{dt} = -D_{\text{EF}}A\rho_s \frac{dm}{dx} \quad (17)$$

III. AIR-DRYING OF A SLAB UNDER CONSTANT CONDITIONS

A. Idealized Mechanisms of Drying of a Slab

It is instructive to consider the air drying of a food model under conditions that simplify analysis. We will consider the dehydration of a slab under conditions in which the air is in large excess so that its properties may be considered constant. Under these conditions the drying time may be divided into a constant rate and a falling rate periods.

1. Constant Rate Period

As is the case with most rate processes, the rate of drying obeys the principle rate = driving force/resistance.

The driving force for drying is the partial pressure of water in the food minus the partial pressure of water in the air: $p_{\text{food}} - p_{\text{air}}$. Since in our model the conditions of air, notably its temperature T_a and RH are constant, p_{air} remains constant throughout drying. During the constant rate period p_{food} remains constant, because the slab surface is saturated with water, and remains at $T = T_w$, and $p = p^\circ$ in a manner similar to what we described for drying of a water film.

During the constant rate period the only resistance to drying is in the air since the internal resistance in the food is low enough to maintain the surface at saturation. Since the conditions in the air are constant, the resistance is also constant and so is the rate, which is controlled entirely by transfer of heat and mass in the air.

The loss of water per unit area of the slab is given by [Eqs. (5) and (6)]

$$-\frac{dw}{dt} = k_g A (p^\circ - p) = k_g' A (Y_S - Y) = \frac{hA(T_a - T_w)}{\Delta H_V}.$$

The constant rate period continues as long the supply of water to the surface suffices to maintain saturation of the surface, that is, a surface temperature remaining at T_w , and water partial pressure at p at p° . One explanation for the cessation of constant rate period is the appearance of “dry” patches, reducing the area for evaporation. In our model slab however we assume that the conditions are uniform at any given slab depth (direction opposite to the direction of water transport) including depth *zero*, the surface level. There are also good physical

reasons to assume that in surface plane there are no significant differences in p , so that our assumptions seem justified.

It is useful to divide materials to be dehydrated into two categories: hygroscopic and nonhygroscopic. Our definition of a nonhygroscopic material is one in which at all water contents $p = p^\circ$. In hygroscopic materials, however, $p < p^\circ$ below a moisture content m_h characteristic for given material.

Therefore, for nonhygroscopic materials, $p = p^\circ$ for all values of m . For hygroscopic materials, $p = p^\circ$ for $m_h < m$ and $p < p^\circ$ for $0 < m < m_h$.

In the idealized situation of a slab we can divide the drying of nonhygroscopic materials into two periods and of hygroscopic into three periods as shown in Figs. 10.10 and 10.11.

In the first period the water removed from the surface is constantly resupplied by flow to the surface as shown in Eq. (18) [based on Eqs. (5) and (16)] resulting in constant drying rate $(dw/dt)_1$.

$$-\left(\frac{dw}{dt}\right)_1 = k_g A (p^\circ - p_a) = -D_L A \rho_s \frac{dm}{dx} \quad (18)$$

where p_a = partial pressure of water in air. The first period ends when the internal water supply fails to saturate the surface. The set of conditions which result in

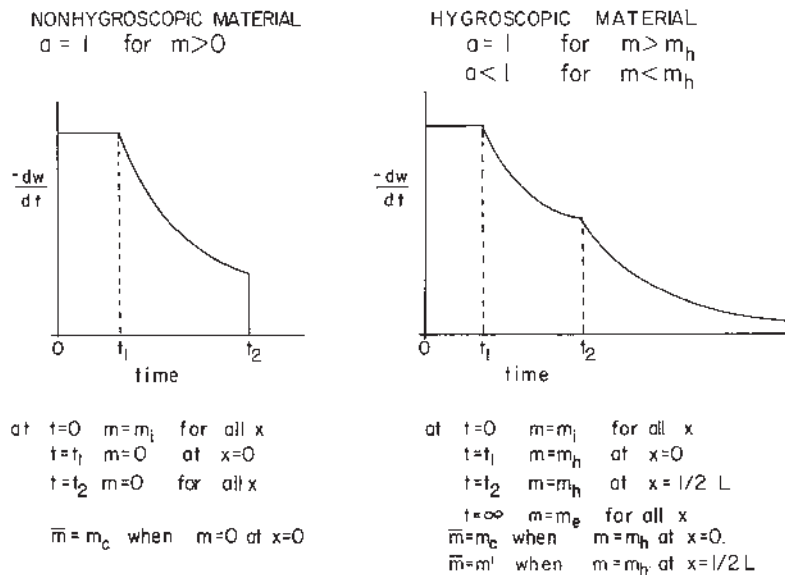


FIGURE 10.10 Drying rates in hygroscopic and nonhygroscopic materials.

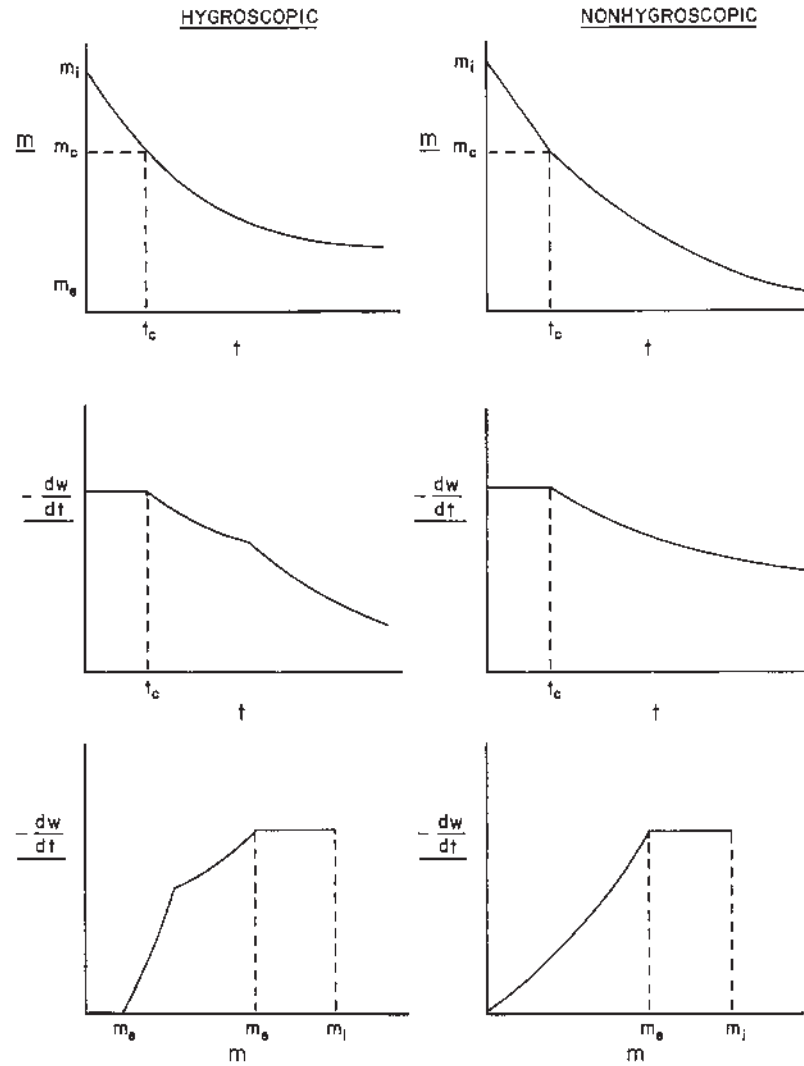


FIGURE 10.11 Drying curves for hygroscopic and nonhygroscopic materials.

the onset of the second period (falling rate period) may be presented in the form of so called break-point curves.

Under our idealized conditions the average moisture content at which the constant rate period end (m_c) is given by

$$m_c = \frac{1}{3} \frac{k_g(p^\circ - p_a)L}{D_L \rho_s} = \frac{1}{3} \frac{h(T_a - T_w)L}{(\Delta H_V)D_L \rho_s} \quad (19)$$

where L = slab thickness (m).

As illustrated in Fig. 10.12, the above relation allows the correlation of the critical moisture content with properties of air and properties of the material being dried. Note that the critical moisture content is not a property since it depends on air properties as well as on geometry (e.g., slab thickness). The reasons for deviations from linearity shown in Fig. 10.10 are due to nonconformance of actual conditions with the ideal conditions assumed in the model underlying Eq. (10). These ideal assumptions include

1. m at the slab surface is zero at the end of the constant rate period.
2. Liquid diffusivity is assumed to be independent of moisture content.
3. Bulk density of solids and slab thickness remain constant (i.e., no shrinkage).

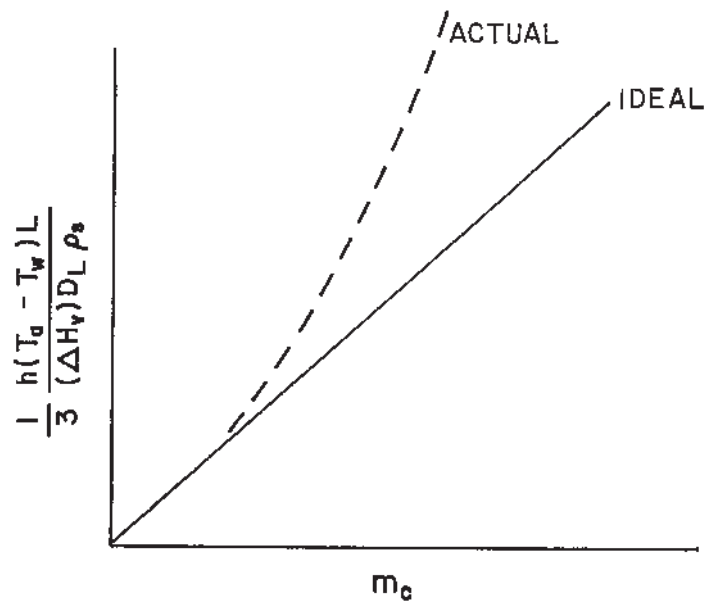


FIGURE 10.12 Ideal and actual relations determining the critical moisture.

2. Diffusion Model for the Falling Rate Period

The constant rate period is followed by the *falling rate period*. Analysis of the rate of drying in this period is less simple than in the situation during the constant rate period.

If it is assumed that below m_e drying is entirely mass transport limited (insignificant effect of heat transfer resistance) and that the transport occurs by diffusion, the following differential equation (Fick's second law) may be used:

$$\frac{dm}{dt} = D_{EF} \frac{d^2m}{dx^2} \quad (20)$$

The solution of the above differential equation is often difficult. The effective diffusion coefficient D_{EF} may depend on process variables and may change during the falling rate period. In addition shrinkage, which may not be isotropic, changes the geometry of the system. Simple solutions are readily available in the literature for the following simplified boundary conditions:

1. Unchanging geometry.
2. At the beginning of the period, m is the same throughout the object (e.g., slab).
3. Constant D_{EF} .

Series solution for slabs, spheres, and cylinders are available in literature. Eq. (21) gives a solution for a slab (m is the average moisture content at time t , m_e is the moisture content in equilibrium with the air, and m_i is the moisture content at beginning of the falling rate period).

$$\phi = \frac{m - m_e}{m_i - m_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp - \frac{(2n+1)^2 \pi^2 D_{EF} t}{L^2} \quad (21)$$

An approximate solution for a slab over an extended period of drying is given by

$$\phi = \frac{8}{\pi^2} \exp - \frac{\pi^2 D_{EF} t}{L^2} \quad (22)$$

Equation (22) predicts a linear relation between the natural logarithm (\ln) of the unaccomplished moisture change (ϕ) and time (t), with a slope proportional to $(-D_{EF}/L^2)$. This equation is best applied to "long times," that is, to periods when fractional unaccomplished moisture change $(m - m_e)/(m_i - m_e)$ is less than 0.6. The equations for short times as well as for long times are shown in Fig. 10.13 for accomplished moisture change: $(m_i - m)/(m_i - m_e)$. In Fig. 10.14 we show schematically the ranges of applicability of the two approximate solutions.

Full solution for the **slab**:

$$\frac{M(t)}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \cdot \pi^2} \exp\left(-\frac{D(2n+1)^2 \pi^2}{4l^2} t\right)$$

↑
Inconvenient: infinite series

Approximate solutions for the **slab**:

'Short times'

$$\frac{M(t)}{M_\infty} = \frac{2}{\pi^{1/2}} \left(\frac{Dt}{l^2}\right)^{1/2} \sim t^{1/2} \quad \frac{Dt}{l^2} \ll 1$$

'Long times'

$$\frac{M(t)}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{D^2}{4l^2} t\right) \quad \frac{Dt}{l^2} \gg 1$$

Dimensionless diffusion number:

$$\frac{Dt}{l^2}$$

FIGURE 10.13 Approximate solutions of the diffusion equation.

3. Receding Plane Models

In considering the drying of a nonhygroscopic, nonshrinking solid it is possible, and often convenient, to assume a receding plane in the slab dividing a dry layer from a layer at which the solid contains water. The assumed model is shown schematically in Fig. 10.15. At the dry and wet layer interface the absolute humidity of the air in the pore solids is in equilibrium with water in the wet layer, and its value is defined as Y_E . At the interface between the dry layer and air

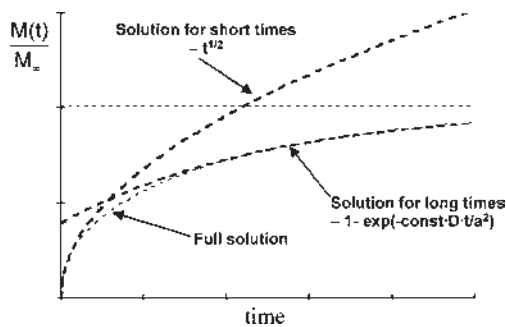


FIGURE 10.14 Graphical representation of approximate solutions of the diffusion equation.

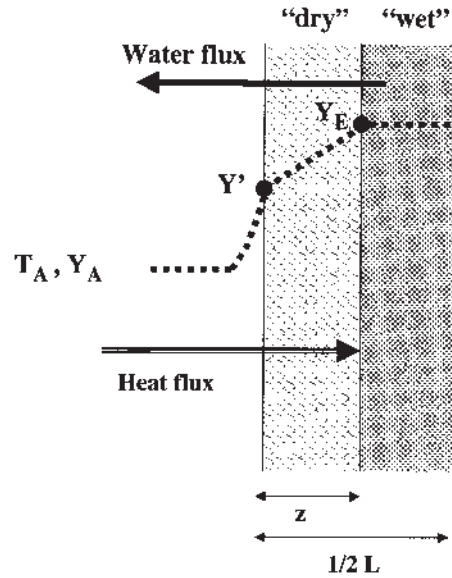


FIGURE 10.15 Heat and mass transport in air drying of a slab.

the absolute humidity is Y' . The water flux is then given by

$$-\frac{dw}{dt} = K(Y_E - Y_A) \quad (23)$$

The model allows the representation of the drying process in a humidity chart and the calculation of drying rates. These calculations are beyond the scope of the present chapter, but the reader is referred to Pakowski and Mujumdar (1995).

B. Calculation of Drying Rates Using Experimental Results

In Fig. 10.10 we noted the complex drying behavior of hygroscopic solids. It is possible, however, to simplify the analysis of drying rates of slabs, by representing the drying curves as shown in Fig. 10.16. Two periods of drying are assumed. The first is the constant rate period during which the rate is given by Eq. (18).

The second period is the falling rate period in which the drying rate is given by Eq. (24) in which we use the symbols $r(c)$ for the constant rate and $r(f)$ for

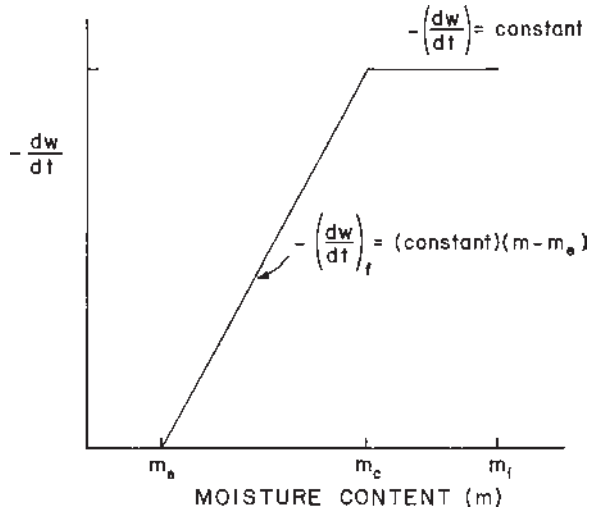


FIGURE 10.16 Simplified rate curve for drying of a slab.

the falling rate period

$$r(f) = \text{constant}(m - m_e) = \frac{r(c)}{m_c - m_e}(m - m_e) \quad (24)$$

where m_e is the moisture content in equilibrium with the humidity of the air.

For simplicity's sake we shall consider drying from one side of the slab only. Since $dm/dt = (dw/dt)/(\text{weight of solids per unit area face area of slab})$,

$$\frac{dm}{dt} = \frac{dw/dt}{A(1/2L)\rho_s} \quad (25)$$

Since the quantity $A(1/2L)\rho_s$ is constant in the slab model assumed in our derivation it is evident that the rate of moisture content m change with $m - m_e$ may be represented by a graph analogous to that in Fig. 10.15. This plot is shown in Fig. 10.17.

We can now combine Eq. (25) and Eq. (18) to obtain Eq. (26) valid in the constant rate period (for $m_c < m < m_i$):

$$-\frac{dm}{dt} = K_1 = \frac{k_g'(Y_s - Y_a)}{\rho_s(L/2)} = \frac{k_g(p^\circ - p_a)}{\rho_s(L/2)} = \frac{h(T_a - T_w)}{\rho_s(L/2)(\Delta H_V)} \quad (26)$$

The constant K_1 is thus readily obtainable if bulk density of solids, slab thickness, and properties of air are known.

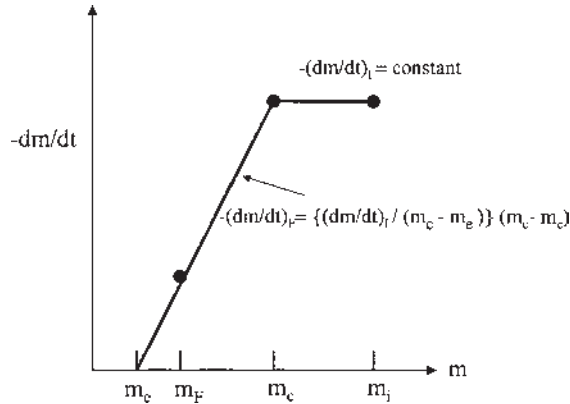


FIGURE 10.17 Graphical representation of drying rates in constant and in falling rate periods.

Integration of Eq. (26) shown below gives the duration of the constant rate period (t_c).

$$\int_{m_c}^{m_i} dm = \int_{m_i}^{m_c} -dm = K_1 \int_0^{t_c} dt \quad (27)$$

The integration yields

$$t_c = \frac{m_i - m_c}{K_1} \quad (28)$$

By inspection of the geometry of Fig. 10.13 it is apparent that the falling rate portion of the drying curve follows the relation

$$-\frac{dm}{dt} = \left(-\frac{dm}{dt}\right)_l \frac{m - m_e}{m_c - m_e} \quad (29)$$

We can now combine Eqs. (26) and (29) to obtain

$$-\frac{dm}{(m - m_e)} = \frac{K_1}{m_c - m_e} \quad (30)$$

Integration of this equation gives the drying time in the falling period t_F .

$$t_F = \frac{m_c - m_e}{K_1} \ln \frac{m_c - m_e}{m_f - m_e} \quad (31)$$

This relation is sometimes described in literature as the proportional-to-thickness law because t_F is proportional to $1/K_1$ and thus directly proportional to L .

The relation is then contrasted with the so-called diffusion law [Eq. (22)], which gives for t_F

$$t_F = \frac{4L^2}{\pi^2 D_{EF}} \ln \frac{m_c - m_e}{m_F - m_e} \quad (32)$$

The difference, however, is only apparent. In Eq. (31) t_F is proportional to $L(m_c - m_e)$, and when $m_c \gg m_e$, it is proportional to Lm_c . Since m_c is proportional to L [Eq. (19)], in effect the drying time in the falling rate is proportional to L^2 in both “laws.”

Very often in the drying of food materials there is no discernible constant rate period, and the usual practice is to use Eq. (32), with the effective diffusion coefficient estimated from the drying data itself. Often several segments of the drying curve with different values of D_{EF} are used to estimate the drying time. In any case the total drying time is equal to $t_C + t_F$.

C. Characteristics and Significance of the Slab Model

Most of the drying operations are performed on materials which are not slabs. However the model is useful in revealing the nature of the mass transfer–heat transfer coupling in the drying operation. The drying relations developed on the basis of this model can also be used directly in drying of a number of geometries of products. They may be applied directly not only to slabs but also to “beds,” that is, to layers of particles which collectively are slab-like. With relatively minor modifications Eq. (21) may also be applied to drying of spheres and of cylinders. The values of D_{EF} have been tabulated for many materials so that a preliminary estimate of drying times can be made on the basis of literature values. However, since D_{EF} depends on properties specific to specific batches and preparations of materials (e.g., porosity, cell structure, and in the case of beds, particle size) these values must be confirmed experimentally. Most of the values reported in the literature for a variety of food products range from 10^{-11} to 10^{-9} cm^2/s for typical drying conditions (Okos and Narsimhan, 1992). The effective diffusivity depends on temperature and in most materials on moisture content. Diffusivity to water for most materials drops at very low water contents, as shown in Fig. 10.18. Dependence of diffusivity on temperature is usually assumed to follow the Arrhenius equation with activation energies in the range of 20 to 40 kJ/mol for porous materials. Materials with low porosity may have much higher activation energies at low moisture contents, and it has been suggested that the WLF equation (cf. Chapter 5) may be applicable to the temperature dependence of such materials.

The representation of gradients within the drying material is also greatly simplified by assuming the slab model.

During the falling rate period the temperature rises from the initial level equal to T_w , and the moisture content changes throughout the drying material.

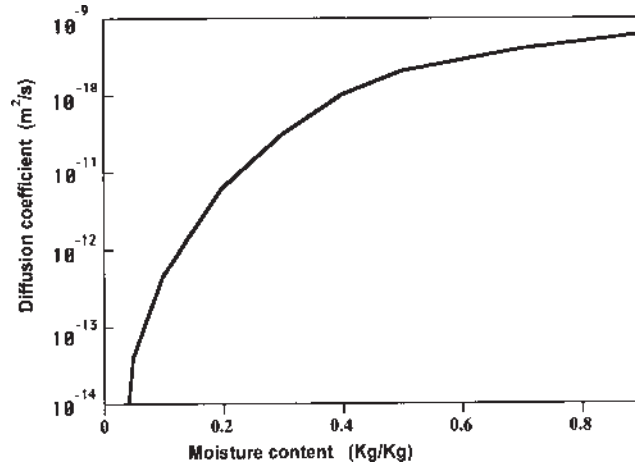


FIGURE 10.18 Typical dependence of water diffusivity in hydrophilic materials on the moisture content.

The relative magnitude of the gradients depends on the relative importance of the mass transport and heat transport limitation as expressed by the Lewis number $Le = \alpha/D$, where α is thermal diffusivity $= k/c_p\rho$.

For air drying, Le is large, the drying is primarily limited by mass transfer, and the temperature gradients in air-drying are minimal while the moisture content gradients are steep. A schematic diagram for temperature and moisture gradients in a slab is shown in Fig. 10.19, and moisture gradients during drying of potato slab, based on experimental data are shown in Fig. 10.20.

D. Shrinkage During Drying

A serious and significant deviation from the assume idealized situation lies in changes of geometry and structure of drying food materials. In dehydration processes other than freeze drying, structural changes in the food materials occur readily since there is the opportunity for viscous flow, solute redistribution, and shrinkage. As a result, the mass transport properties change drastically during the dehydration process, and the geometry deviates from the initial condition. Among the most dramatic changes is the decrease in the effective diffusion coefficient with decreasing moisture content. The effective diffusion coefficient for water in potato starch gel was reported to decrease from 10^{-8} to 10^{-7} cm^2/s . At water contents of 20% to 10^{-10} at water contents below 1% (Fish, 1958).

Fish also described modeling procedures for diffusion in shrinking dehydrating systems, which have been applied subsequently in many forms to

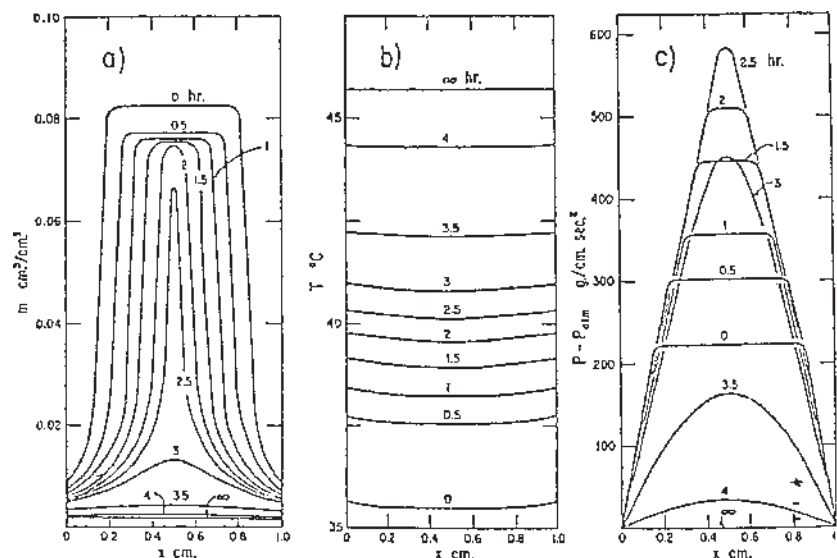


FIGURE 10.19 Typical (a) moisture, (b) temperature, and (c) pressure profiles during drying of a slab.

estimate drying times and moisture gradients. A simplified model for treating drying of shrinking solids was presented in 1986 (Coumans and Thijssen, 1986). Two papers present models for consideration of shrinkage and its effect on drying of apples and of carrots (Crapiste and Whitaker, 1988; Mulet and Bernal, 1989). A more recent paper presented models and experimental results for drying of potato strips. The models considered nonideal behavior features including: shrinkage during drying and properties as functions of local moisture content and temperature. Experimental results were found to conform to the expectations based on the modeling. (Wang and Brennan, 1995a,b). A comprehensive listing and classification of drying models for porous solids was published in 1993 (Waananen and Litchfield, 1993).

The quality of dehydrated foods is often limited in their texture and rehydration capacity. Tough, “woody” textures and loss of juiciness are among these defects. Shrinkage, as well as loss of plasticization by water, contribute to these defects. Changes in structure, density, and porosity of potato during dehydration were related to drying conditions including temperature and rate of drying and to shrinkage (Wang and Brennan, 1995a,b). The inability of water to fully hydrate and plasticize dehydrated materials may be due in part to crystallization and aggregation of the structural food polymers

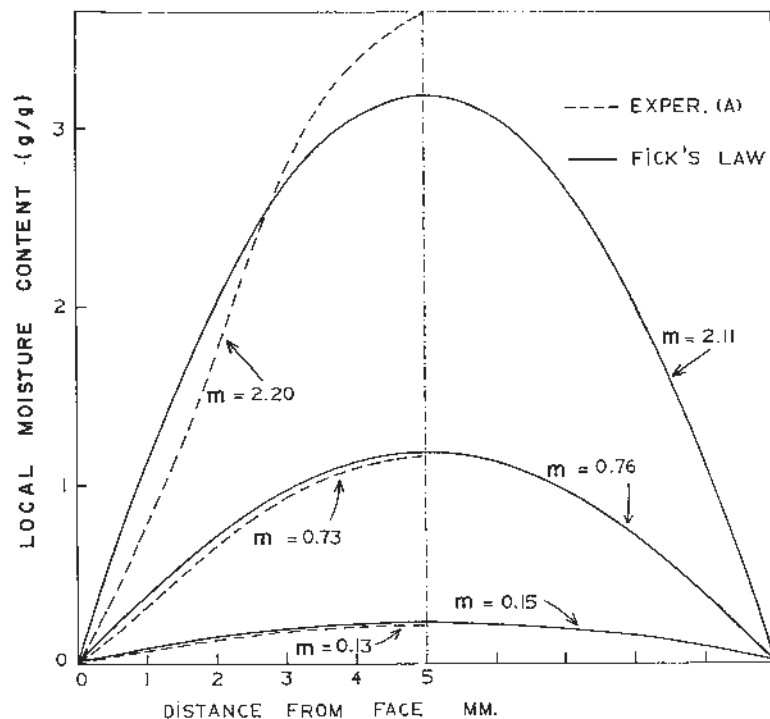


FIGURE 10.20 Experimentally determined and theoretical moisture profile during drying of a slab.

(polysaccharides and proteins) and in part to kinetic effects, which are due to greatly reduced permeability of the matrix through which water must penetrate. Freezing and thawing prior to dehydration are occasionally capable of improving rehydration rates probably because the freeze-thaw process generates porosity through crystal formation. The effectiveness may however be limited, by the ease of “squeezing out” the rehydrated water from the large pores created by freezing.

An interesting method for preventing shrinkage during dehydration of plant tissues was developed and patented by Haas (1977).

In this procedure the tissue is pressurized with certain gases (pressures up to 100 bar), then freezing, then depressurizing, then thawing either prior to or during drying. The effectiveness of different gases was reported to depend on their solubility and diffusivity. The mechanism of the shrinkage-reducing

effect of this procedure was elucidated by King (1974) and appears to be as follows:

1. Upon pressurization the tissue becomes saturated with gas at the high pressure. The amount of gas dissolved depends on its solubility at the high pressure (Bunsen coefficient).
2. Upon freezing the presence of ice crystals promotes gas nucleation and formation of gas bubbles.
3. The ice crystals provide a rigid structure during depressurization preventing the gas bubbles from either expanding or diffusing out of the tissue.
4. Thawing removes the ice structure and allows the bubbles to expand by a factor as much as 70 for the highest pressures used.
5. The growth of bubbles within intact cells creates an internal pressure that pushes some water out by reverse osmosis, it also generates cell wall rigidity. This is probably true for only a part of the bubbles: others disappear as gas leaks out through defects in cell walls.
6. Once thawing and displacement of water is complete, subsequent gas exchange occurs by diffusion; hence, *permeability* of the gas used is the property that along with solubility determines its effectiveness. The retention of the gas during drying is required for the improved texture after drying.

King proposed that the explanation suggested by him predicts that best effects would be obtained by pressurizing with gases that have a high solubility in water and a permeability coefficient for the gas that is equal to or lower than that for air.

The criteria suggested by King were in line with experimental results for most gases used. Methane, air, nitrogen, and ethane gave best results; helium and carbon dioxide were least effective.

IV. DRYING TECHNOLOGY

A. Introduction

Processes for dehydration of foods and biomaterials are very diverse. A detailed description and analysis of these processes and the associated equipment is well beyond the scope of this book. The following sections will introduce some of the key drying methodologies, and outline the principles of their operation. The reader interested in deepening her or his knowledge of drying is encouraged to consult more specialized books. Fortunately some very excellent recent works are available. An excellent review covering the drying principles and applications is the chapter by Okos and Narsimhan (1992). A comprehensive reference on the subject of dehydration is the two volume handbook edited by Arun Mujumdar

TABLE 10.1 A Classification of Some Dryers

| Mode of heat transfer | Batch dryers | Continuous dryers |
|--------------------------|--|---|
| Convection dryers | Tunnel dryers Cabinet dryers | Kiln dryers Belt dryer Rotary dryers Spray dryers Fluidized bed Drum dryer |
| Conduction | Heat shelf dryer Agitated pan dryer | |
| Radiation | IR-heated shelf dryer | IR-heat belt dryer |
| Internal heat generation | Microwave oven | Dielectric dryer Microwave tunnel |
| Mixed | Shelf dryer | Rotary dryer |

(1995). This work is likely to replace the work of Krischer and Kroll (1963) as the “bible” of drying. Mujumdar is also the editor of the series of *Advances in Drying* (Karel and Flink, 1983), which provides reviews of drying research and applications. Readers interested in industrial equipment will find a good introduction in the book by van’t Land (1991). Details of equipment specifications for industrial dryers may also be obtained from manufacturers by searching the “web.”

B. Classification of Drying Processes

Dryers and drying operations may be classified in different ways, such as classification on the basis of mode of heat transfer, operating pressure, and method of conveying materials. Dryers operating at atmospheric pressure may be contrasted with those operating under vacuum. Table 10.1 shows a classification of some atmospheric pressure dryers on the basis of the dominant heat transfer mode and the type of operation (batch or continuous).

An important difference between different types of dryers is the residence time in the dryer. In flash dryers, spray dryers, and drum dryers the residence time is usually well below 1 min. Most continuous dryers operate with a residence time of 1 h or less, batch dryers may require residence time of several hours.

Dryers may also be classified on the basis of the type of transport of the material being dried, as shown in Table 10.2.

C. Convective Dryers

In this section we shall review the operational principles of a number of types of dryer, which have in common the following characteristics:

TABLE 10.2 Types of Material Transport in Dryers

| Transport | Typical dryers | Materials dried |
|-----------------|----------------------------|--------------------------|
| Stationary | Shelf dryer | Suitable for most solids |
| Gravity feed | Rotary dryer | Granules, cubes |
| Mechanical | Belt dryer | Pastes, cubes |
| Carts, trucks | Tunnel dryer | Suitable for most solids |
| Sheets, layers | Drum dryer | Liquids, pastes |
| Air suspended | Fluid bed | Particles |
| Atomized in air | Spray dryer Flash dryer | Liquids, suspensions |

1. The material to be dried is either solid or very viscous liquid and is dried as either as a bed of particles, pieces, a sheet, or pastes of slurries contained in trays.
2. The material is dried in a stream of air.
3. The primary mode of heat transfer is convection, and most or all of the energy is supplied by the air. In some dryers additional heat may be supplied by radiation.
4. The material may be conveyed on belts, conveyors, trays, or trucks or may conveyed pneumatically by the air. We shall discuss the case of fluidized bed dryers in a separate section.

We will consider both batch and continuous dryers. The types of equipment vary enormously in size, design, and operating characteristics. As an example we consider the capacity for convective drying of vegetables (such as chopped parsley or diced peppers, both of which represent important industrially dehydrated materials). A small cabinet or shelf dryer might be suitable for drying a charge of 100 kg of the wet material in a cycle of several hours. Thus its drying capacity might be of the order of 2–3 kg/h of dried material. Continuous process lines in industrial systems may be typically capable of processing several tons of such materials per hour, and the dried product output is of the order of several hundred kg/h.

Atmospheric batch dryers are used when different types of materials are to be dried in a small or seasonal operation. An example is the kiln dryer, which is very old and simple dryer type, but still used in many parts of the world. The dryer is shown in Fig.10.21. It consists of a two story building with a slotted floor separating the drying rooms in the upper story from the rooms in the lower level, which contain burners which heat air. The air containing the combustion gases supply heat to a layer of the product (typically fruit) that is placed on the slotted floor in a layer which may be 20–40 cm deep. The loading and unloading

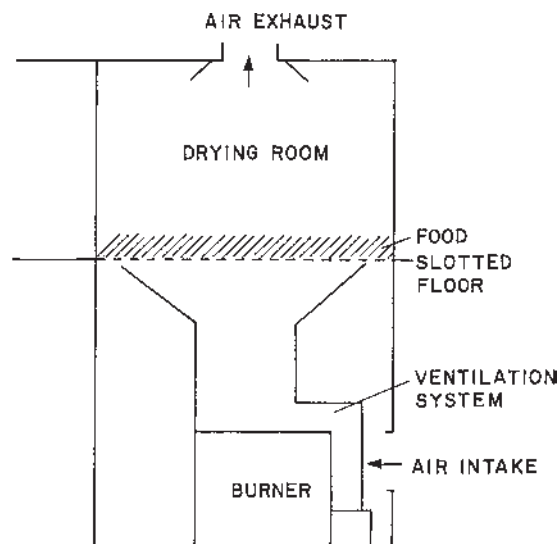


FIGURE 10.21 Kiln dryer.

and periodic raking to assure more or less uniform drying are labor intensive, accounting for much of the cost of the operation. Drying times are long, and the drying is usually carried out only to an intermediate moisture level. (typically 20% water). At this moisture content fruit are quite prone to nonenzymatic browning and are usually treated with sulfite prior to drying. The traditional procedure involved burning sulfite, thus generating SO_2 in combustion gases. Modern procedure rely on sulfite dipping. The semidried product is equilibrated in bulk containers and shipped as "evaporated fruit." It also serves as an intermediate stage for production of dehydrated fruit pieces, which are usually dried in tunnel dryers or in vacuum dryers. Similar designs known as bin dryers are used for drying of grain. Cabinet or shelf dryers are also useful in small scale operations.

Figure 10.22 shows a schematic diagram of a convective shelf dryer. Drying of layers on the shelves may be considered adiabatic if the dryer is well insulated (line A-D in Fig. 10.4). Cabinet dryers may also be supplied with auxiliary heaters as shown in Fig. 10.23. In this case additional heating of the drying material and of the air occurs in the dryer and drying follows a line in the schematic diagram in Fig. 10.4, which lies between A-D and A-C. Batch dryers are useful in evaluating the drying characteristics of the drying material, and can also be used to demonstrate effects of operating variables. The performance of shallow beds on shelves or trays approximates the idealized conditions discussed for drying of slabs and is useful in preliminary design of scaled up continuous

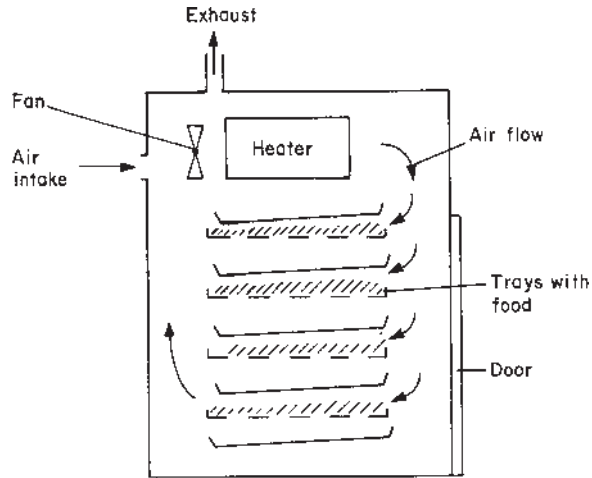


FIGURE 10.22 Drying cabinet.

operations. Table 10.3 shows the expected effects of several process parameters on drying rates of food pieces dried in layers in a batch convective dryer. The symbols used are $(-dw/dt)_I$ is drying rate in constant rate period, t_c is duration of constant rate period, and $(-dw/dt)_F$ is drying rate in the falling rate period.

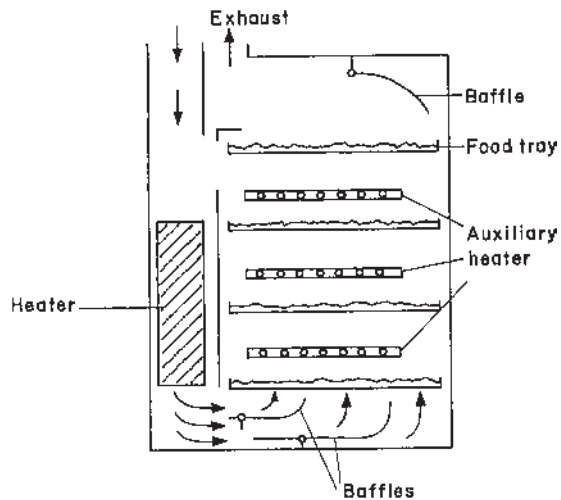
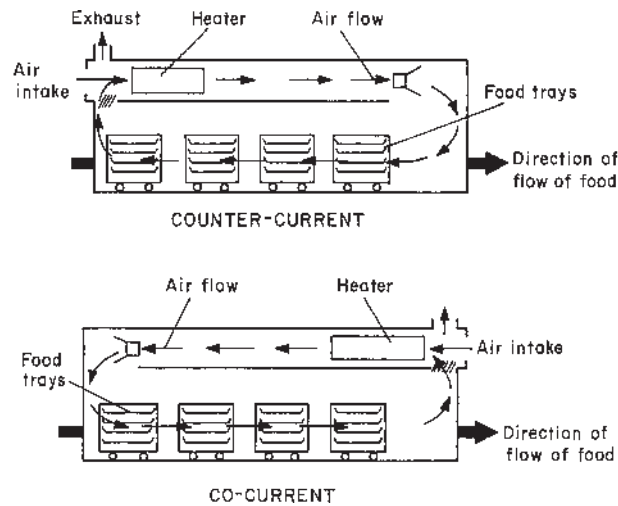


FIGURE 10.23 Drying cabinet with auxiliary heaters.

TABLE 10.3 Effects of Increasing Process Parameters on Rates of Drying

| Parameter | $(-dw/dt)_F$ | t_c | $(-dw/dt)_F$ |
|-------------------------|----------------------------|-----------|--------------|
| Air velocity (G) | Varies with $\sim G^{0.8}$ | Decreases | Minor effect |
| Air temperature (T) | Proportional to $T - T_w$ | Decreases | Increases |
| Air humidity (Y) | Decreases | Increases | Decreases |
| Piece size | Decreases | Decreases | Decreases |
| Bed depth | Increases | Varies | Varies |

There exist many variants of product and air flow in continuous convective dryers. The principle is illustrated in Figs. 10.24 to 10.26, which show different arrangements of product and air flow. The industrial equipment is however much more sophisticated than the simplified schemes show in these diagrams. Computer-assisted instrumentation and state-of-the-art sensors allow variation of process parameters with time and with distance (or stage) in the drying system. However, the simplified analyses we have presented for representation of

**FIGURE 10.24** Schematic representation of flows in co-current and counter-current tunnel dryers.

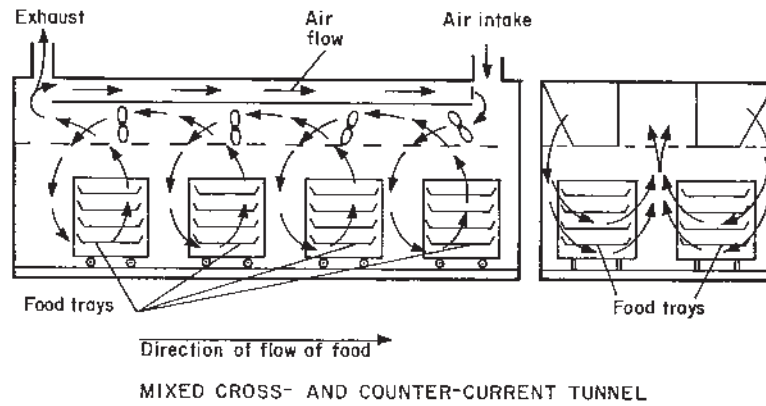


FIGURE 10.25 Schematic representation of flows in a mixed cross-current and counter-current tunnel dryer.

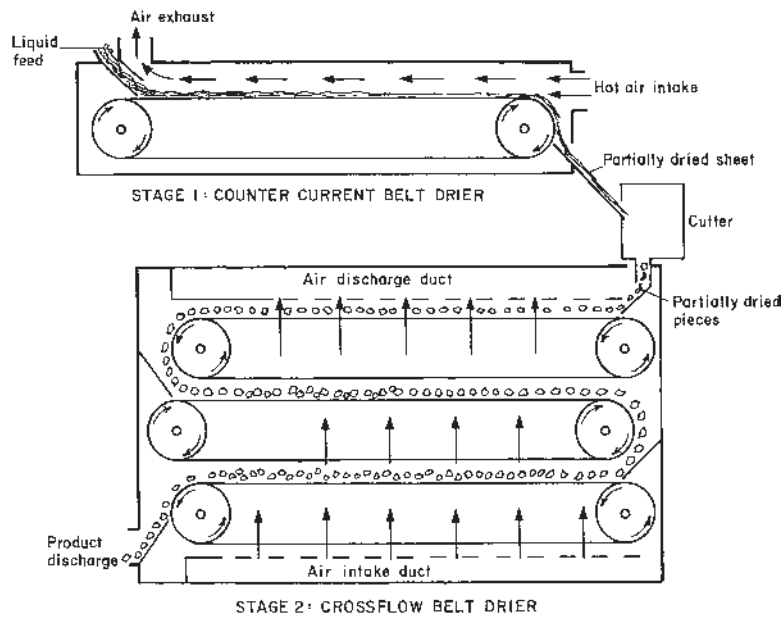


FIGURE 10.26 Belt dryers.

processes in humidity diagrams can be readily applied to continuous convective driers. Figure 10.27 shows the expected pattern of local temperature in convective driers.

The convective driers lend themselves to simplified design calculations based on the simplified approaches we considered for the case of a slab being dried in excess air, even though the actual drying operation are certainly not carried out using excess air at constant conditions. It should be obvious that doing so would mean discharging hot air from the driers without utilizing most of their drying capacity (which depends of temperature difference). It is desirable to discharge the air as cold and as wet as can be done without impairing the efficiency of the drying process.

The following illustrative example may be useful in understanding how simple analyses can aid in drying process design.

1. Illustrative Example

Part 1. Consider a drying process in which 1000 kg/h of sliced onions are to be dried in continuous, convective dryer. Their initial water content is 83%

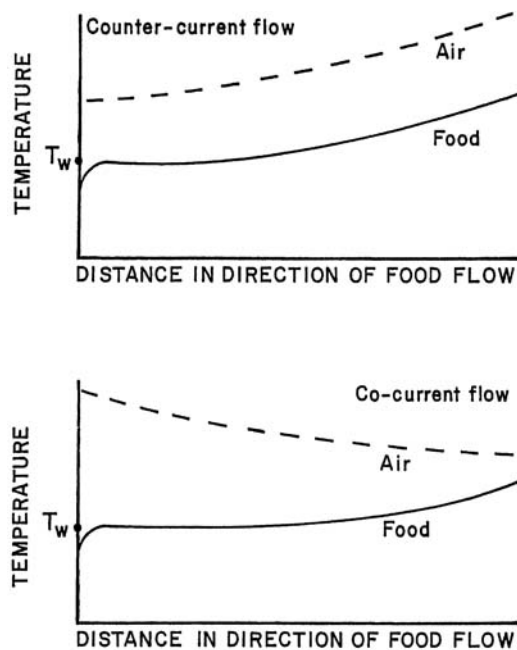


FIGURE 10.27 Temperature profiles in tunnel driers.

and the final water content 8%. The air enters at a temperature of 120°C and an RH of 1.2%. It exits at a temperature of 50°C and an RH of 55%. Assume that all the energy for drying is provided by the cooling of the air and that the losses to the dryer wall are insignificant. We can also assume that the food enters at T_w .

The first calculation we perform is the amount of air flow required by doing a mass balance given by

$$sm_i + GY_i = sm_e + GY_e$$

The amount of solids entering and exiting ($s = 0.17(1000) = 170$ kg/h). The initial moisture content (m_i) is $0.83/17 = 4.9$ kg water/kg solids. The exit moisture content (m_e) is $8/92 = 0.087$.

We use the psychrometric chart shown in Fig. 10.5 to determine the values of Y_i and Y_e using the known values of T and of RH. They are 0.015 and 0.045 kg/kg respectively.

$$G = \frac{s(m_i - m_e)}{Y_e - Y_i} = \frac{170(4.81)}{0.045 - 0.015} = 27250 \text{ kg dry air/h}$$

Assuming a density of air of 1.2 kg/m³ the required air flow is 22710 m³/h.

Part 2. Consider the dryer in example part 1. It is desired to reduce the required air flow. However, the initial temperature of the air must not exceed its current value of 120°C, and it is not feasible to lower the exit temperature below 50°C because the driving force for heat transfer would be lowered too much. What other steps could be taken? It is clear that the amount of water picked up per kg of air must be increased. However the entering air is already at a very low RH, and further dehumidification would be of little value. A solution would be to have the air exit at the same temperature but at a higher RH. This of course would deviate the humidification path from adiabatic saturation (which is equivalent to the T_w line). Such a deviation requires additional heat. Assuming that we allow the air to exit at 80% RH, Y_e would rise to 0.065 kg/kg, and the mass balance would give

$$G = \frac{s(m_i - m_e)}{Y_e - Y_i} = \frac{170(4.84)}{0.065 - 0.015} = 16500 \text{ kg dry air/h}$$

We have managed to reduce the amount of required air by approximately 11000 kg/h. Of course there is a price to pay. We need a heater to supply

the additional energy. We can obtain the amount of required energy directly from an enthalpy–humidity diagram shown in Fig. 10.6.

$$\begin{aligned}
 \text{Power required} &= G[(\text{enthalpy at } 50^\circ\text{C } 80\%\text{RH}) \\
 &\quad - (\text{enthalpy at } 50^\circ\text{C, } 55\%\text{RH})] \\
 &= (16500 \text{ kg dry air/h})(220 - 180)\text{kJ/kg dry air} \\
 &= 660 \text{ MJ/h} = 183 \text{ kJ/s}
 \end{aligned}$$

This power output corresponds to 183 kW.

Part 3. In the calculations in parts 1 and 2 we postulated a desired throughput and calculated the corresponding requirement for air flow. These calculations, however, tell us little about dryer size. To estimate that extremely important design factor, we require additional information. The first critical parameter to be estimated is the drying area required. To estimate it we need the drying rate (per unit drying area) and a loading factor determining the mass of product per unit area. We will consider the situation postulated in part 1 of the present example, that is, adiabatic drying, with no additional heat source. The wet bulb temperature of the air remains constant in such a process, and as long as the surface of the food is saturated (i.e. in the constant rate period), the food remains at that temperature as well. To simplify the estimation we will consider a two-stage process as shown in Fig. 10.28. We can now apply the constant rate Eq. (6) to estimate the drying rate: $-dw/dt = hA(T_a - T_w)/\Delta H_V$. We can estimate the value of the heat transfer coefficient (h) on the basis of literature values. We will assume a value of $100 \text{ (W m}^{-2} \text{ s}^{-1}\text{)}$, and a value of ΔH_V of 2.4 MJ/kg . From the psychrometric chart we obtain $T_w = 40^\circ\text{C}$. However we need to consider the change in the air temperature. In the simplified analysis of drying in excess air, that temperature remained constant. In our example the air enters at 120°C and exits at 50°C . We overcome this difficulty by using the log mean temperature difference $(\Delta T)_m$ between air and the food surface in modified Eq. (6):

$$\begin{aligned}
 -\frac{dw}{dt} &= \frac{hA(\Delta T)_m}{\Delta H_V} \\
 (\Delta T)_m &= \frac{(\Delta T)_{\text{exit}} - (\Delta T)_{\text{entrance}}}{\ln[(\Delta T)_{\text{exit}}/(\Delta T)_{\text{entrance}}]} = \frac{10 - 80}{\ln(10/80)} = 37^\circ\text{C}
 \end{aligned}$$

We enter the value in modified equation

$$\frac{h(\Delta T)_m}{\Delta H_V} = \frac{100(37)}{(2.4 \times 10^6)} = 0.00154 \text{ kg m}^{-2} \text{ s}^{-1} = 5.55 \text{ kg m}^{-2} \text{ h}^{-1}$$

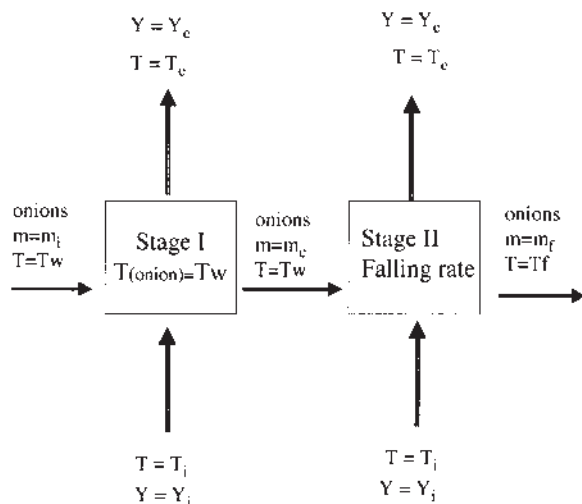


FIGURE 10.28 Conditions in a hypothetical two-stage dryer.

In order to complete the estimates for the size of the first stage, we require an additional parameter: the critical moisture content. To estimate the value of m_c we could use Eq. (19) with a literature estimate of D_L and a specification of L , or the m_c value could be estimated in preliminary experiments. We will assume a value of $m_c = 2.5$ kg water/kg solids. We will also assume a bed thickness of 0.05 m (a layer of onion slices approximately 2 in thick). We will also assume a bulk density of solids of 85 kg/m^3 corresponding to approximately 50% porosity.

The total amount of water to be removed in stage I is equal to $s(m_i - m_c) = 170(4.9 - 2.5) = 408$ kg/h. Since the drying rate is $5.55 \text{ kg m}^{-2} \text{ h}^{-1}$ the area required is 74 m^2 .

Estimating the area in stage II is somewhat more complicated. During the falling rate period the temperature both of the air and of the drying material change continuously, as shown schematically in Fig. 10.27. There are two short cut approaches. One is to assume the validity of Eq. (31), in spite of the fact that this equation assumes constant air temperature. The other approach is to assume validity of Eq. (22), and using a literature value of D_{EF} that is most appropriate to the drying material and the temperature range and moisture content range of the material during the drying period. The third and most accurate approach would be to carry out an iterative numerical calculation, which with assistance of an appropriate computer program could provide an accurate drying profile. In all of above cases we also need information about the equilibrium moisture content for the exit air conditions. This is best obtained experimentally. We will assume

$m_{\text{eq}} = 0.04$ kg water/kg solids and will assume that the rate of drying in stage II depends on local moisture content as shown in Fig. 10.16 and given by Eq. (24):

$$r(f) = \frac{r(c)}{m_c - m_e} (m - m_e)$$

We now obtain the average $r(f)_{\text{av}}$ for stage II, using log mean rate average.

$$r(f)_{\text{av}} = \frac{r(f)_{\text{exit}} - r(f)_{\text{entrance}}}{\ln[(r(f)_{\text{exit}})/r(f)_{\text{entrance}}]}$$

$$r(f)_{\text{entrance}} = r(c) = r(f)_{\text{av}} = 5.55 \text{ kg m}^{-2} \text{ h}^{-1}$$

$$\begin{aligned} r(f)_{\text{exit}} &= \frac{r(c)}{m_c - m_e} (m_{\text{exit}} - m_e) = \frac{5.55}{2.5 - 0.04} (0.08 - 0.04) \\ &= 0.105 \text{ kg m}^{-2} \text{ h}^{-1} \end{aligned}$$

$$r(f)_{\text{av}} = \frac{0.105 - 5.55}{\ln(0.105/5.55)} = \frac{-5.45}{-3.96} = 1.37 \text{ kg m}^{-2} \text{ h}^{-1}$$

Water to be removed in stage II is $(m_c - m_{\text{exit}})(s) = (2.5 - 0.08)(170) = 411$ kg/h. The area required is therefore $411/1.37 = 300 \text{ m}^2$. The total area of the two stages (almost 400 m^2) may seem very large, however, by using multiple and wide conveyor belts, the tunnel length need not be enormous. A drawing of a process line for drying vegetables shown in Fig. 10.29 (courtesy of Sandvik Co.) may provide a perspective.

D. Flash Dryers and Fluidized Bed Dryers

Very high rates of drying may be achieved by drying individual particles surrounded by a stream of hot air. Dryers performing these operations are called *dispersion dryers*.

There are several types of dispersion dryers, and we shall discuss three of them, namely flash dryers, fluidized bed dryers, and spray dryers.

Very high drying rates are achieved in *flash drying*, defined as a process in which particles are carried by a stream of hot air. The system is relatively simple and a schematic diagram of it is shown in Fig. 10.30. Gas velocities are in the range of 10–30 m/s, and the method is suitable for particles smaller than 1–2 mm. The residence time is extremely short, typically 1 s or less. The drying occurs usually only in the constant rate period, with the product temperature at T_w . Since the critical moisture content is proportional to particle radius and the radius is very small, it is possible to achieve low water content in the flash dryer exit. If the exit

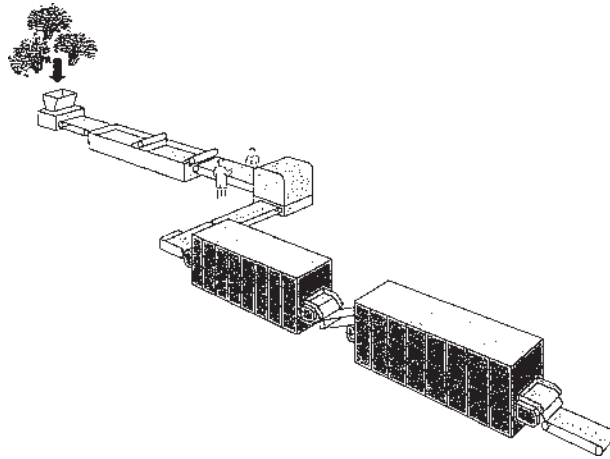


FIGURE 10.29 A dried parsley line. (Courtesy of Sandvik Co.)

moisture content is above the desired final condition, finish drying may be accomplished by following the flash drying with fluidized bed drying.

Fluidized bed drying is a process in which the drying stream of air is passed through a bed of the particles, which are to be dried. The distinctive feature of the fluidized drying is that the bed behaves as a fluid. A simple fluidized dryer diagram is shown in Fig. 10.31. The interaction between the air stream and

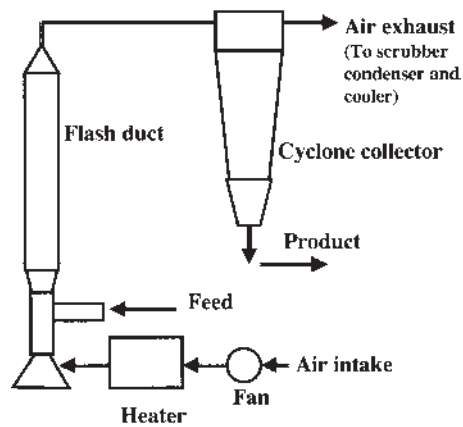


FIGURE 10.30 Schematic representation of a flash dryer.

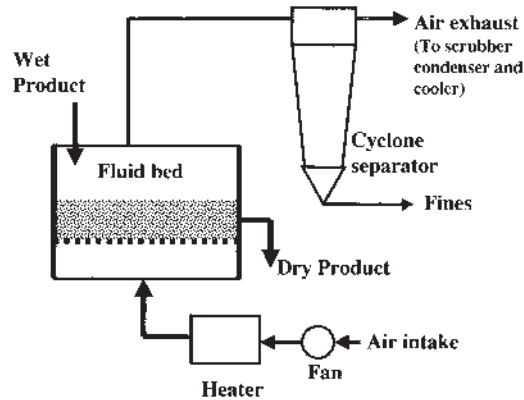


FIGURE 10.31 Schematic representation of a fluidized bed dryer.

the particles assumes different forms depending on particle size and gas velocity. At low velocities the air percolates through the fixed bed of particle. As the velocity of the gas increases, the particles become suspended in the gas stream, and the particle bed behaves as a fluid. The velocity at which the fluidization occurs is known as the velocity of incipient fluidization (U_o), and is determined by the pressure drop across the bed, which then equals the weight of the particles per unit the area of the bed. At velocities much in excess of (U_o) bubbles of the gas pass through the fluidized bed. The bubbles contribute to bed mixing. At still higher velocities the particles are entrained in gas and move with it, as was the case in the flash drying. The heat and mass transfer are greatly facilitated by the fluidization. The heat needed for evaporation may be supplied entirely by the air, in which case the drying follows the path of adiabatic saturation, or it may be also supplied by heated surfaces. Figure 10.32 shows schematically the dependence of the heat transfer coefficient on the air velocity in the bed dryer. It is evident that fluidization drastically amplifies the heat transfer. The equations relating U_o and the pressure drop at incipient fluidization (ΔP_o) to air and particle properties are shown below:

$$\Delta P_o = (\rho_s \rho_g)(1 - \varepsilon)Lg \quad (33)$$

where ρ_s and ρ_g are densities of particles and of the gas, respectively, ε is the bed void volume, L is the bed height, and g is acceleration due to gravity.

The value of U_o corresponding to (ΔP_o) depends on void volume, particle shape factor, and particle size fluid viscosity. Many equations have been proposed to estimate this velocity. Strumillo and Kudra cite 12 different equations (Strumillo and Kudra, 1986 p. 227).

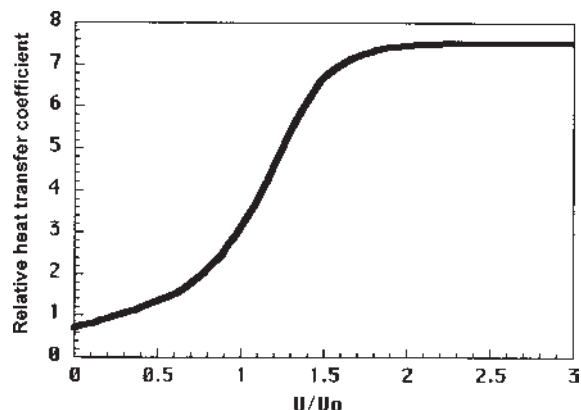


FIGURE 10.32 Effect of air velocity in a fluidized bed dryer on the heat transfer coefficient.

According to Hovmand (1995) the Kozeny Carman equation for flow in porous media may be applied as a good approximation:

$$U_o = \frac{\varepsilon^3}{5(1 - \varepsilon)^2} \left(\frac{\Delta P_o}{S\mu L} \right) \quad (34)$$

where S specific area of the particle and μ is fluid viscosity. Fluidized bed drying is applied to many different products. Materials suitable for fluidization generally have particle sizes between 20 μm and several millimeters, have a regular shape, must be able to withstand vigorous mixing, and not be sticky.

Fluidized beds are available in various sizes and adaptations from a number of equipment manufacturers. Okos in his review of food dehydration (Okos and Narsimhan, 1992) lists a number major variations in fluidbed design. Among these is the vibrated fluid bed dryer, often used for sticky or fragile products.

In this dryer the particles are transported by vibration of the chamber at 5 to 25 Hz, and the velocity of air is relatively low, often below U_o .

Among the applications to foods, he notes drying of grains, legumes, milk, potato granules, and cocoa. Air velocities used were between 1.8 and 16 m/s. The final moisture content of dried food items ranged from 4 to 20%. Drying times are reported to be in the range of 5 to 30 min and depend on particle size and the desired final water content. Drying is most rapid if all of the dehydration occurs in the constant rate period. Strumillo and Kudra report the range of gas velocities in fluid bed dryers at 0.1 to 10 m/s (Strumillo and Kudra, 1986).

Specifications of various dryers ranging from table top laboratory dryers to fluidbed dryers 30 m long are readily available from the manufacturers, most of whom post these on their sites on the internet.

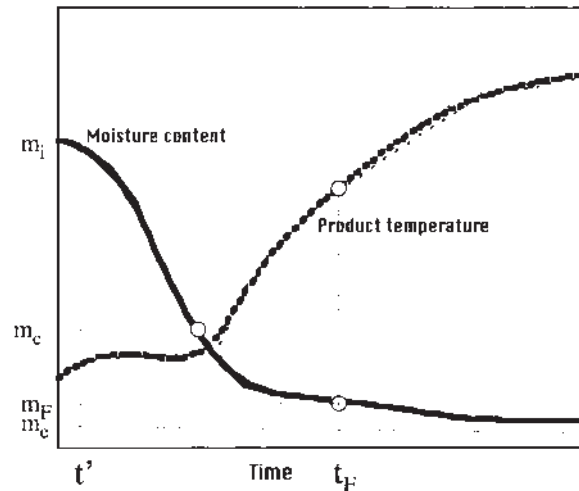


FIGURE 10.33 Schematic representation of moisture and temperature profiles in a fluidized bed dryer.

Figure 10.33 shows the pattern of moisture content decrease and temperature rise under air conditions existing in a fluidized bed. It also shows the typical range of fluidized bed operation from t' (the onset time of fluidization) to t_F (the end of drying in a batch dryer or product exit time in a continuous dryer). As mentioned previously the range of drying in a flash dryer is usually narrower and does not extend much below the critical moisture content (m_c).

E. Spray Drying

1. Principles of Spray Dryer Operation

Spray drying is the most important method for drying liquids including solutions and suspensions. Among the most important applications in the food industry are drying of dairy products, including skimmilk as well as full fat milk, and of coffee. Many other food products are spray dried, including fruit juices and purees, eggs, protein, and starch hydrolyzates. Spray drying is a dispersion drying process since it involves drying of droplets surrounded by air.

The principle of spray drying seems simple, but the actual operations are among the most sophisticated and technically accomplished food processing methodologies. In principle spray drying consists of the following. A liquid or slurry is sprayed (atomized) into a drying chamber, where it comes in contact with air at controlled temperature and humidity. The dry particles surrounded by the air are pneumatically conveyed to separation equipment where they are

separated from air, collected, and either packaged or conveyed to additional processing steps (e.g., “instantizing”). A schematic diagram presenting the process is shown in Fig. 10.34.

Each of the steps, so simply described, actually constitutes a complicated and delicately balanced engineering operation, requiring close control. This control requirement starts with the feed pumping. Thus the properties of the feed, including temperature, viscosity, surface tension, and chemical composition, must be controlled. Even at this first stage special operations may be necessary to optimize subsequent process steps and the properties of the final product. Some of these operation may included homogenization of the liquid feed and incorporation of air or of other gases prior to atomization. Atomization is of critical importance and may require specialized equipment. Mass and heat transfer in the drying chamber are complex and are affected by the flow pattern imparted to the air and on the paths of the drying particles. The characteristics of the materials may complicate the operation, for instance, materials that become sticky at an intermediate moisture content may adhere to dryer walls, and materials of this type may require specialized design, such as “air brooms,” which sweep particles away from the walls, or jacketed walls providing for cooled wall surfaces.

Atomization is a key part of spray drying, since it controls in large measure particle size distribution as well as particle flight patterns in the chamber. Three types of atomizers are employed. *Centrifugal atomizers* consist of spinning discs or vaned wheels or cups. Liquid is fed into center of the centrifugal atomizer and is ejected in the form of droplets at very high velocities (up to 100 m/s).

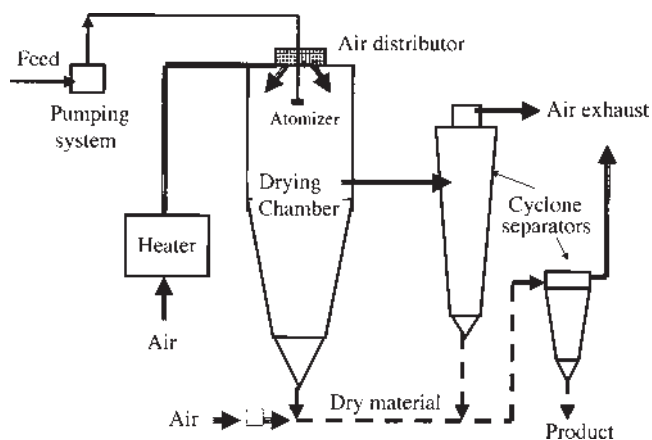


FIGURE 10.34 Schematic representation of a spray dryer.

These atomizers have very high capacity and can handle dispersions as well as solutions. The droplet size is controlled by wheel speed, feed rate, liquid properties, as well as specific atomizer design. Droplets in the range of 1 to 600 μm can be produced.

The mean droplet diameter depends in a complex manner on process parameters and feed properties. The following equation is suggested by Filkova and Mujumdar (1995):

$$d_{av} = c_1 N^{-0.53} M^{0.21} (2r)^{-0.39} \quad (35)$$

where

- d_{av} = droplet diameter
- c_1 = constant depending on liquid properties
- N = rotational speed (rps)
- M = mass feed rate kg/s
- $2r$ = disk diameter (m)

Pressure nozzle atomizers atomize liquids by forcing them through a narrow orifice under high pressure. With these atomizers it is possible to achieve a narrow particle size distribution and to direct the stream of ejected droplets. The range of achievable droplet size is reported as 10 to 600 μm .

The pressure drop across the nozzle is the determining factor in droplet size, as given in the equation

$$d_{av} = \frac{c}{\Delta P^{0.33}} \quad (36)$$

where c is a constant.

Two fluid nozzles produce a spray by using a second fluid, such as compressed air or steam, to atomize the feed. The range of droplet sizes produced in these atomizers is 6 to 600 μm . In these atomizers the droplet size may be related to the volumetric flow rates of the feed fluid and the atomizing fluid (usually air) by

$$d_{av} = \frac{c'}{u} + c'' \left(\frac{V_F}{V_{air}} \right)^{1.5} \quad (37)$$

where c' and c'' are constants depending on feed fluid properties, u is linear velocity of air, and V_F and V_{air} are volumetric flow rates of feed fluid and atomizing air, respectively.

The sprayed droplets encounter the hot air in several possible modes, the air flow may be co-current, counter-current, or mixed. The temperature distribution and rate of initial drying are strongly affected by these arrangements.

The course of subsequent drying and the properties of the dry powders produced depend critically on the physical processes occurring during this initial contact between the spray and the hot air used for dehydration. Figure 10.35 presents schematically the possible structures developing from the droplet.

The pattern of drying in the spray dryer is complex and difficult to model theoretically—a number of recent computer modeling and experimental studies are, however, likely to make the task more manageable. The complexity arises from the great number of variables that affect the process.

Typical operating parameters reported for spray drying of dairy products are

Entering moisture content is 48 to 85%.
 Exit moisture content is 2.5 to 5%.
 Inlet air temperature is 150 to 220°C.
 Outlet temperature of air is 50 to 100°C.

The drying is considered to follow the adiabatic saturation line during the constant rate period, and the rate falls once the diffusion in the particle becomes controlling.

The factor controlling the conditions adapted for drying is the quality of the product.

The key quality determinants of dairy powders include ease of reconstitution, reduction of free fat content in fat-containing powders (free fat is not encapsulated within the glassy sugar-protein matrix of the powder), appropriate bulk density, and absence of defects due to nonenzymatic browning during drying.

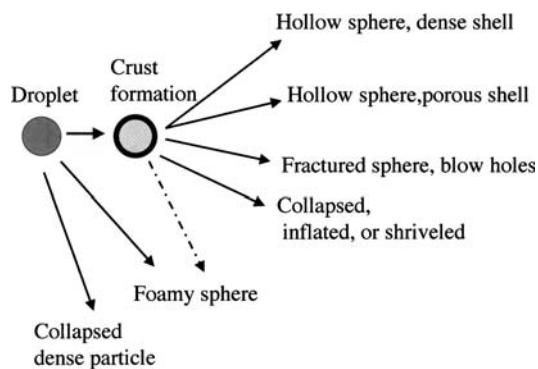


FIGURE 10.35 Morphology of particles produced in spray drying.

Methodology of testing for the quality indicators of spray dried milk is presented by Pisecky (1986).

All of the above factors are strongly affected by temperature and the droplet size. Knipschildt (1986) studied some of these effects. In one trial a constant inlet temperature of 195°C was used to dry homogenized whole milk with 48% solids. The outlet temperature was varied from 75 to 105°C by reducing the feed rate (thus increasing the drying effect by having a greater ratio of hot air to the sprayed liquid). The effects were as follows:

Outlet moisture decreased from 4.75% at 75°C to 1.76% at 105°C.

Solubility was acceptable up to an outlet temperature of 90°C, but was very poor above 105°C.

Free fat content increased from 2.15% to 5.43%.

These quality defects could be overcome to some extent by producing droplets with a very low diameter and therefore a very large surface area.

Smaller particles may also be obtained by decreasing the viscosity of the inlet feed, either by reducing the solids content or by increasing the feed temperature. Both measures have serious disadvantages. Feeding less concentrated liquids is economically undesirable; the cost of evaporation in evaporators is much lower than the cost of drying. Increasing feed temperature is of concern in terms of potential deleterious effects on powder quality.

An extremely important quality factor in spray drying of coffee, tea, juices, and various flavor extracts is the retention of flavor. Because this factor is equally significant in the production of freeze dried materials, we shall consider the principles of flavor retention in both types of drying in a later section of this chapter.

A potential risk in spray drying operations is that of fires and explosions. Powders of combustible materials and food powders, especially those containing fats, are in this category and present a fire hazard. The dependence of these hazards on operational parameters has been analyzed, and steps can be taken to eliminate or reduce these hazards (Synnott and Duane, 1986).

2. Instantized Powders

In most cases it is desirable to have powders that disperse rapidly and completely in water. Powders to which such properties were imparted are known as *instantized powders*. Such powders have the following properties:

- Large wettable area
- Sinkability (do not float on surface)
- Dispersibility or solubility
- Resistance to sedimentation

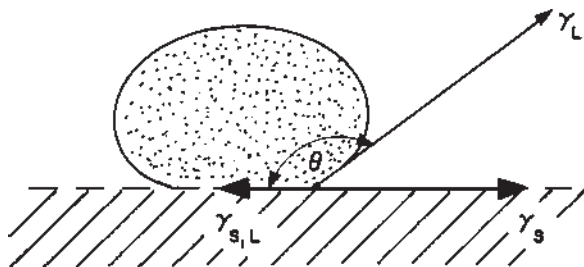


FIGURE 10.36 Representation of the contact angle of a droplet on a solid surface.

The wettability depends on total surface area and on the surface properties of the particles. Figure 10.36 is a schematic representation of forces acting on a drop of liquid on a solid surface. The balance of forces results in formation of a contact angle θ . Equation (38) gives the ideal dependence of this angle on surface properties:

$$\cos \theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l} \quad (38)$$

where γ is the free surface energy (mJ/m^2) and the subscripts s , sl , and l refer, respectively, to solid-air, solid-liquid, and liquid-air interfaces.

Wetting of a solid by liquid, as shown in Fig. 10.37, occurs when the spreading coefficient σ' is positive. Equations (39) and (40) below define σ' and its relation r to the contact angle:

$$\sigma' = \gamma_s - \gamma_{sl} - \gamma_l \quad (39)$$

$$\sigma' = \gamma_l(\cos \theta - 1) \quad (40)$$

Thus the spreading coefficient is positive when the contact angle is zero. To increase the spreading coefficient, we have the options of increasing the surface free energy of solids (increase its polarity) or decreasing the free surface energy of the suspending liquid (e.g., by adding surfactants). In practice problems with poor wetting due to nonpolar nature of the particles are usually due to free fat and are often controlled by addition of lecithin. Assuming that the polarity of the surface is as high as possible, the other obvious course of action is to increase the surface area by creating very small powder particles. This approach, however, is counterproductive. An assembly of small particle tends to clump upon wetting, creating clumps which are wet on the outside, but incompletely wetted inside, and may incorporate air, which makes them float on the surface. This has

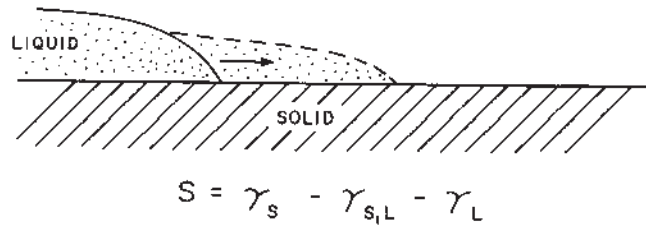


FIGURE 10.37 Representation of forces causing spreading (S = spreading coefficient).

the additional defect of poor sinkability. A sinkable product readily penetrates the liquid and stays submerged.

The most effective and widely used method that is effective in powders with a wide range of polarities is *agglomeration*. In agglomerated products very small particles are fused into large aggregates in which the points of contact between the particles are very limited, so that practically the entire surface area is available to wetting. The aggregates must be stable enough to support this porous aggregate structure through the process of dispersion to assure adequate liquid penetration and to break up only after liquid penetration is complete. Figure 10.38 shows diagrammatically the agglomeration objective. Aggregates of dairy powders produced by agglomeration are typically in the 200 to 1000 μm range. The optimal size depends on the material. Schubert (1990) presents data showing that dispersibility of skim milk powders in water at 21°C increases from 60 to nearly 100% by producing agglomerates larger than 200 μm . In the case of whole milk powders dispersibility was less than 20% at 50°C and rose to over 50% in aggregates over 500 μm in average diameter. Dispersibility greater than 80% required aggregate particles greater than 1 mm.

Instantized powders are produced in processes in which the surface is softened, usually by localized rewetting. Localized rewetting of many food

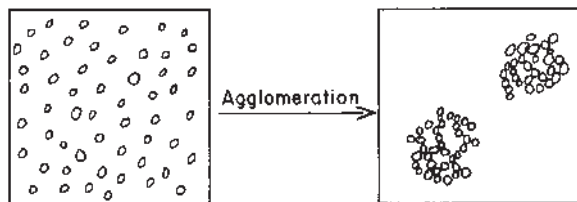


FIGURE 10.38 Schematic representation of agglomeration of particles.

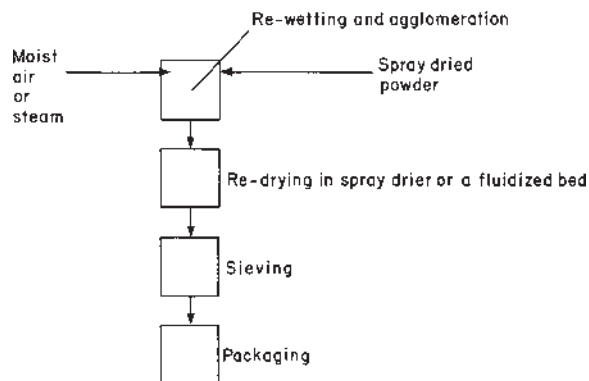


FIGURE 10.39 Schematic representation of an agglomeration process.

powders, including dairy products and coffee, results in localized transition from a glassy to a rubbery state. The degree of rewetting must be controlled very carefully. The rewetted particles are brought into contact and allowed to fuse at the contact points and cooled or dried rapidly in this state resulting in stable aggregates. Many different instantizing processes have been developed that follow this general principle but vary in methodology. Thus rewetting may be a separate stage in the process of part of the spray drying. If a separate process is used, rewetting may be accomplished by exposing free-falling particles to low-pressure steam or by conveying the particles into a chamber and exposing them to a controlled humidity, or a bed of particles may be exposed to a stream of humidified air. Subsequent drying and the time of exposure to the elevated humidity may vary from process to process. A schematic diagram for the process is shown in Fig. 10.39.

Several recent reviews deal with agglomeration and are recommended to the reader. They include papers by Schubert and Pietsch (Pietsch, 1996; Schubert, 1990; Schubert, 1993).

F. Drum Dryers

Among the dryer types in which heat is transferred by conduction are drum dryers. They consist of hollow drums made of high grade cast iron, cast iron plated with chrome alloys, or stainless steel. The drums are heated internally by steam. The feed must be in liquid or slurry form and is applied to the outer surface by one of the several methods schematically shown in Fig. 10.40, namely by dipping, splashing, or spraying or by application devices such as spreading rollers. The dryer may consist of single, twin, or double drums as shown in

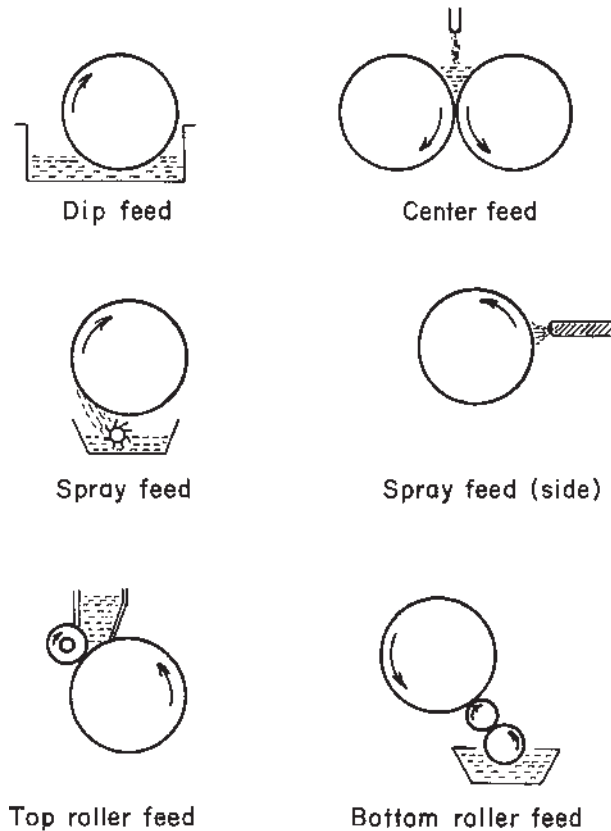


FIGURE 10.40 Application of fluid to drum surfaces in drum drying.

Fig. 10.41. With double drums the thickness of the spread film is controlled by the clearance between the drums, which can be adjusted. When the feed is applied by dipping the thickness depends on physical properties of the feed and the peripheral velocity of the drum. The important physical parameters include the surface tension and the contact angle with drum surface. Efficient spreading of the film is facilitated by very low contact angles and low surface tension of the liquid. The properties of the drum surface are important. Greasy films or spots on the drums can have deleterious effects on the drying rate for several reasons: drying may be slow, thick films may be produced, which dry slowly; heat resistance may increase; and parts of the total drum surface may not be covered.

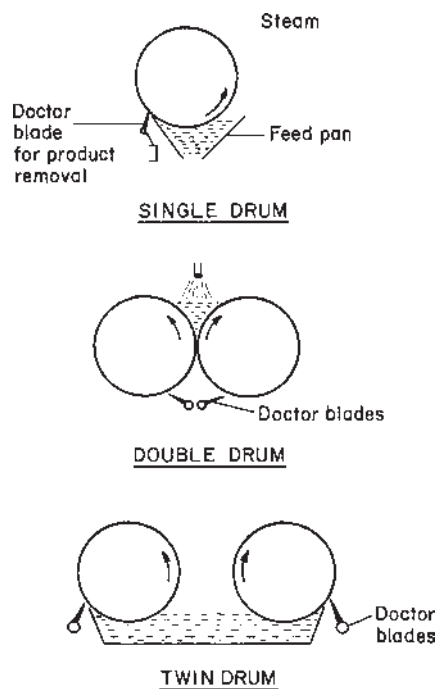


FIGURE 10.41 Some types of drum dryers.

In efficient operations the drying rate is controlled by heat transfer from the interior of the drum to the film and is given by

$$-\frac{dw}{dt} = \frac{UA\Delta T}{\Delta H_v} \quad (41)$$

where U is overall coefficient of heat transfer ($\text{kJ m}^{-2}\text{°C}^{-1}\text{h}^{-1}$), A is drum surface area (m^2), and ΔT is difference between the temperatures of steam and the evaporating surface (°C). The value of U depends on film thickness, drum wall thickness, and its conductivity, on thickness and properties of the condensate on the inner drum surfaces, and on degree of perfection in contact between drum surface and the film.

The most important factors in obtaining a high rate of drying are a large temperature difference and a high value of U . The temperature difference is limited primarily by heat sensitivity of the material being dried. U depends on properties of the drum and thickness and thermal properties of the film.

Under optimal conditions drying capacities can be of the order of 5 to 30 kg of product/m²/h (van't Land, 1991). In addition to assuring an adequate heat supply, drum drying requires efficient removal of water vapor. At atmospheric pressure the removal of 1 kg/h requires a minimum dry air flow of approximately 70 m³/h.

The removal of solids may present special requirements for materials that tend to be plastic at the temperature of discharge (above their glass transition temperature for amorphous materials). In these situations the product may be cooled at the point of discharge by a directed stream of cool, dry air. Additional modifications may include controlled temperature zone at drum periphery by controlling the air flow.

Among the most important drum drying applications are drying of cereals and of potatoes. In 1982 in the United States 48% of the 16-million-ton potato crop was used in processed food products, compared to 34% used unprocessed. Sixteen percent of the processed potatoes were dehydrated in the form of powder, slices, dice, strips, flakes, and granules (Grabowski and Mujumdar, 1992).

Among the most important forms of dried mashed potatoes are potato flakes. In this process potato pulp achieved by mashing is mixed with several additives, which may include milk solids, emulsifiers, chelating agents, and antioxidants. Degree of cell breakage during preparation is important to drying and is controlled by conditions of mashing. The water content at which the slurry is deposited on the drums is typically 78 to 82%. Drum drying on single-drum and double-drum dryers is the methodology applied to producing the granules. The clearance between the drums, drum speed, and drum temperature are controlled, and the final flakes are several mm thick and have a water content of 6 to 7%.

Drum drying is also important in production of cereals, including production of instantized products.

G. Infrared and Solar Dryers

In addition to conduction and convection, heat for drying may be supplied by radiation. The radiation may be supplied by electrically heated elements made of several materials, including tungsten and chromium–nickel alloys. These elements are usually placed inside of quartz tubes. The temperatures of the elements themselves are in the range of 1000 to 2000°C. Radiators may also be gas fired, with the flames heating the radiator surface to temperatures approaching 1000°C.

The fundamentals of radiant heat transfer were discussed in a previous chapter, we may simply note that in drying applications the heat transfer may be assumed to be given by

$$q = K(T_1^4 - T_2^4) \quad (42)$$

where

T_1 is temperature of radiating surface.

T_2 is temperature of food surface.

K is a constant depending on properties of the radiator and the food and on equipment geometry.

q is heat flux in $\text{kJ m}^{-2} \text{s}^{-1}$.

Dryers operating with adequate rates of vapor removal and operating in the constant rate period may be almost entirely limited by heat transfer. The sizing of dryers and prediction of heating rates is usually based on pilot experiments (van't Land, 1991).

Radiant heat supply for drying is of course also available from the sun. Solar radiation has been used in drying of harvested staples for millennia, and in regions in which sunshine is plentiful and the air humidity low, open air drying represents a convenient and least expensive mode of drying. Some crops are dried this way around the world, at least partially, including the technologically advanced countries. Modern solar drying is a recent development and allows to make the process more efficient and capable of producing high quality products. In addition to solar energy collectors, such dryers may include fans for maintaining air flow, energy storage devices, and auxiliary energy generating equipment.

A simple solar dryer is shown schematically in Fig. 10.42, and consists simply of a drying enclosure, and sun-energy collecting surface, and ducts directing convective air flow through a bed of material to be dried.

An array of much more sophisticated systems has been described, engineering principles of operation have been developed, and this methodology

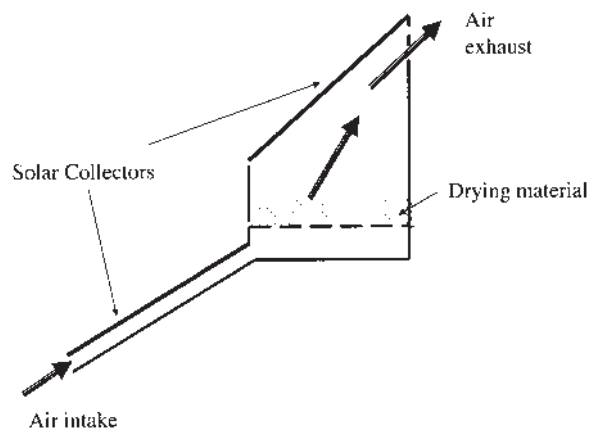


FIGURE 10.42 Schematic representation of a solar dryer.

may continue to increase in importance, especially in view of energy price increases (Imre, 1995).

V. FREEZE-DRYING

A. Introduction

Freeze-drying is a process in which water is transferred from the solid to the vapor state by sublimation, as indicated schematically in Fig. 10.43. To achieve this transfer, the pressure and temperature must be below the triple point for water. The relationship between vapor pressure of ice and its temperature is shown in Fig. 10.44. The partial pressure of water in foods containing ice crystals must equal the vapor pressure of ice when an equilibrium is in existence. Therefore the diagram in Fig. 10.44 also represent the relation between pressure of water in all parts of foods containing ice crystals. The structure of foods is affected differently from that in other forms of dehydration because of the absence of liquid water during the process.

Figure 10.45a represents an idealized freeze drying situation in a slab. There is an interface between the frozen portion of the slab and the dried portion. Water sublimates at the interface, and the water content drops from the initial value m_i to the final value m_f . The dry layer is assume to be at equilibrium with water vapor pressure of the surrounding space. The ideal representation is not realistic, and a more realistic representation is given by Fig. 10.45b, in which a transition zone is postulated in which there is a gradient of water content.

Because in freeze drying the temperature of the drying layer is relatively low and its water content very low, the mobility in it is minimal. The drying is

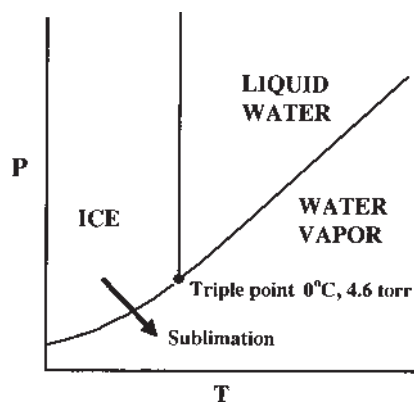


FIGURE 10.43 Representation of sublimation during freeze-drying.

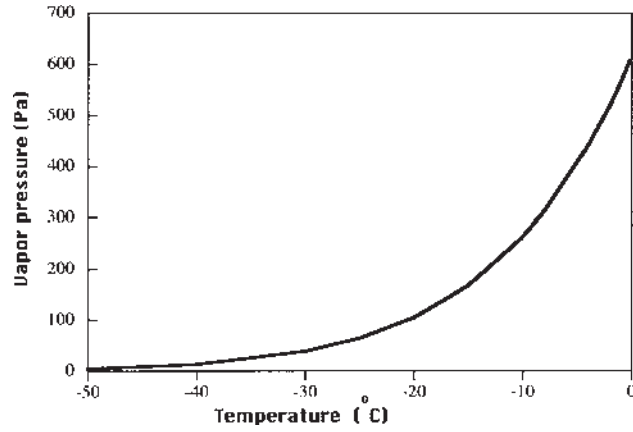


FIGURE 10.44 Vapor pressure of ice as a function of temperature.

conducted below the so-called collapse temperature at which structure changes, porosity decreases, and shrinkage is evident. The collapse temperature depends on material composition and properties as well as on time interval over which the conditions are maintained. In most cases it is very close to the glass transition

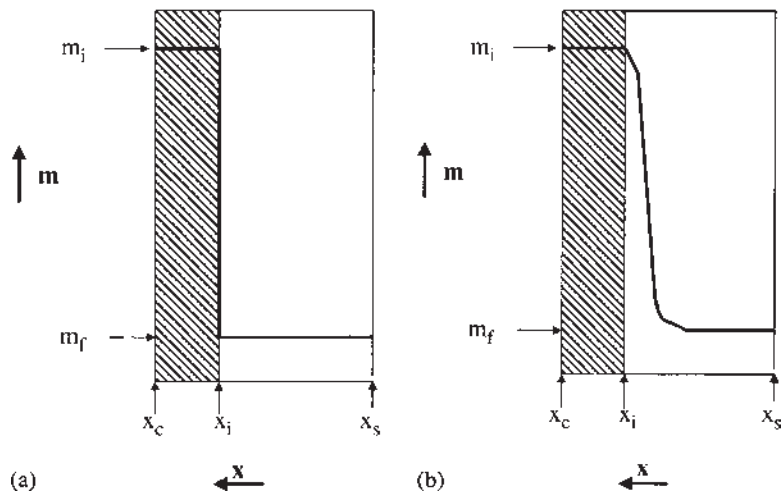


FIGURE 10.45 Moisture gradient in freeze drying of a slab: (a) idealized and (b) actual.

temperature. By conducting the drying under conditions in which the drying material remains in the glassy state several features which benefit quality are obtained: The mobility of the matrix remains low, porosity is maintained and mass transfer of water vapor is facilitated, and the appearance and structure of the original foods are preserved to a large extent. The changes due to chemical reactions are minimal because of limitation on reactant mobility. At the same time, organic compounds, such as flavors, that are contained within the glassy matrix are retained.

These quality considerations and the effect of drying conditions on quality maintenance are discussed in a later section.

B. Heat and Mass Transfer in Freeze-drying

As shown schematically in Fig. 10.46, freeze drying is a coupled heat transfer and mass transfer process. The relative importance of the mass transport and heat transport limitations are expressed by the Lewis number: $Le = \alpha/D$, where α is thermal diffusivity $= k/(c\rho p)$. For air drying Le is large, the drying is primarily limited by mass transfer, and the temperature gradients in air-drying are minimal, while the moisture content gradients are steep. In most freeze drying situations the transfer occurs through a porous layer with a high effective diffusivity and very low thermal conductivity. The value of Le is then low, and heat transfer is often limiting.

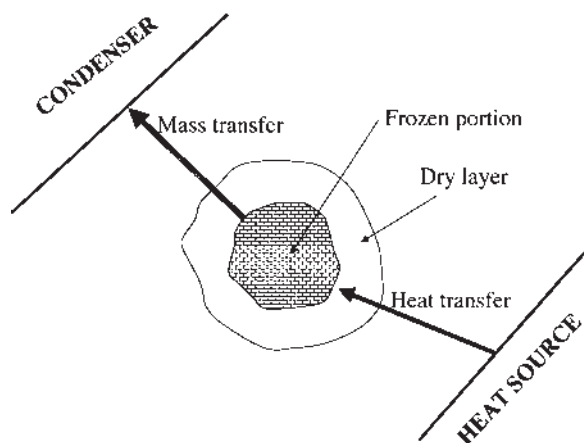


FIGURE 10.46 Heat and mass transfer in freeze-drying.

The coupling of heat and mass transfer may be summarized in

$$\frac{G}{A} = \frac{(p_i - p_c)}{\sum R} = \frac{q}{\Delta H_s} \quad (43)$$

where

G/A = sublimation rate per unit area (kg/m^2).

q = heat transfer per unit area (kJ/m^2).

p_i = partial pressure of water at the sublimation interface (Pa).

p_c = partial pressure of water at the condenser surface (Pa).

$\sum R$ = total resistance to vapor transfer between sublimation interface and condenser ($\text{Pa m}^2 \text{ s}/\text{kg}$).

q = heat transfer to sublimation interface (kJ/m^2).

ΔH_s = latent heat of sublimation (kJ/kg).

The drying rate is dependent on the mode of heat transfer. We shall consider three possible modes of heat transfer feasible in vacuum freeze drying. As we have done in the case of air drying, we will use the example of drying of a slab (Fig. 10.47).

1. Heat transfer and mass transfer take the same path (through the “dry” layer) but in opposite directions.
2. Heat transfer occurs through the frozen layer; mass transfer, through the dry layer.

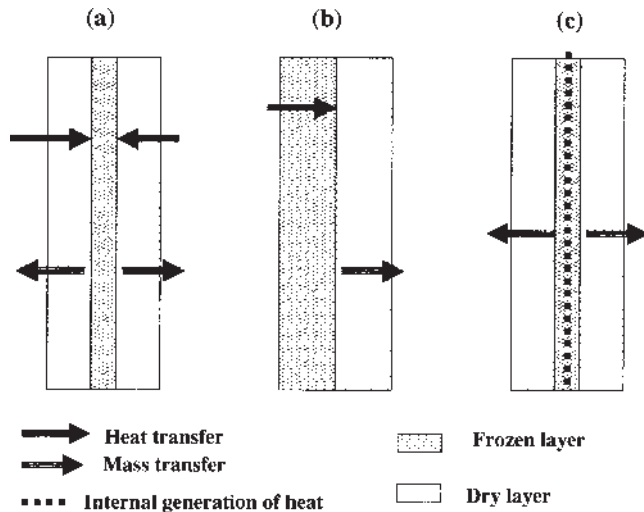


FIGURE 10.47 Three types of heat transfer in freeze-drying of a slab.

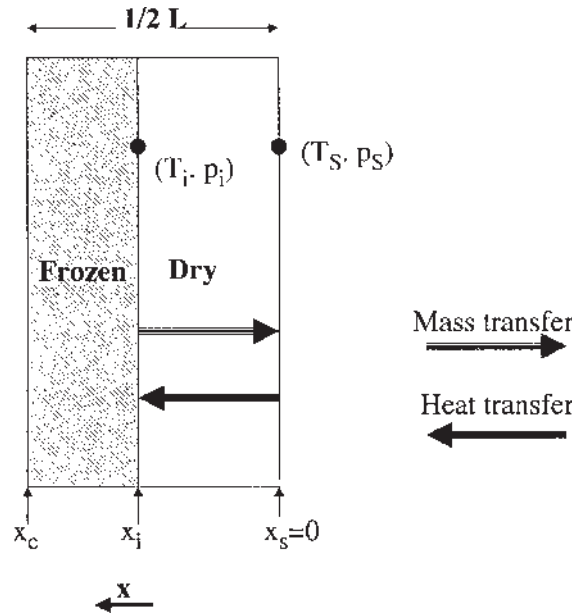


FIGURE 10.48 Heat and mass transfer in freeze-drying of a slab.

3. Heat generation occurs within the frozen layer (by microwave heating).

An additional possibility closely related to the first case exists when freeze drying is conducted at atmospheric pressure.

1. Heat and Mass Transfer Through the Dry Layer

Consider the arrangement, which is simplified but nevertheless typical of most vacuum freeze-drying operations, shown in Fig. 10.48. The slab to be dried is heated by radiation to the dry surface, and its frozen layer temperature T_i is determined by the balance between heat and mass transfer. For simplicity's sake, we consider a slab with negligible end effects. Assume that the surface temperature T_s is reached instantly and is maintained at constant level (e.g., at the maximum temperature permissible for the dry layer because of quality considerations). We assume also that the partial pressure of water in the drying chamber p_s , including at the surface of the dry layer, is constant. Under these conditions the heat transfer at any given time is given by

$$q = Ak_d(T_s - T_i)x^{-1} \quad (44)$$

where k_d is thermal conductivity of the dry layer ($\text{kJ m}^{-1} \text{s}^{-1} \text{°C}^{-1}$), A is sublimation surface area (m^2), and x is dry layer thickness at the given time (m).

The drying rate is given by

$$G = -\frac{dw}{dt} = Ab(p_i - p_s)x^{-1} = \frac{Ak_d(T_s - T_i)}{\Delta H_s} \quad (45)$$

where w is mass of water in the slab (kg), t is time (s), and b is dry layer permeability ($\text{kg m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$).

Assuming slab geometry and a drop of moisture at the sublimation interface from m_i to m_f we obtain a relation between rate of drying and the rate of increase in thickness of dry layer.

$$-\frac{dw}{dt} = A\rho(m_i - m_f)\frac{dx}{dt} \quad (46)$$

In this equation, ρ is the bulk density of solids in the slab (kg m^{-3}). By combining Eqs. (45) and (46), we obtain

$$x dx = \frac{b}{\rho(m_i - m_f)}(p_i - p_s)dt \quad (47)$$

Assuming that the rate of mass transfer is equal to the rate of heat transfer divided by latent heat of sublimation we obtain

$$Ak_d(T_s - T_i)x^{-1} = Ab(p_i - p_s)x^{-1}\Delta H_s \quad (48)$$

And after rearrangement we obtained a relationship between partial pressure and temperature:

$$p_i = p_s + \frac{k_d}{b\Delta H_s}T_s - \frac{k_d}{b\Delta H_s}T_i \quad (49)$$

Since we assume that p_s , b , ΔH_s , T_s , and k_d are constant, we have a linear equation relating p_i to T_i , as plotted in Fig. 10.49. In the same figure we also plot the thermodynamic relation $p_i = f(T_i)$ shown previously in Fig. 10.45. We can see that there is only one point at which the lines representing the two equations intersect. This means that for the idealized assumptions we made, the frozen layer temperature remains constant throughout the drying process until there is not ice left; within the simplified scheme shown in Fig. 10.46a, which is the basis of our calculation, this applies to the entire drying cycle.

As a consequence, Eq. (47) may be readily integrated to give the drying time since it contains only two variables x and t .

We show this in

$$\int_0^{L/2} x dx = \frac{b(p_i - p_s)}{\rho(m_i - m_f)} \int_0^{t_d} dt \quad (50)$$

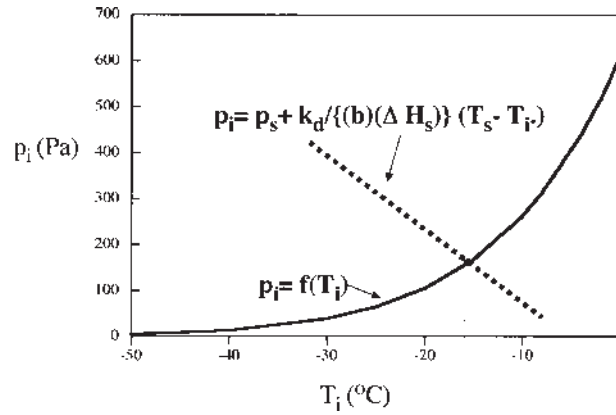


FIGURE 10.49 Representation of equations governing the temperature of the frozen layer in a freeze-drying slab with heat transfer through the dry layer.

The drying time is then

$$t_d = \frac{L^2 \rho (m_i - m_f)}{8b(p_i - p_s)} \quad (51)$$

where t_d is drying time (s) and L is slab thickness (m).

Because of coupling of heat and mass transfer, we could also calculate the drying time based on heat transport rate:

$$t_d = \frac{L^2 \rho (m_i - m_f) \Delta H_s}{8k_d (T_s - T_i)} \quad (52)$$

We see therefore that the drying time depends only on the following properties and variables:

1. Slab thickness (the thicker the slab the longer the process).
2. The difference between the initial and the final moisture contents multiplied by bulk density of solids is proportional to amount of water to be removed. Drying time increases with this quantity.
3. Latent heat of sublimation.
4. Thermal conductivity of the dry layer which decreases with porosity and depends also on pressure of gases other than water vapor.
5. Permeability of the dry layer, which increases with porosity.
6. Maximum permissible surface temperature drying time decreases with increases in this temperature.

7. Partial pressure of water at the surface. Drying time decreases as that pressure, which depends on condenser temperature and on resistance to vapor flow between drying surface and the condenser.

Note that the frozen-layer temperature and corresponding vapor pressure are independent of slab thickness and do not change during drying. While most food do not conform to strict slab geometry, the conditions during industrial freeze-drying of many foods including layers of frozen liquids and slurries, beds of vegetables, and other foods, are not too different from those expected from the above model. During freeze-drying with heat input to the dry surface and conduction through the dry layer, the surface temperature is ideally brought very quickly to the maximum permissible temperature T_s (by radiation from a radiator maintained at very high temperature) and then maintained at T_s by progressively lowering the radiator temperature. T_s chosen is usually determined by quality considerations, especially by the need to minimize undesirable color and flavor changes. The temperature of the frozen layer is determined by dry-layer transport properties and by T_s and p_s . In well designed freeze dryers the resistance to vapor transport in the chamber is kept low, and p_s is only slightly higher than the vapor pressure of water at the condenser (p_c). In freeze drying with conduction through the dry layer therefore the condenser temperature (T_c) is the key determining factor of the frozen layer temperature (T_i) during drying. T_i must remain low to avoid the structural changes lowering product quality. Ideally it should remain below T_g . In materials forming so-called strong glasses (see Chapter 6 for discussion of glass formation), the collapse may be avoided by maintaining the temperature of freeze-drying product somewhat higher than T_g , but fragile glasses such as those formed by most solutions present in foods require drying at T_g or below (Fig. 10.50).

The softening of the food matrix in the vicinity of T_g can be utilized to achieve desirable structural changes. The U.S. Army found it useful to have compressed freeze-dried products, which would be convenient as low weight and low volume field ration components (Emami and Flink, 1979). The original procedure developed by the Army researchers was to rehumidify the freeze dried materials to a level at which they became plastic and allowed compression; the compressed food required an additional rehydration step. Joint work by the U.S. Army and MIT resulted in two variants of the procedure that eliminated the rehumidification requirement. In one variant the drying process was stopped when the average water content of the material corresponded to the collapse temperature at the desired compression. Of course, at a point the gradient in the food was very steep with portions very much below the average and some portion still containing ice, hence existing at the initial water content. The redistribution of the moisture to achieve uniformity was carried out by a controlled microwave treatment, followed by air drying (Karel and Flink, 1983).

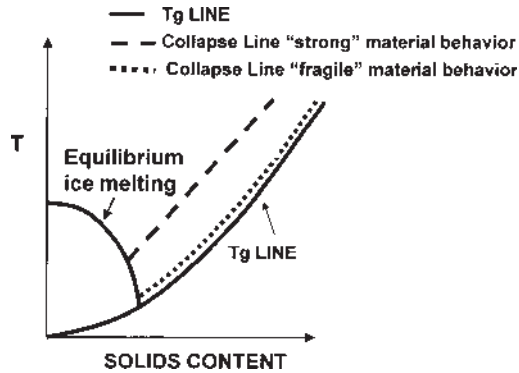


FIGURE 10.50 Collapse of structure during freeze-drying of “strong” and of “fragile” amorphous systems. (Adapted from Witschi, 1999.)

The second variant took advantage of the existence of the gradient in the food during the freeze-drying. In this process illustrated in Fig. 10.51, compression was maintained continuously during the freeze-drying process. At any time during the freeze-drying there existed a gradient of moisture, temperature, and of the corresponding mechanical properties of the material. It was determined that the tangent modulus illustrated in Fig. 10.52 was an appropriate measure of the relevant mechanical properties in compression. Figure 10.53 shows how the tangent depends on moisture and temperature. Figure 10.54 shows the moisture, temperature, and tangent modulus profiles at any given drying instant. The minimum of the tangent curve is located near the ice interface, and it is at this continuously receding location, that the actual compression is continuously

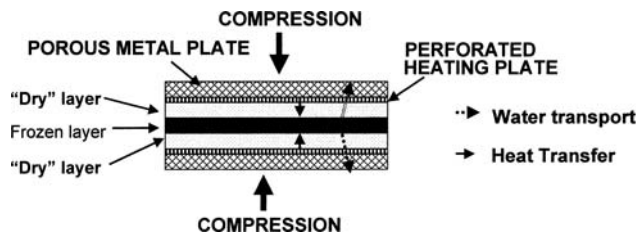


FIGURE 10.51 Compression of foods during freeze-drying. Preparation of freeze-dried compressed military rations. (Emami and Flink, 1991.)

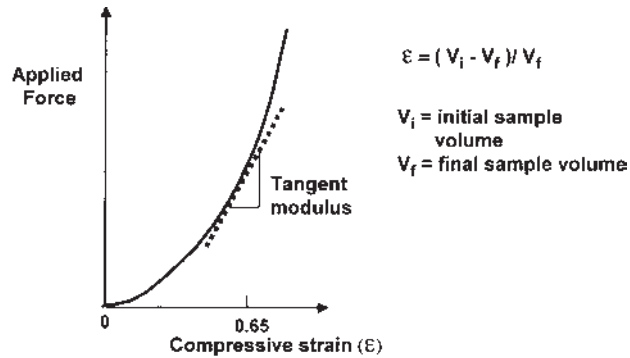


FIGURE 10.52 Tangent modulus defining mechanical properties of freeze-drying materials.

occurring. The procedure has the advantage of requiring neither rehumidification nor secondary drying (Emami and Flink, 1991).

Some typical surface and frozen layer temperatures in freeze drying of foods are shown in Table 10.4. The idealized process model discussed above may be brought closer to reality by postulating three drying periods. During the first the radiator temperature T_r remains constant, and T_s rises to approach the maximum permissible level. In the second period T_s is kept constant by progressively lowering T_r . In these two periods T_l is assumed to remain constant. In the third

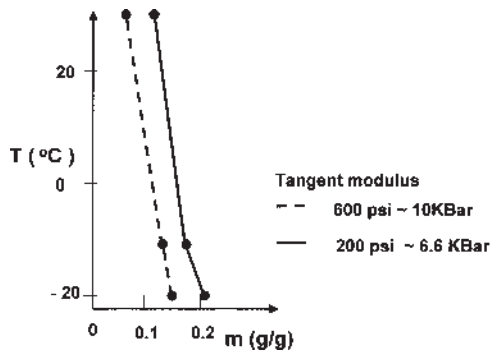


FIGURE 10.53 Temperature and moisture conditions in the dry layer during freeze-drying that result in equivalent tangent modulus at a strain of 0.65. (From Emami and Flink, 1991.)

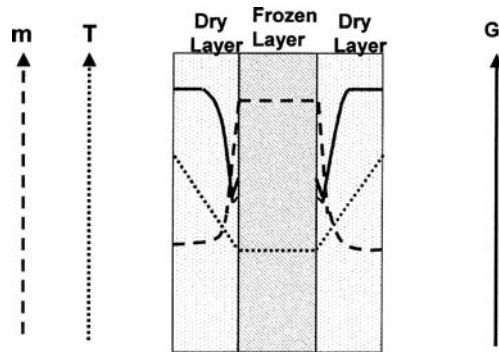


FIGURE 10.54 Gradients of moisture (m), temperature (T), and tangent modulus (G) at a given strain in freeze-drying of a slab.

period all the ice disappears, and the heat supplied by radiation is assumed to be used in raising the temperature of the dry layer. The assumption is made here that the fraction of the heat supplying latent heat for desorption of remaining water is not significant, an assumption which is not justified when the amount of water remaining in dry layer at the time all ice is gone is relatively large. For operations in which the average temperature in the dry layer is high, the assumption is reasonable, because the gradient of moisture in the dry layer is very steep.

During the first period the solution to be provided by the calculations using the models is the rate of rise of T_s and the location of the sublimation interface (r).

The following equations have been suggested as useful guides to the location of the interface and the rate of its recession:

$$r = \frac{(T_s - T_i)k_d}{(T_r^4 - T_s^4)\epsilon\sigma} \quad (53)$$

TABLE 10.4 Typical Frozen Layer and Surface Temperatures in Freeze-Drying

| Food | Surface temperature (°C) | Ice temperature (°C) |
|--------------|-----------------------------|-------------------------|
| Chicken dice | -20 | 60 |
| Orange juice | -45 | 45 |
| Shrimp | -20 | 75 |
| Beef | -15 | 60 |

where

r = interface location (m).

T_r, T_s, T_i = temperatures of radiator, surface and ice, respectively.

ε = emissivity.

σ = Stefan Boltzmann constant.

It should be noted that during the first period T_r and T_i are constant but r and T_s change with time.

Equation (54) gives the rate of recession of interface, which is proportional to rate of drying:

$$\frac{dr}{dt} = \frac{k_d}{\rho(m_i - m_f)\Delta H_s} \frac{T_s - T_i}{r} \quad (54)$$

The second period can be analyzed using one of the following two assumptions:

1. If ice disappears before a constant surface temperature (maximum permissible temperature T_s^*) is reached, there is no "second period."
2. When T_s^* is reached, ice is still present beyond location r . The following equations apply: For location of r as a function of time

$$t = t_1 + \frac{\rho(m_i - m_f)\Delta H_s}{2k_d(T_s^* - T_i)} (r^2 - r_1^2) \quad (55)$$

where t_1 is duration of first period and r_1 is r at end of first period. During the second period T_s and T_i are constant and Eq. (45) gives the rate of drying. However, the radiator temperature must be changing in order to maintain surface temperature at the maximum permissible level. The required radiator temperature as a function of time is given by

$$T_r = [(T_s^*)^4 + \frac{k_d}{\varepsilon\sigma}(T_s^* - T_i)]^{1/4} \quad (56)$$

Analytical and numerical solutions are available for shapes other than slabs and for various assumptions more complicated than the model analyzed here.

One of the key requirements for prediction of drying behavior is the knowledge of food properties. Table 10.5 presents some typical thermal conductivities and Table 10.6 shows permeabilities of freeze-dried foods, which may be considered to be equivalent to the properties of the dry layers during the freeze drying process.

TABLE 10.5 Thermal Conductivity of Freeze-Dried Foods

| Food | Gas and pressure | Thermal conductivity J/(m s K) |
|-------------|----------------------|-----------------------------------|
| Turkey meat | Air, or He, 0.1 torr | 0.03 |
| Turkey meat | Air, 10 torr | 0.078 |
| Turkey meat | He, 10 torr | 0.12 |
| Haddock | Air, 0.5 torr | 0.02 |
| Beef | Air, 1.0 torr | 0.02 |
| Apple | Air, 0.1 torr | 0.017 |
| Coffee | Air, 1.0 torr | 0.034 |

Freeze-drying of foods is usually carried out with T_s^* in the range of 50 to 80°C, and chamber pressures in the range of 0.1 to 2 torr, and the resulting ice temperatures are in the range of -40 to -20°C. Biological and pharmaceutical preparations require lower temperatures and are usually at room temperature or below in the dry layer, and below the T_g in the frozen layer. This requires chamber pressures well below 0.1 torr and condenser temperatures of -60°C or lower. The average moisture content in these material is still unacceptably high at the time all ice is sublimed, and a long vacuum drying period is required.

Freeze-drying with heat input through the dry layer is also feasible at atmospheric pressure and is also feasible provided that gas temperatures are low and partial pressure of water in the air is very low. This may require use of desiccant beds to remove water from the air. The theoretical relations discussed above are valid for this case as well, but the mass transfer resistance of air becomes significant and the Lewis number increases. The drying rates are usually low.

TABLE 10.6 Water Vapor Permeability of Freeze-Dried Foods

| Food | Total pressure (torr) | Permeability [kg/(Pa m s)] |
|----------------------------------|-----------------------|-------------------------------|
| Beef | 1.6 | 1.4×10^{-8} |
| Turkey breast | 0.1 | 1.6×10^{-8} |
| Turkey breast | 100 | 7.7×10^{-10} |
| Coffee (20% solids) ^a | 1 | 3.1×10^{-11} |
| Coffee (10% solids) ^a | 0.15 | 6.2×10^{-11} |

^a Concentration of coffee prior to freeze-drying.

2. Freeze-Drying with Heat Input Through the Frozen Layer

Freeze-drying of liquids and of solids capable of maintaining an intimate contact with a heating surface can be conducted with heat input through the frozen layer. The mass and heat transfer conditions in this case are different from the previously discussed case of heating through the dry layer.

The mass transfer is as described in Eq. (45)

$$\frac{-dw}{dt} = Ab(p_i - p_s)x^{-1}$$

The rate of recession of the ice–dry layer interface is also as given previously in Eq. (47).

$$x dx = \frac{b}{\rho(m_i - m_f)} = (p_i - p_s) dt$$

The coupling of heat and mass transfer is now given by

$$Ak_i(T_H - T_i)(L - x)^{-1} = Ab(p_i - p_s)x^{-1}\Delta H_s \quad (57)$$

The relevant heat transfer resistance is now in the frozen layer with time dependent thickness $(L - x)$, and the relevant heat conductivity is k_f , the conductivity of the frozen layer.

The drying equation is now somewhat more complicated than in the previous case because the interface temperature T_i varies with time as the dry layer increases, and the frozen layer decreases in thickness. The resistance to heat transfer $[(L - x)/k_f]$ decreases, and the resistance to mass transfer (x/b) increases as drying progresses. The heat conductivity of the frozen layer is up to two orders of magnitude higher than that of the dry layer, and mass transfer becomes limiting. The other limitation lies in the maximum permissible frozen layer temperature, which reaches T_H . If the material is sensitive to changes induced by glass transition, this mode of drying is not suitable because the permissible heater temperatures are too low to make drying feasible at reasonable rates. However, for materials in which the frozen layer is allowed to remain at temperatures close to the melting point (e.g., at temperatures a few degrees below the freezing point of water), the method allows drying at fairly substantial rates, provided that the contact with heating surfaces is maintained. These rates may be enhanced further by continuously removing the dry layer by a rotating knife or similar devices (Greaves, 1960).

A calculation for the case of different types of drying of a hypothetical slab 1 in thick was carried out using thermal and permeability properties typical of freeze-drying food solutions, and assuming a maximum permissible dry layer temperature of 125°F (52°C) (Karel, 1974).

The following drying times were estimated:

Heat input through dry layer from two sides of the slab: time = 8.75 h.

Heat transfer by conduction to the frozen layer with T_H at -12°C : time = 13.5 h.

Heat transfer by conduction to the frozen layer with T_H at -2°C : time = 7.2 h.

Heat transfer by conduction to the frozen layer with T_H at -12°C : with the dry material removed continuously: time = 4.0 h.

3. Freeze-Drying with Heat Input by Microwaves

The limitation on heat transfer rates in conventional freeze dryers led early to attempts to provide internal heat generation by microwaves. The generation of heat by microwaves in material placed in their electric field is given by

$$\frac{\text{Power}}{\text{unit volume}} = KE^2 \nu \epsilon'' \quad (58)$$

where

K = a constant.

E = electric field strength (V/m).

ν = frequency (Hz).

ϵ'' = loss factor.

Of the frequencies permitted for use in processing only two are suitable as internal heat generators 915 MHz and 2450 MHz. The loss factor is a property of foods and depends very strongly on water content and the state of water. Ice has a much lower loss factor than liquid water, and water sorbed on surfaces also has a lowered loss factor. Table 10.7 presents values of the loss factor for several food materials.

TABLE 10.7 Dielectric Loss Factor for Selected Materials at 2000 to 3000 MHz

| Material | Temperature ($^\circ\text{C}$) | Loss factor |
|-------------------|----------------------------------|-------------|
| Raw beef | -40 | 0.083 |
| Raw beef | 5 | 10.56 |
| Freeze dried beef | 5 | 0.12 |
| Ice | -12 | 0.003 |
| Water | 25 | 12 |
| Cooked beef | -20 | 0.65 |
| Cooked beef | 25 | 12 |

Successful generation of heat within the frozen layer would greatly reduce time required for freeze drying. If we apply the calculations we cited above for a 1-inch-thick slab, and assume that it would be feasible to maintain a temperature of -12°C in the frozen layer, then the drying time we estimate is 1.37 h, very much lower than that attainable by the other heat transfer modes. The calculations seem to be realistic since experimental work by Hoover et al. gave a drying time of 2 h for a 1-in beef slab dried in a laboratory microwave freeze dryer. (Hoover and Markantonates 1966).

In spite of the advantages of microwave heating in freeze drying, this method has remained largely unused because of several inherent difficulties, which we noted in the first edition of the present book (Karel, Fennema, and Lund, 1975).

1. Energy supplied by microwave is very expensive.
2. Unless the freeze dryer is operated at very low pressures, which are not economical, there is a tendency for so-called glow discharge, which results in loss of useful power, ionization of gases in the dryer, and deleterious changes in the food.
3. Control of microwave heating during vacuum freeze-drying is difficult because of the very large difference in the properties of dry and wet components and between frozen and liquid water.

Most recent reviews of microwave drying, and of freeze drying show that the above problems have not yet been overcome (Liapis and Bruttini, 1995; Schiffmann, 1995).

VI. QUALITY ASPECTS OF DEHYDRATED MATERIALS

The quality of dehydrated foods and the preservation of activity of biopreparations depend on conditions of dehydration as well as on condition and length of storage. In this chapter we are focusing primarily on events occurring during the dehydration processes. Three types of quality altering phenomena will be discussed:

1. Changes in structure and texture during drying
2. Changes due to chemical reactions occurring during drying
3. Retention of volatile organic compounds and in particular of flavor compounds

The quality of dehydrated foods is often limited by changes in their texture and their rehydration capacity. Tough, woody texture, slow and incomplete rehydration and loss of the typical fresh food juiciness are most common defects of such foods. The physicochemical basis for these changes is complex.

In the case of plant-derived materials loss of cellular integrity, crystallization, cross-linking of polysaccharides, and flow and redistribution of components are considered to play important roles in creating these defects. Crystallization of starch and of some other polysaccharides is known to be promoted by removal of sorbed water. In baked products retrogradation of starch is a well-known mechanism.

In dehydrated foods of animal origin loss of characteristic tenderness is often due to aggregation of muscle proteins. These defects are found in both air-dried and freeze-dried products and may be due to loss of water.

Many of the structural changes may be avoided if dehydration is carried out below the glass transition temperature. Bulk flow and redistribution of components, as well as loss of original structure and shrinkage may then be avoided.

In experiments on freeze-drying apple slices it was demonstrated that collapse and resulting shrinkage could be prevented only at or below T_g . The extent of collapse could be moderated, however, by increasing the total solid content of the apple tissue by osmotic dehydration prior to freeze-drying (Fig. 10.55) (Anglea and Karathanos, 1993; Karathanos and Anglea, 1996). Similar results were observed with potato, carrot, and banana (Krokida and Karathanos, 1998).

Foods containing a cellular network containing polymers may retain their shapes somewhat above T_g of the solutions they contain, but the collapse of the glasses within the network and the resultant increase in mobility may cause deleterious changes even if the overall external structure retains its original appearance.

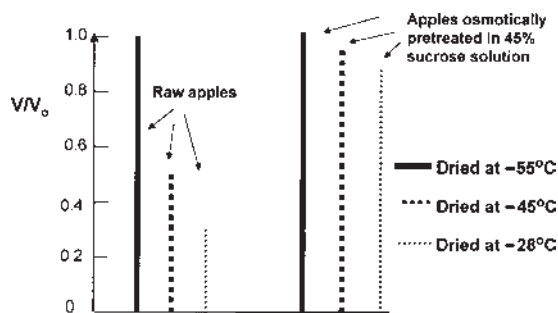


FIGURE 10.55 Shrinkage of apples during freeze-drying (frozen apple $T_g \sim -45^\circ\text{C}$).

A. Changes Due to Chemical Reactions Occurring During Drying

Reactions occurring during drying can result in quality losses, in particular due to the complex set of reactions known as nonenzymatic browning. The extent of these reactions is largely dependent on the time course of changes in temperature and moisture content. If the dependence of important deteriorative reactions on temperature and moisture content are known as well as the temperature and moisture gradients during drying, it is possible to calculate the extent of quality loss occurring during the process.

Two limiting cases that facilitate these calculations may be recognized:

1. In air dehydration it is usually feasible to assume that the temperature gradient within the food is negligible. Thus, it is possible to calculate the moisture–temperature profiles by an assumption that moisture content varies with time and location but temperature varies only with time.
2. In freeze drying, within the ‘ice-free’ layer (deterioration in the frozen layer during drying is extremely slow and may be neglected), it may be assumed that the temperature varies with time and location but that the moisture gradients are small. It may often be adequate to assume that as long as ice is present anywhere within the drying material, the temperature difference across the dry layer is *constant*.

Simulation of quality losses in a given dehydration process and more significantly, the ability to optimize dehydration processes with respect to quality retention have been greatly facilitated by the application of computers (Karel, 1983).

We shall illustrate typical approaches to simulation by an example based on our work on browning during dehydration of potatoes. In this study browning during dehydration was predicted by a computer iteration procedure. To introduce the reader to the approach we shall consider a much simplified version of this simulation (Karel, 1983, p. 265).

The rate of browning r is assumed to be a function of the **average** moisture content m and temperature T .

This function was assumed to be expressed by the set of Eqs. (59a) to (59e), which was based on published experimental data. (Hendel and Silveira, 1955)

$$\ln r(50^\circ\text{C}) = K_{11} - K_{11}(\ln m) \quad \text{for } m < 20\% \quad (59a)$$

$$\ln r(50^\circ\text{C}) = K_{13} + K_{12}(\ln m) \quad \text{for } 1\% < m < 20\% \quad (59b)$$

$$\ln \frac{r(T)}{r(50^\circ\text{C})} = -\frac{E}{R} \left(\frac{1}{323} - \frac{1}{T} \right) \quad (59c)$$

$$E = 26 \text{ kcal/mol} \quad \text{for } m > 16\% \quad (59d)$$

$$E = (42 - m) \text{ kcal/mol} \quad \text{for } m < 16\% \quad (59e)$$

A further assumption is made that the m can be calculated using the diffusion [Eq. (32)]

$$t_F = \frac{4L^2}{\pi^2 D_{EF}} \ln \frac{m_c - m_e}{m_F - m_e}$$

The diffusion coefficient D_{EF} is considered to be a function of temperature and independent of m . For the system under study,

$$D_{EF} = 1.67 (10^{-5}) \exp \frac{-7500}{RT} \quad (60)$$

The temperature of drying potato is given by

$$\ln(T_d - T_p) = \ln(T_d - T_w) - \beta t \quad (61)$$

The subscripts d, p, and w, refers to air dry-bulb temperature, potato temperature, and air wet-bulb temperature, respectively. β is given by

$$\beta = \frac{\Delta \ln(m/m_I)}{\Delta t} \quad (62)$$

These equations may now be used to estimate the extent of browning during drying using the iteration procedure showing the flow chart in Fig. 10.56. The flow chart shows the following steps.

1. Input contains information about conditions of air (T_d , T_w , m_e), the initial water content (m_I), the final water content (m_f), and the slab half-thickness (L).
2. D is calculated using Eq. (60).
3. Total drying time is calculated using Eq. (32).
4. β is calculated using Eq. (62).
5. The iteration begins using an arbitrary time interval (Δt).
6. T_p is calculated using Eq. (61).
7. m is calculated using Eq. (32).
8. r is calculated Eqs. (58) and (59).

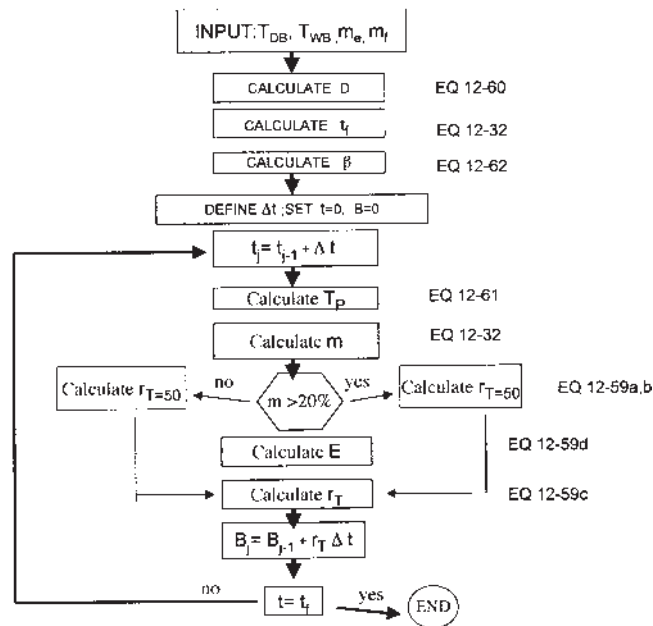


FIGURE 10.56 Flow chart for simulation of browning in a drying slab.

9. ΔB is added to the extent of browning B existing at the beginning of the interval.
10. The iteration is repeated until $t = t_f$.

More complicated numerical procedures allow us to calculate the extent of browning, or of any other reaction for which the kinetic parameters are known, as a function of time and location within the material being dried. The estimates based on integration of the extent of the reaction at each location with the estimate based on average moisture content are shown in Fig. 10.57.

Figure 10.58 shows the distribution of the extent of browning reaction in a potato slab dried at an air temperature of 96°C, for different extents of drying shown as average water content m (g/g dry matter) (Aguilera et al., 1975). Similar techniques were applied to estimate losses of nutrients during dehydration (Mishkin and Saguy, 1984a,b). The fact that retention of nutrients is dependent on conditions during dehydration allows the optimization of dehydration processes with respect to quality (Mishkin and Saguy 1984a,b). The optimization may consider several quality factors allowing us to optimize with respect to one factor but keeping other factors as constraints, assuring that their level is in acceptable range (Karel, 1988).

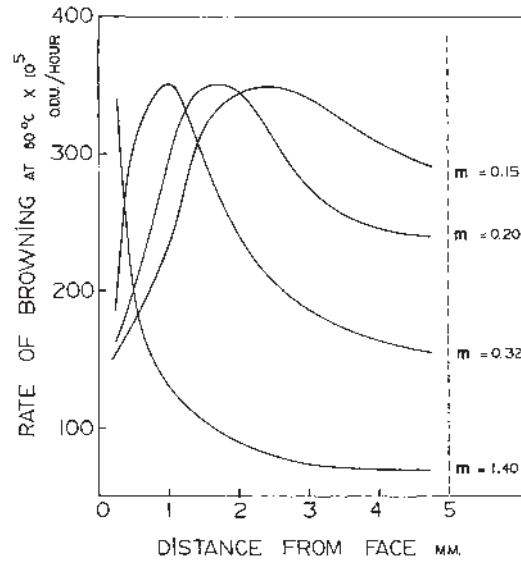


FIGURE 10.57 Local rates of browning in a drying potato slab for various extents of drying.

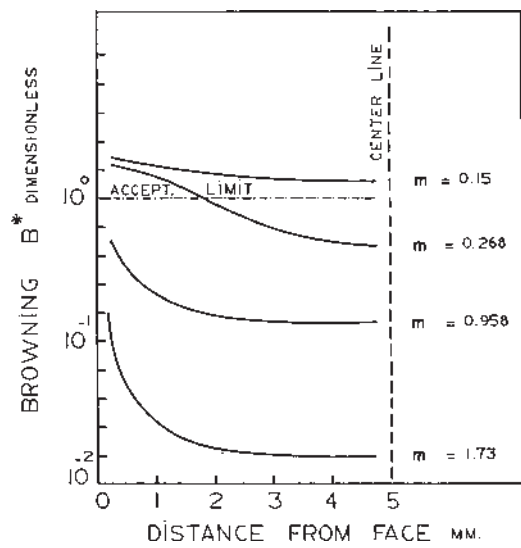


FIGURE 10.58 Distribution of brown color in potato slab during dehydration at an air temperature of 96°C.

Figure 10.59 shows the results of calculation of an optimal air temperature as a function of time in a model system for two different objectives. As a consequence of different sensitivity to temperature and moisture of ascorbic acid degradation, and of non enzymatic browning, the optimal profiles for reducing the extent of reaction are different for the two reactions. If the minimizing browning is considered as the objective, profile A is relevant, and the results are browning limited to 0.021 units (arbitrary measure useful here for purposes of comparison), and vitamin C retention is 24%. If we optimize with respect to ascorbic acid, we obtain profile C, and the browning is 0.032 units and vitamin C retention is 84.5%. If we place a constraint on browning, requiring that it does not exceed 0.025 units, and then optimize for vitamin C, we obtain profile B, with vitamin C retention only 30%.

Other constraints may derive from the maximum permissible drying time (due to economic considerations) and the maximum permissible final moisture content. One way to implement such a process is by using multiple stages with different temperatures. For example a 6-h process for drying a model slab to a final moisture of 0.05 kg/kg with minimal ascorbic acid destruction was shown to be achieved conveniently in a three-stage operation with stages 1 and 3 at 65°C and stage 2 at 57°C.

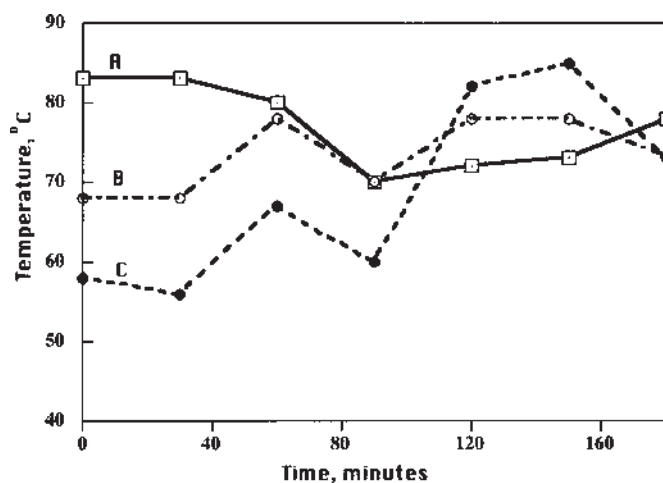


FIGURE 10.59 Optimal air temperature control profiles for optimizing quality factors in a drying potato slab for different objectives: (A) objective: minimize browning; (B) minimize loss of vitamin C, with constraint on browning; (C) minimize loss of vitamin C. No constraints.

Progress in optimization of dehydration has been rapid in the past decade because of availability of computers and of on line instrumentation. The examples shown here provide only an introduction to a rapidly advancing field.

B. Retention of Volatile Organic Compounds—Flavor Compounds

Retention of flavor compounds in dehydrated foods is an important attribute of quality. In some food products, such as instant coffee it is the most important aspect of quality. Conversely it is often desirable to remove organic compounds by volatilization during drying, as is the case in removing solvent residues from solvent-treated oilseeds. The factors controlling the retention and loss of volatile organic compounds during drying are therefore of fundamental importance in dehydration processing.

The body of knowledge in this field is extensive, and much of it is based on work conducted by three groups during the 1970s. These are mentioned below.

The group of Hans Thijssen in Eindhoven is credited with the development of the *selective diffusion* theory governing flavor retention (Thijssen, 1971).

C. J. King and his group at Berkeley developed much of the knowledge about flavor retention in spray drying (King, 1988). Freeze-drying was the focus of work on flavor retention of the MIT group (Flink and Karel, 1972).

The principle of retaining volatile organic compounds during drying is the entrapment of these compounds, either as individual molecules, or as part of nonaqueous droplets, in an impermeable matrix of hydrophilic food components. The matrix was shown to retain the flavor as long as it remains in the glassy state (Levy and Karel, 1995). The possibility of retaining volatile compounds with vapor pressures far higher than that of water, while removing water depends on the selective diffusivity of the matrix during dehydration, its water content decreases, and it approaches the glass transition temperature, the matrix composed of various hydrophilic glass-forming components such as sugars, polysaccharides, and proteins, decreases in its permeability to all compounds, including water. However—and therein lies the principle of selectivity—the diffusivity of organic compounds is more sensitive to water content of the matrix than that of water itself. Figure 10.60 shows the dependence on moisture content of maltodextrin on diffusivities of acetone and of water in that matrix, which is typical of dehydrated foods. In Fig. 10.61 presented the ratio of diffusivity of acetone to that of water in maltodextrin as a function of water content at three different temperatures. It is evident that the lower the temperature, the greater the difference between the two diffusivities. It should also be evident that there exist domains of temperature and moisture in which water removal can be accomplished, while the organic flavor compounds possess very low diffusivities and are retained. Figure 10.62 shows the conditions at which the ratio of

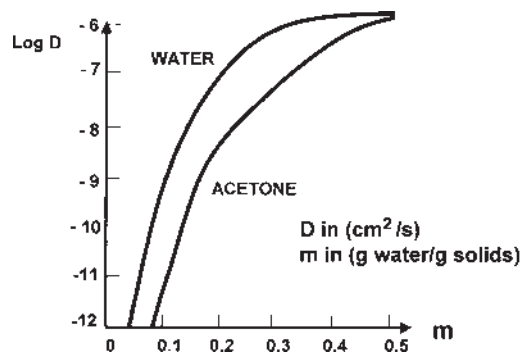


FIGURE 10.60 Diffusivities of water and of acetone in maltodextrin at 25°C. (From Thijssen and Rulkens, 1968.)

diffusivities of organic compounds to that of water in maltodextrin drops to 0.01. The figure presents data for several alcohols and for acetone. It also shows the glass transition line for maltodextrin. Methanol has the highest likelihood of loss, and the higher alcohols, the least. It has also been established that below T_g the diffusivities of organic compounds drop to extremely low levels. Carbon tetrachloride, and hydrocarbon were reported to D values as low as $10^{-17} \text{ m}^2/\text{s}$ in glassy polystyrene and as low as $10^{-22} \text{ m}^2/\text{s}$ in glassy polymethyl methacrylate. Similarly low values are reported for flavors in sugar and maltodextrin glasses. The diffusivity of water below T_g is however, much higher. As an example in

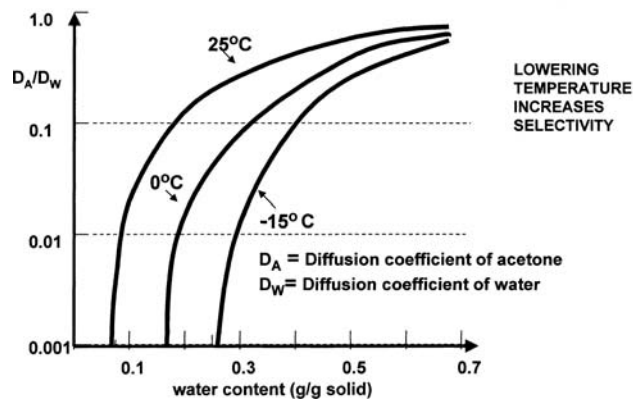


FIGURE 10.61 Selective diffusion in maltodextrin. Ratio of diffusivity of acetone to that of water at different temperatures. (From Thijssen, 1971.)

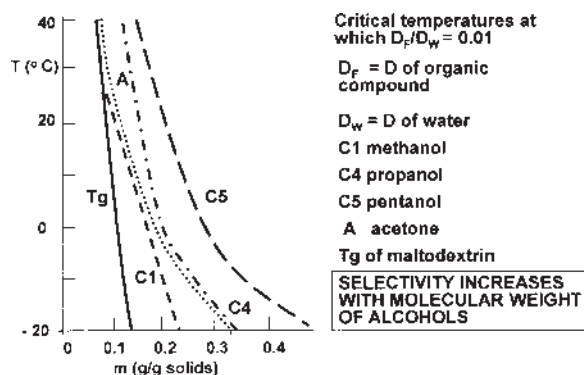


FIGURE 10.62 Selective diffusion in maltodextrin. Temperature and moisture conditions at which the diffusivity of organic compounds drops to 1% of that of water. The T_g line for maltodextrin is also shown. (From Thijssen, 1971 and Roos and Karel, 1991.)

the case of maltose-water system below T_g the value of D is reported in the range of 10^{-14} m²/s to 10^{-12} m²/s (Parker and Ring, 1995). It is therefore feasible to essentially seal in flavors while water is still capable of being removed at reasonable rates.

The two methodologies most effective in this respect are freeze-drying and spray drying. The course of events resulting in flavor retention during freeze drying is shown schematically in Fig. 10.63. During freezing there is a separation of ice and concentrated solution. The flavor is contained within the concentrated solution either as individual molecules or as dispersed droplet. The schematic representation in Fig. 10.63 shows the case of droplets. During freeze-drying the sublimation results in the ice layer being replaced by air, and the droplets remain entrapped within the solid layers which are below T_g . The loss of flavor during freeze-drying is limited to the fraction exposed to the ice-solid interface during drying. Ideally, the entrapped flavor is retained as long as the storage conditions allow the material to remain below T_g . If the conditions are changed by raising the temperature of water content and T_g is exceeded, loss occurs typically as shown in Fig. 10.64. If there is crystallization of the matrix, complete loss occurs rapidly because the matrix molecules assemble in crystals, which usually exclude the flavor, except in some rather nontypical situations where some flavor molecules may be accommodated in sugar crystals. If the material remains amorphous above T_g , a two-phase course of loss is usually evident. In the first stage bulk flow of the matrix results in loss of porosity and increase in density, as shown in Fig. 10.65.

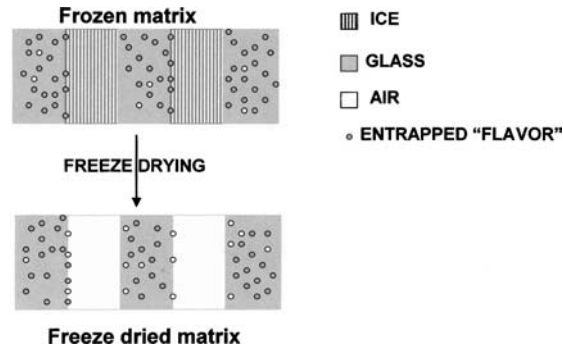


FIGURE 10.63 Schematic representation of encapsulation of flavors during freeze-drying.

During that stage some flavor loss occurs rapidly. Once the densification of the matrix due to elimination of porosity is complete the flavor loss occurs only by diffusion through the dense matrix, and may be sufficiently slow to allow substantial flavor retention. The two stage nature of the flavor release allows the design of optimal controlled release systems. Amorphous materials may be allowed to soften after flavor entrapment and become nonporous by raising the temperature. If they are then cooled rapidly, part of the flavor remains within a dense matrix and may be retained indefinitely if material remains below T_g , or released slowly at a rate dependent on $(T - T_g)$.

The conditions of freeze-drying have a significant impact on flavor retention.

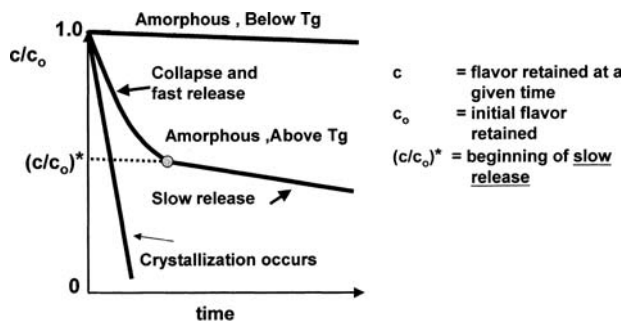


FIGURE 10.64 Effect of phase transitions in an amorphous matrix on release of encapsulated flavors.

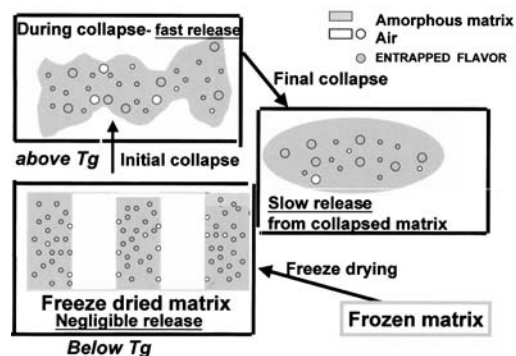


FIGURE 10.65 Collapse of freeze-dried matrix above T_g and flavor release.

The freeze-drying conditions that promote flavor retention include low temperature, slow rates of freezing, low pressure, and increased solids content (Karel, 1974).

Spray drying is also effective in retaining volatile compounds. The principle governing retention is the same as in freeze drying: the drying achieves entrapment of organic volatiles in a glassy state in the matrix by drying under conditions in which diffusion of volatiles is selectively retarded. Ideally the atomization and initial exposure to air in the spray dryer produces a “skin” on the droplet surface that provided the diffusion selectivity discussed previously. The understanding of the processes involved in retention has resulted in the development of guidelines for operation of spray dryers allowing optimization of flavor retention. A review of such guidelines has been published recently (King, 1995). The following aspects were stressed:

1. Atomizers should be operated at a high pressure (for pressure atomizers) or rotation speeds (for disk atomizers). These conditions cause rapid onset of the selective diffusion regime.
2. The spray angle should be chosen so that the spray fills as much of the dryer cross section without wetting the walls. This maximizes initial exposure to hot air and the formation of the selective skin.
3. Air input distribution and temperature profile affect retention. To the extent feasible, the temperatures of air should be high in the initial contact area and low in the dryer regions, where morphological development of particles occurs. High gradients of temperature may be achieved by “tall form” dryers (large height to diameter ratio) or by having a secondary stream of cooler air lower in the dryer.

4. As in the case of freeze-drying, high solids concentrations in the feed promote flavor retention, provided that viscosity remains sufficiently to give efficient formation of small droplets.

The same principles that apply to entrapment of flavor are valid for entrapment of oil droplets, i.e., to minimize their exposure to oxygen during storage, and to avoid presence of free fat on the surface which interferes with rehydration.

SYMBOLS

| | |
|--------------|--|
| A | area |
| b | permeability |
| c | concentration |
| c_p | specific heat (subscripts: A = dry air; H = humid air; s = solid; v = vapor) |
| D | diffusion coefficient (subscripts: L = liquid; EF = effective D) |
| d | diameter |
| E | activation energy [in Eq. (58) electric field strength] |
| G | mass flow rate of air |
| g | gravitational constant |
| h | heat transfer coefficient |
| H | enthalpy |
| K | constant |
| k | thermal conductivity, $kd = k$ of dry layer |
| k_g | mass transfer coefficient based on pressure difference |
| k_g' | mass transfer coefficient based on pressure difference |
| L, l | thickness |
| Le | Lewis number |
| M | mass flow rate |
| m | moisture content (subscripts: c = critical, f = final, h = hygroscopic, I = initial) |
| N | rotational speed |
| P | total pressure |
| P_o | fluidization pressure |
| p | partial pressure of water (subscripts: o = vapor pressure; i = ice) |
| Q, Q' | heat supplied to dryer |
| q | heat flux |
| r | radius [in Eq. (53), interface location in Eq. (59) rate of browning] |
| $r(c), r(f)$ | drying rates in constant and falling periods, respectively |

| | |
|-----------------|---|
| RH | relative humidity |
| S | specific area |
| s | mass flow rate of solids |
| T | temperature (subscripts: s = surface; S = saturation; w = wet bulb; d = dry bulb) |
| t | time |
| U | Overall heat transfer coefficient |
| U_o | velocity at onset of fluidization |
| V | volumetric flow rate |
| Y | absolute humidity (subscripts: s = saturation; e = equilibrium; i = initial) |
| x | distance |
| ΔH | latent heat (subscripts: v = vaporization, s = sublimation) |
| ΣR | sum of resistances |
| α | thermal diffusivity |
| β | constant |
| ε | porosity, void volume, [emissivity in Eqs. (53) and (56)] |
| ε'' | dielectric loss factor |
| ϕ | unaccomplished moisture change [Eqs. (22) and (27)] |
| γ | surface tension |
| μ | viscosity |
| ν | frequency |
| θ | contact angle |
| ρ | density (subscripts: L = liquid, s = solid, g = gas) |
| σ | Stephan Boltzman constant |
| σ' | spreading coefficient |

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Nonthermal Methods

I. NONTHERMAL PHYSICAL PROCESSES FOR FOOD PRESERVATION

The existence of undesirable side effects of thermal processing and the desire for flexibility in process and storage methodology have provided the incentive to explore nonthermal methods of food processing. In the present chapter we limit ourselves, in line with the objective of this book, to physical treatments which *may be considered* nonthermal. The qualification implied in the previous sentence arises from the fact that all of the physical treatments proposed have some thermal effects, but the preservation effect is not primarily due to the thermal component of the treatment.

None of the treatments discussed in this chapter have achieved, as of this time, wide commercial utilization. The state of development varies. We consider the following potential food processing technologies:

1. Preservation using ionizing radiation
2. High-pressure processing
3. Irradiation with ultraviolet (UV) light
4. Pulsed application of broad spectrum light
5. Application of high-intensity pulsed electric fields
6. Application of oscillating magnetic fields

The status of the current development of these processes varies considerably between them. Ionizing radiation processing is very well developed,

a basis exists for process control, commercially sized processing facilities are available in many countries, and a firm basis exists for regulation of irradiated products brought on the market. The process has been used in several commercial applications, and while most of them have not proved commercially viable, most of the failures have been those of marketing, economics, and consumer perception, not failures of the technology itself. The literature on both the fundamental and applied topic in the field is extensive, and several books summarize the subject.

Ultraviolet radiation is a fairly well documented method, albeit with limited applicability because of its lack of penetration into matter. Ultrasonics have a history of use in industry for purposes other than preservation, but their use as a preservation method is still to be developed (Urbain, 1986). The other nonthermal preservation technologies are still in need of research and development (IFT, 2000b).

High-pressure processing has shown the most development. The basis of the effect of this process are understood, progress has been made in quantitative assessment of its lethal effects on microorganisms, pilot plant scale and some small commercial scale equipment is available, and a few products have appeared on the market.

Pulsed electric field application, and applications of pulsed light have been demonstrated to have the capability to produce lethal effects on microorganisms, but kinetics of these effects is not established, and the design of a feasible preservation procedure is still to be developed.

Oscillating magnetic fields have been reported to have effects potentially capable of aiding in food preservation, but these reports are still to be convincingly confirmed in peer reviewed literature, and at this time the method can only be characterized as an interesting subject for further study.

II. RADIATION PRESERVATION OF FOODS

A. Introduction

The possibility of using radiation for food preservation was recognized soon after Roentgen's discovery of x-rays in 1895 and of natural radioactivity by Becquerel in 1896. In 1904 Samuel Prescott reported studies at MIT on bactericidal effects of ionizing radiation. United States and European patents were issued for this purpose in the 1920s and 1930s. In 1943 MIT researchers, working under U.S. Army contracts demonstrated the feasibility of sterilizing beef by irradiation with x-rays. Subsequently extensive work was conducted at MIT, at the laboratories of the United States Army, at the Federal Research Center for Food Preservation in Karlsruhe, Germany and at Michigan State University. This work initiated a much broader effort involving many dozens of institutions throughout the world,

and resulting in thousands of scientific papers and other documents dealing with the subject. The present author agrees fully with the statement by Thakur and Singh (1994) that “food irradiation is one of the most extensively and thoroughly studied methods of food preservation.” A number of international scientific bodies and agencies of national governments have evaluated this well documented body of research and approved the use of the process in various preservation applications. Nevertheless, and in spite of enormous progress in its science and technology the status of use of food irradiation is not basically different from the status as described in the 1975 edition of the present work: “In spite of this massive effort, radiation is still not a widely used preservation method.”

B. Properties of Ionizing Radiations

Several types of radiation have the characteristic ability to ionize individual atoms or molecules, thereby producing an electron and a positively charged ion:



where M is an atom or molecule, and $h\nu$ a quantum of energy delivered by radiation.

The types of ionizing radiation and their properties are shown in Table 11.1. Of the types of radiation listed the only electromagnetic radiations and high-energy electrons which are considered suitable for use in food preservation are

1. Gamma rays from radioactive isotopes of Cobalt and Cesium
2. Electron beams from machine sources
3. X-rays from machine sources

1. Photons

Light, x-rays and γ rays are part of the electromagnetic spectrum shown schematically in Fig. 11.1. Electromagnetic radiations possess a dual nature. According to quantum theory they may be considered as waves or as packets of energy, or *photons*. Energy and wave properties are related as shown in

$$\nu = \frac{c}{\lambda} \quad (2)$$

$$E = h\nu \quad (3)$$

where:

c = velocity of light in vacuum (cm/s).

ν = frequency (1/s).

λ = wavelength (cm).

E = energy of the photon (J).

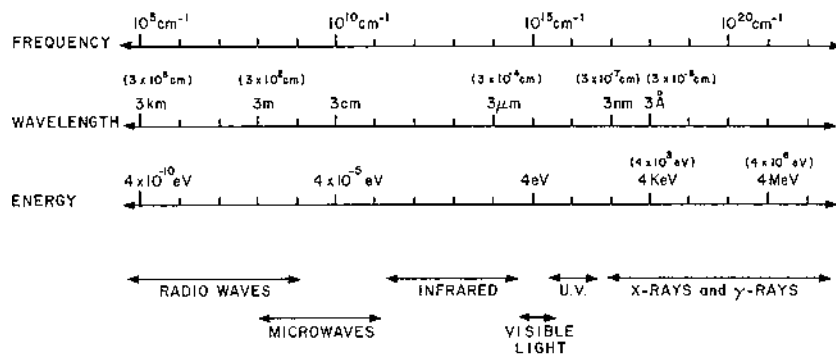
h = Planck's constant = 6.626×10^{-34} J s.

TABLE 11.1 Nature and Properties of Some Ionizing Radiations

| Radiation | Nature of rays | Typical energy (MeV) | Penetration ^a |
|---------------|-----------------------------------|----------------------|--------------------------|
| x rays | Man-made photons | 0.01–10 | 20–150 |
| γ rays | Photons from isotopes | 0.1–several MeV | 30–100 |
| β rays | Electrons from isotopes | 0.01–1 | 0.1–0.5 |
| Cathode rays | Electrons from accelerators | 0.1–10 | 0.1–5 |
| Protons | Protons from accelerators | MeV range | 0.003 |
| Neutron | Neutrons from fission or isotopes | MeV range | ~ 10 |
| α rays | He nuclei from isotopes | 1–10 | ~0.005 |

^a Depth of absorber of unit density (water) required to reduce radiation intensity by a factor of 100.

Energy of a photon is often measured in electron volts (eV), the energy acquired by an electron in a potential fall of 1 V. One eV is equal to 1.602×10^{-19} J. An often used unit is MeV equal to 1×10^6 eV. As shown in Fig. 11.1, the lower the wavelength, the higher the energy of the photon. The total energy

**FIGURE 11.1** Electromagnetic spectrum.

impinging a material being irradiated by photons is equal to the product of the number of photons and the energy of each photon.

The types of interactions between matter and photons depend on the photon energy. Three modes of interaction of significance are the Compton effect, pair production, and the photoelectric effect. In the Compton effect the photon behaves as a particle undergoing collision with an orbital electron. The electron is ejected with a kinetic energy derived from the photon and the photon retains a reduced kinetic energy (Fig. 11.2).

In the photoelectric effect all of the energy of the photon is absorbed by an atom, the photon disappears, and an orbital electron is ejected. The energy of the photon is partly used up in overcoming the binding forces holding the electron in its orbit, and is partly converted into the kinetic energy of the electron. The pair production is possible when photons of high energy (high-energy x rays) are converted into an electron, and a positron.

Figure 11.3 shows the contribution of the three effects to interaction of photons, such as gamma rays, with matter.

The interaction of the photons with matter results in absorption of the energy which can be described by the following equation:

$$I = I_0 \exp(-\mu X) \quad (4)$$

where I is intensity of radiation at distance X within the absorber, I_0 is the intensity at the surface of the absorber (where the radiation impinges upon it), and μ is the coefficient of absorption, which depends on the photon energy and the nature of the absorber.

Coefficients of absorption for several materials are shown in Table 11.2.

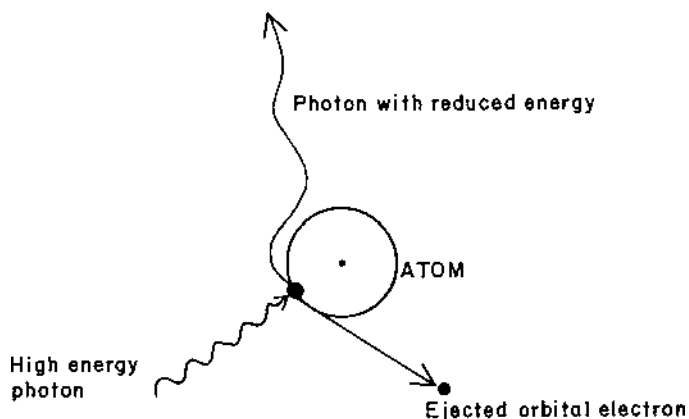


FIGURE 11.2 Schematic representation of the Compton effect.

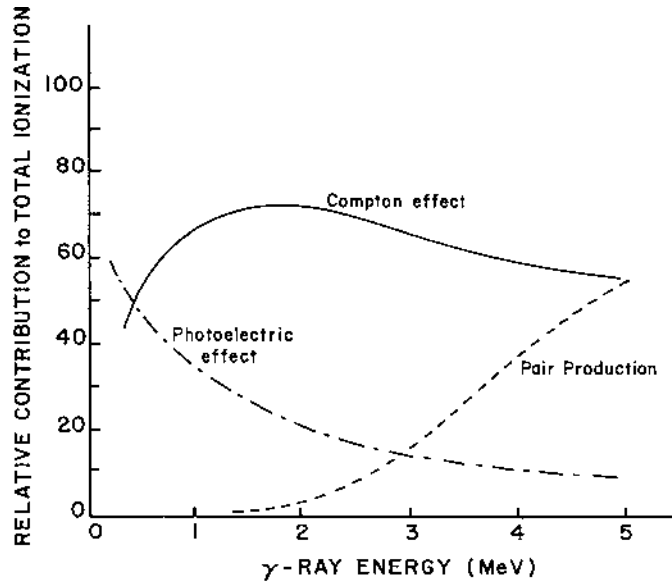


FIGURE 11.3 Relative intensity and relative number of electrons at different depths of absorber.

The exponential nature of Eq. (4) results in an attenuation pattern shown in Fig. 11.4. It should be evident that the intensity never reaches zero as long as the exponential relation applies, and that each additional equal thickness of the absorber will reduce the intensity by the same factor. A useful value is the half-thickness which reduces the intensity by a factor of 2. Half-thickness value is equal to $0.693/\mu$.

TABLE 11.2 Absorption Coefficient μ (in cm)

| Material | Energy of photons (MeV) | | |
|-----------|-------------------------|---------|---------|
| | 0.5 | 1.0 | 4.0 |
| Air (STP) | 0.00008 | 0.00005 | 0.00004 |
| Water | 0.09 | 0.067 | 0.033 |
| Aluminum | 0.23 | 0.16 | 0.082 |
| Iron | 0.63 | 0.44 | 0.27 |
| Lead | 1.7 | 0.77 | 0.48 |

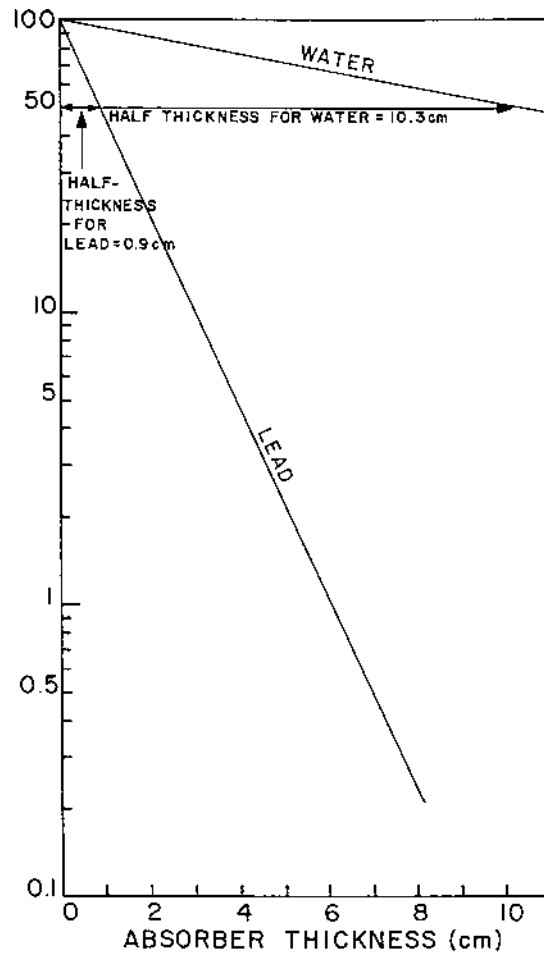


FIGURE 11.4 Penetration of 1-MeV gamma rays in water.

2. High-Energy Electrons

Electrons emitted by a hot cathode can be accelerated to very high velocities by electron accelerators, such as a Van De Graaf accelerator, and linear accelerator discussed in a subsequent section. The relation between electron velocity and its energy is shown in Table 11.3.

High-energy electrons are also produced in disintegration of some radioactive atoms. As an example, ^{24}Na emits an electron and is converted to ^{24}Mg . Electrons produced by radioactive isotopes are called β rays in contrast to

TABLE 11.3 Relation Between Electron Velocity and Energy

| Velocity (% of speed of light) | Energy (MeV) |
|-----------------------------------|--------------|
| 13.9 | 0.005 |
| 36.6 | 0.05 |
| 86.7 | 0.5 |
| 94 | 1.0 |
| 99.6 | 5.0 |
| 99.87 | 10.0 |

cathode rays which are electrons produced by machines. There is an important difference between them, cathode rays can be produced with a uniform energy, but β rays have an energy spectrum. Radioactive isotopes are also emitters of high-energy gamma rays with energies specific to a given isotope.

Electrons lose energy and slow down as they interact with matter. As more and more electrons in a beam slow down to negligible velocities, the number of fast electrons decreases with the depth of the absorber. If a monoenergetic beam of electrons enters the absorber, the relative number of remaining initially falls linearly with depth. However, not all of the electrons at a given depth have the same energy. As a result the relative ionization (or relative energy dissipation) at any point does not vary linearly with distance. Figure 11.5 shows how the relative number and relative ionization vary with depth in an absorber. In the case of β rays, which are not monoenergetic when they enter the absorber the attenuation of intensity is similar to that of gamma rays as shown in Fig. 11.4. The maximum range of an electron beam is related to its energy by the Feather equation, which is valid for energies above 0.5 MeV:

$$R_{\max} = \frac{0.542E - 0.133}{\rho} \quad (5)$$

where R_{\max} is maximum range (cm), E is energy (MeV), and ρ is absorber density (g/cm^3).

C. Dosimetry of Ionizing Radiations

It should be evident from the preceding discussion that the amount of energy absorbed by an irradiated object and the amount of ionization produced depend on a number of variables, including the number of particles or photons passing through the object, energy of the radiation and the nature of the absorber. Measurement of the radiation dose is therefore a complex matter. The unit first

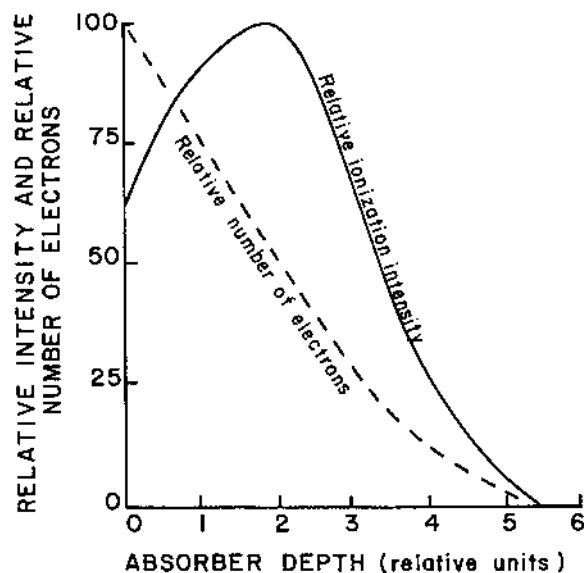


FIGURE 11.5 Absorption of a monoenergetic electron beam by matter.

suggested for this purpose was the Roentgen, defined as that quantity of radiation which produced one electrostatic unit per cubic centimeter of air under standard conditions. The amount of energy delivered by γ or x rays to a gram of dry air in delivering 1 roentgen is 83.8 ergs (83.8×10^{-7} J). This led to the development of a unit of absorbed radiation called rep (roentgen equivalent physical), originally defined as the amount of energy absorbed in biological tissue exposed to 1 roentgen. Originally this was considered equal to 93.8 ergs/g, but it was soon determined that different materials absorbed different amounts of energy when exposed to the same number of roentgens (typically 93 ergs in water, as much as 150 in bone). Subsequently the unit based on absorption of 100 ergs of energy per gram was adapted and called the *rad*. At present the unit adapted internationally is the *Gray* (Gy) equal to 100 rad, or 1 J/kg. In practical applications it is more convenient to use multiples of this unit, and kGy equal to 1000 Gy is often used.

A different kind of unit basic to radiation measurement is the curie (cu), which is a measure of radioactivity of a substance. One Curie is equal to 3.7×10^{10} disintegrations per second. It should be noted that since the unit does not take into account the number of particles emitted in each disintegration, or their energies, the actual radiation intensity is not defined by this unit.

The measurement of absorbed dose of radiation is critical to evaluation of effects of radiation processing, and is an essential control measure in industrial applications. A number of methods has been developed and is available commercially for research and industrial applications. The methods may be classified as physical and chemical.

The physical methods include calorimetry, ionization, and scintillation measurements. Most of the energy absorbed by irradiated materials is converted to heat, and calorimeters are considered a primary method. In early food research applications we used this method to calibrate a ^{60}Co radiation source, and calibrated secondary dosimeters against it (Davison et al., 1953). Another physical method uses ionization. Ionizing radiations produce ions of both signs. By filling a chamber with a gas and establishing an electric field between two electrodes it is possible to collect the ions produced by ionization of the gas at the two electrodes. Since ionizing radiation ionizes gas molecules, the ions are attracted to the oppositely charged electrodes; and their presence causes a momentary drop in the voltage, which is recorded by the external circuit. The observed voltage drop helps identify the radiation because it depends on the degree of ionization, which in turn depends on the charge, mass, and speed of the photon, or electron. The dose rate may be measured by the electric current flowing between the electrodes.

Another method suitable for measuring intensity of radiation is *scintillation*. In this method an incident photon of ionizing radiation is allowed to impinge on liquids containing materials which effectively convert a constant fraction of the incident energy to visible light which is measured by a sensitive light meter.

In addition to the physical methods, and often more convenient in the applications involving food irradiation are chemical dosimetric systems. The most widely used reference method is the oxidation of ferrous ion to ferric ion in an acid aqueous solution. This dosimeter (known as the *Fricke dosimeter*) is widely used for calibration of routine methods, the ferric ion is readily measured spectrophotometrically at 305 nm, the peak wavelength for absorption. The oxidation is proportional to dose in the range of 40 to 400 kGy, and is independent of dose rate over a wide range of rates, it is also independent of temperature between 1 and 60°C. It is also independent of electron or photon energy levels within the range of 0.5 to 16 MeV. The method has a reported precision of $\pm 1\%$ (Urbain, 1986).

For routine purposes it is convenient to use one of the many commercially available dosimeters. Most of these consist of plastic or glass sheets which the light absorbance of which changes upon irradiation in a manner which allows to obtain a calibration curve relating absorbance to absorbed radiation. These as well as various solution dosimeters must be calibrated against a primary dosimeter, and these routine measurements must be frequently checked against such primary methods.

For personnel protection it is required to utilize devices which alert to low doses of radiation. Among these one of the most widely used is the Geiger Mueller counter, based on ionization.

Accumulated doses in the very low dose range are monitored by the use of radiation badges worn by personnel, which are in essence chemical dosimeters based on changes in the spectroscopic characteristic of a film or strip which is checked periodically.

D. Chemical Effects of Ionizing Radiations

Ionizing radiation initiate a vast array of chemical reactions, and a detailed discussion of these is outside the scope of the present book. Certain features of the chemical effects require mention, however, since they are central to the food preservation applications.

Most foods are aqueous systems and the primary effect of irradiation is the splitting or *radiolysis* of water. Irradiation results primarily in production of the following intermediates:

Excited water (H_2O)*
Free radicals OH^\cdot and H^\cdot
Aqueous electron e_{aq}^-

These species react with each other and with other solution components. In pure water and in presence of oxygen they produce in particular the following:

Hydrogen gas H_2
Hydrogen peroxide H_2O_2
Water H_2O
Ions H_2O^+ and OH^-

Reaction of these intermediates with water are numerous and complex and form the subject of radiation chemistry (Thakur and Singh, 1994).

In addition to water radiolysis irradiation can produce free radicals by scission of bonds in compounds other than water. The most important reaction is the formation of radicals by scission of $-\text{CH}$, $-\text{SH}$ and $-\text{NH}$ bonds in food polymers and proteins. $\text{C}-\text{C}$ bonds may also be broken producing alkyl radicals. Different groups in food polymers including proteins and polysaccharides have different radiation sensitivities. The radicals can undergo further reactions as indicated schematically in Fig. 11.6 for the case of proteins. Lipids are sensitive to irradiation and in particular lipid oxidation rates are greatly enhanced because of initiation of this chain reaction by radicals preformed by irradiation. Carbohydrates are also sensitive to irradiation. The consequences of these reactions to wholesomeness, and their role in producing the desirable preservation effects are discussed in subsequent sections.

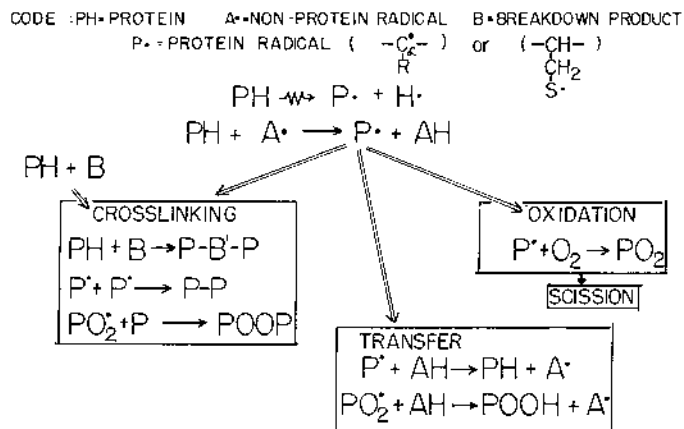


FIGURE 11.6 Radiation-induced reaction of proteins.

E. Effects of Radiation on Living Organisms

The potentially lethal effects of ionizing radiations were realized soon after the discovery of x-rays by Roentgen and of natural radioactivity by Becquerel in the late nineteenth century. The sensitivity of organisms to radiation increases with their complexity. The following is a listing of approximate ranges of lethal effects on various organisms. (It should be noted that chronic, or genetic effects may occur in organisms showing no acute effects immediately after the irradiation.)

Humans: Lethal in the range of 2 to 10 Gy (depending on individual sensitivity)

Plants: Sprouting inhibited in the range of 5 to 100 Gy

Insects: Lethal to specific developmental stages in the range of 10 to 1000 Gy

Vegetative bacteria: 500 to 10,000 Gy

Spores: 10,000 to 50,000 Gy

Viruses: 10,000 to 200,000 Gy

Biological effects of radiation are usually divided into **direct** effect in which it is assumed that a single "hit" on a sensitive target in a cell results in cell death, and **indirect** in which the cell death is ascribed to reactions with the various reactive species generated by irradiation. The direct hit theory does not apply well to multicellular organisms, but even in unicellular organisms indirect effect may predominate. The mechanisms are therefore very complex and far beyond the present discussion. However certain key features of biological response to

irradiation are crucial to the understanding of the radiation preservation process and will be discussed below.

1. Lethal Effects on Microorganisms

In the case of lethal effects of thermal processing the logarithm of the surviving fraction of organisms exposed to a given constant temperature decreases linearly with time. Similarly a plot of the logarithm of the surviving fraction against dose yields a straight line both cases “death” has the meaning of inability of the organisms to grow, that is, to produce new colonies. Death so defined does not necessarily result in immediate cessation of the metabolic activity of the cell. In contrast to thermal processing in which calculation of lethality kinetics require consideration of two factors, the intensity factor–temperature, and the extensive factor–time; in radiation-induced lethality it is possible to relate the kinetics to dose only. Dose rate (intensity of radiation) may have some effects but within the range of intensities of relevance in radiation processing these are of sufficient impact to preclude the relation between dose and lethality.

The relation used, as shown in Eq. (6) results in graphical representation shown in Fig. 11.7.

$$\frac{n}{n_0} = \exp\left(\frac{-D}{D_0}\right) \quad (6)$$

where n/n_0 is the fraction surviving organisms, D is the radiation dose, D_0 is a lethality constant dependent on organism and irradiation conditions.

D_0 may be conveniently thought of as the dose resulting in the destruction of approximately 63.3% of the organisms. A useful related constant is D_{10} or decimal reduction dose, which is the dose, reducing the number of organisms by a factor of 10. D_{10} is equal to $2.303/D_0$.

Different microorganisms have different sensitivities to irradiation. Table 11.4 lists the lethality constants for some microorganisms of particular importance in food processing.

The fairly broad range of lethality values for each given microorganism shown in the above table is due to the fact that lethality is affected not only by the type of microorganism, but also by various other factors.

In particular the following factors affect the survival of irradiated organisms:

1. Water content. Typically the more dilute the medium in which irradiation is conducted the lower the microbial survival. This is due to a higher relative concentration of water-derived radiolytic products. It should be noted that freezing decreases the concentration of unfrozen water and has protective effects.

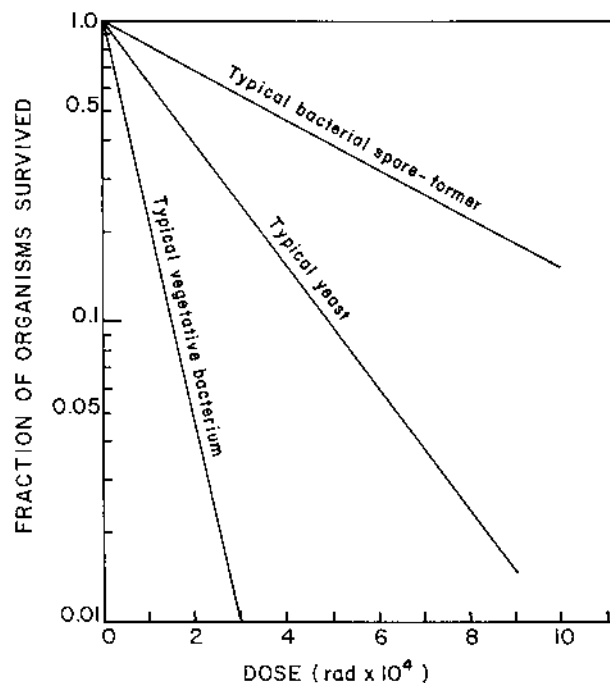


FIGURE 11.7 Typical dose response curves for different types of microorganisms.

2. Specific components of the medium may have protective or sensitizing effects. pH is an important factor affecting sensitivity. Increasing oxygen concentration in the medium usually sensitizes the organisms to radiation-induced lethal effects.
3. Temperature has a very significant effect. The effect of radiation is usually enhanced by increasing temperature during irradiation.
4. Dose rate and kind of radiation (electron, gamma ray, or xray) is not a major factor in affecting dose-dependence of the lethality.
5. Pretreatments have an important effect. In particular creating conditions, which germinate spores, increases sensitivity to radiation of spore forming organisms.

The bactericidal action of radiation on pathogens does not necessarily eliminate the danger of toxins formed before the irradiation. In particular for the toxins produced by *C. botulinum* and *S. aureus* the doses required to inactivate the toxins greatly exceed the lethality requirements.

TABLE 11.4 Typical Values of Lethality Constants for Selected Bacteria

| Microorganism | D ₁₀ (Gy) |
|---------------------------------------|----------------------|
| Vegetative bacteria (range) | 100–2000 |
| <i>Campylobacter</i> species | 100–300 |
| <i>E. coli</i> (including O157:H7) | 200–500 |
| <i>Micrococcus radiodurans</i> | 2500–6000 |
| <i>Pseudomonas fluorescens</i> | 50–200 |
| <i>Salmonella</i> species | 250–2000 |
| <i>Staphylococcus aureus</i> | 200–600 |
| Bacterial spores (range) | 300–6000 |
| <i>Bacillus subtilis</i> | 300–3000 |
| <i>Clostridium botulinum</i> (Type A) | 3000–6000 |
| <i>C. botulinum</i> (Type E) | 1000–1500 |
| <i>C. perfringens</i> | 1100–2200 |
| <i>C. sporogenes</i> PA3679 | ~ 2200 |

Yeasts and molds are important food spoilage agents. They can be controlled by irradiation. However because measurement of individual cells surviving is not as convenient as in the case of bacteria calculations of the lethality is not usually based on Eq. (6). The following radiation doses are considered to effectively eliminate danger of sufficient cell survival to allow significant growth after irradiation. (It is important to note here that irradiation does not prevent growth if the food material is contaminated after the treatment. In this respect thermal and radiation processing are similar.):

Yeast: 5000 to 20000 Gy

Molds: 1000 to 10000 Gy

Parasites, including protozoans and helminths include pathogens transmitted through food consumptions. Among the protozoans *Toxoplasma* and *Entamoeba* are often food borne, and can cause illness. They are readily inactivated by low radiation doses (less than 500 Gy). Helminthic parasites including the cause of trichinosis (*Trichinella*) and the several tapeworms (*Taenia* species) and flukes require higher doses (up to 5000 Gy).

Viruses are difficult to inactivate by irradiation, and their D_{10} values may be in excess of 5000 Gy. Since the viruses are usually quite sensitive to heat, radiation in combination with heating may often be effective in controlling bacteria as well as viruses.

2. Control of Insect Infestation

Insect infestation is one of the major causes of losses of plant derived food products, including grains, and grain-derived products, legumes, fruit and various dehydrated foods. Their control is often dependent on the application of pesticides, and fumigants. Irradiation offers an attractive alternative because insects are quite sensitive to ionizing radiation, and the application of radiation treatments leaves no chemical residues, and at the dose levels required results in negligible change in the desirable properties of the treated materials. Of course in contrast to those chemical pesticides, which persist in the treated matter, irradiation offers no protection against re-contamination by insects, and is therefore useful only if such recontamination is prevented.

Studies on radiation-caused effects on insects have been carried out very extensively, in the United States, Great Britain, and many other countries. The present author was responsible for the insect irradiation effort carried out at MIT as part of the overall irradiation project (Proctor et al., 1954). We found that immediate lethality required substantial doses of radiation, but reproduction, and development of the next insect stage (i.e., larvae from eggs, pupae from larvae, and adults from pupae) could be prevented by doses of only several thousand rad (10–50 Gy). Figure 11.8 shows the survival of adults of two species of insects irradiated with gamma rays. Table 11.5 shows the doses required to kill adults and larvae of two grain-infesting beetles using either gamma rays or machine-produced electrons (cathode rays). It was found in subsequent studies that the minor differences between the two forms of radiation were due to differences in dose distribution within the irradiated samples, (see Fig. 11.5), which were particularly significant for irradiation of adults which were mobile during, and for which a uniform distribution of insects within the sample was not assured. In general, however, the effects of the radiations were similar. Adults and larvae were killed within 1–2 days when irradiated with doses of 1000 to 3000 Gy. It should be noted that further reproduction is inhibited with much lower doses. Table 11.6 shows that irradiation of eggs of beetles with 200 to 500 Gy prevented the hatching and larval development.

Subsequent studies reported by Urbain (1986) showed that development of insects and mites could be completely arrested by doses of 100 to 1000 Gy.

F. Technological Aspects of Food Irradiation

1. Applications of Radiation Processing in Food and Related Materials

a. Sterilization in Hermetically Closed Containers. This application was the first to be explored, and was presented as an alternative to canning, especially in military rations and in space travel. It has more recently been termed

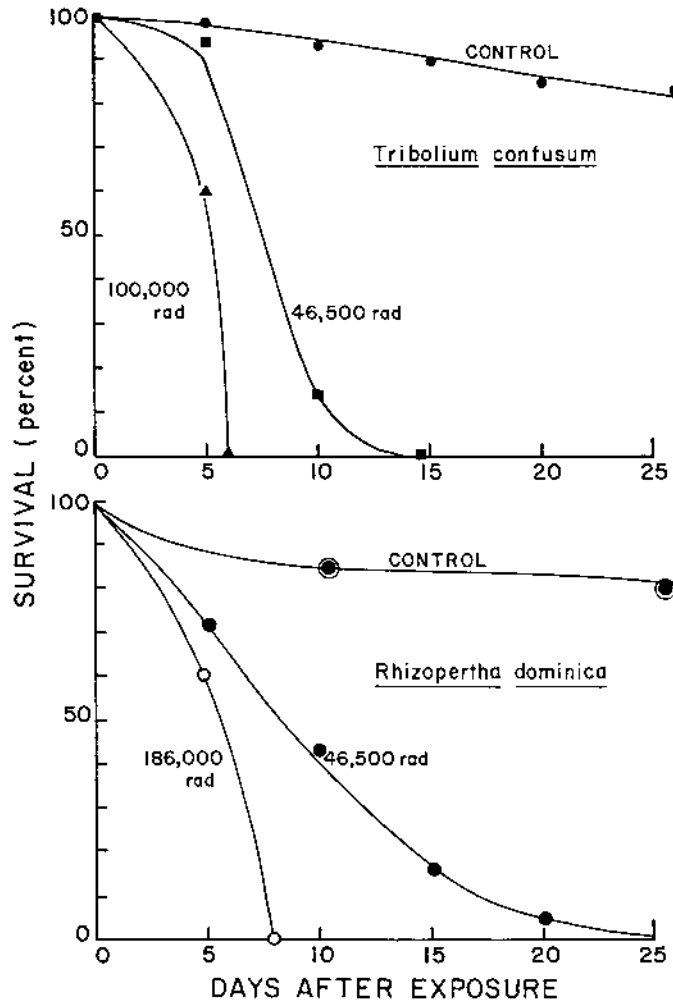


FIGURE 11.8 Survival of irradiated adults of two insects.

radappertization. It involves the application of doses of radiation in the range of 20 to 50 KGy, and is usually designed to be supplemented by a mild heat treatment to inactivate enzymes and viruses. Most of the interest in sterilization of foods has been in processing of meats and some fishery products. A major limitation on doses, which can be applied, is the production of organoleptic defects in the foods. These can be overcome to a large extent by irradiation in the frozen state, which reduces indirect chemical effects producing off flavor and loss of vitamins.

TABLE 11.5 Effects of Radiation on Two Insects: *Tribolium confusum* (Confused Flour Beetle) and *Oryzaephilus surinamensis* (Grain Beetle)

| Insect | Radiation | Dose (Gy) | Mean survival time (days) |
|------------------------|------------|-----------|---------------------------|
| <i>T. confusum</i> | | | |
| Adults | None | — | Over 70 |
| | Gamma rays | 230 | 7 |
| | Gamma rays | 2000 | 1.7 |
| | Electrons | 2430 | 2.4 |
| Larvae | None | — | Over 30 ^a |
| | Gamma rays | 230 | 6.5 |
| | Gamma rays | 1860 | 1.5 |
| | Electrons | 2040 | 1.5 |
| <i>O. surinamensis</i> | | | |
| Adults | None | — | Over 70 |
| | Gamma rays | 1580 | 1.1 |
| | Electrons | 1670 | 1.1 |
| Larvae | Gamma rays | 1580 | 1.5 |
| | Electrons | 1580 | 1.5 |

^a Mean time to development into pupae.

b. Reduction of Concentration of Spoilage Organisms. This is equivalent in its effect to the heat pasteurization methods, and has been termed *radurization* defined as a method to substantially reduce numbers of viable spoilage organisms. This method is usually supplemented with other preservation procedures, in particular with refrigerated storage. Radurization usually is

TABLE 11.6 Effect of High Energy Electrons on Development of Eggs of *T. confusum* (Confused Flour Beetle)^a

| Dose (Gy) | Status following irradiation | | | |
|-----------|------------------------------|-------------|-----------|-------------|
| | Day 5 | | Day 25 | |
| | Unhatched | Live larvae | Unhatched | Live larvae |
| Control | 79 | 21 | 36 | 60 |
| 235 | 98 | 2 | 98 | 0 |
| 465 | 100 | 0 | 100 | 0 |

^a One hundred eggs used in each experiment.

effective in prolonging the shelf life of animal products, and to some extent with plant products, but these often show quality defects due to radurization. The dose range required for this treatment is 1 to 5 KGy.

c. Inactivation of Nonspore-forming Pathogens. This application has been termed *radicidation*, it differs from radappertization in applying doses of radiation much lower than those required to inactivate spores. Among the nonspore-forming pathogens of particular interest here are the *Salmonella* species as well as *Listeria* and most recently the pathogenic *E. coli* species. The doses proposed for this purpose range from 2 to 8 kGy, depending on the food and the expected level of contamination.

d. Inhibition of Sprouting and Delaying the Senescence of Plant Materials. Potatoes, onions and carrots are among vegetables stored for considerable periods of time after harvest, often at ambient temperatures. Substantial losses can occur during storage due to sprouting, fungal diseases, and moisture loss. Sprouting is frequently controlled by application of chemicals such as maleic hydrazide, or by storage at refrigerated temperatures. However chemical treatments are decreasing in desirability because of concerns with health effects of their residues and refrigeration is not only expensive, but it can cause an increase in reducing sugars during storage, thus making potatoes more susceptible to nonenzymatic browning and therefore less suitable for processing as potato chips. Irradiation is an effective method of sprouting prevention, and has been used commercially in Canada and in Japan. The sprouting inhibition by irradiation is attributed to necrosis of growing points of the dormant buds. A dose 0.02 to 0.05 kGy is effective in sprouting control of potatoes and onions. Irradiation is most effective when applied soon after the harvest. Other vegetables in which sprouting can be inhibited include garlic, sweet potatoes, yams, and some other tubers.

Storage life of fruit and some vegetable is often limited by biochemical activity in a post harvest stage known as senescence, characterized by an increase of respiration rate, abnormal metabolic activity and loss of dry matter. The senescence phase can be delayed by irradiation, and in climacteric fruits ripening can be delayed by days, and in some cases weeks.

Doses considered suitable range from 0.2 to 0.5 kGy. It should be noted that fruits are very sensitive to excessive doses of radiation, and the dose chosen must be optimized to obtain the maximum quality of stored fruits.

2. Disinfestation of Grains, Dried Fruits, Nuts, and Other Insect-Infested Materials

As indicated previously doses required to kill insects and mites, or to prevent their reproduction are relatively low, and radiation is a very suitable method of

disinfestation. There are the major potential application types, some of which have in fact been used commercially in some countries, as will be discussed later.

The types are:

1. Disinfestation of bulk shipments of grains, legumes, and other commodities. The most effective method would be to carry out the disinfestation when the materials are loaded into ships, or trains, or when they are received, and before they are transferred into storage silos.
2. Disinfestation of various dry foods, after they are packaged. In this case the recontamination is prevented.
3. Treatment of fruits from areas which harbor insects which are quarantined at the locations to which they are exported.

Disinfestation requires doses in the range of 0.1 to 1 KGy.

3. Treatment of Waste Streams

A number of applications are possible in which the food itself is not treated, but some materials involved in the food processing system are. The doses would of course be adjusted according to the nature of the waste, level of contamination, and the intended end result. Among important suggested applications are elimination of *Salmonella* and related species from the wastes in meat and poultry industries. Sterilization of animal waste derived meals is another potential target since it is considered an important source of contamination. Recent developments in Europe, where animal feeds derived from parts of slaughtered animals are being banned because of the danger of transmission of the "mad cow disease" causative agents, may greatly reduce the utilization of these meals worldwide since prions, which are the causative agents, are not inactivated by currently available techniques.

Another application which has been suggested is treatment of cooling water for fish on board fishing vessels. By maintaining the microbial count at a low level, without heating the water, it should be possible to retard the deterioration of fish prior to the time of their delivery for further processing at the harbor.

4. Other Applications

As indicated previously radiation causes scission of polymer chains especially those of polysaccharides. It has been suggested to use this capability of radiation treatments to enhance the rehydration of dried vegetables. Similar treatments can also be applied improved the texture of vegetables with excessive toughness due to crosslinking.

An interesting application is the possibility of enhancing the aging of whiskey. The flavor and appearance of these beverages is due to oxidative changes accelerated by irradiation prior to storage.

5. Irradiation Sources

a. Radioactive Isotopes. Of the many man-made radioactive isotopes only two are considered suitable for irradiation applications, ^{60}Co and ^{137}Cs . Radioactive cesium can be separated from spent nuclear fuel, and the radioactive cobalt is obtained by neutron irradiation of the non radioactive cobalt isotope ^{59}Co .

Cobalt-60 sources are the only radioactive units available for food processing at the present time. The usual procedure for their production is to machine cobalt metal into shapes suitable for the radiation source design, encapsulating it in a material that does not become radioactive in a neutron flux, and then exposing it to the intense neutron flux in a reactor. A second encapsulation follows the irradiation. The operations involving the handling of the ^{60}Co material must be carried out by remote control, since exposure of humans to the now intensely radioactive material would be lethal.

^{60}Co emits 2 γ rays per disintegration, with energies of 1.17 and 1.33 MeV, and a half-life of 5.3 y. Material with several hundred Ci/g can be produced, and assembled into megacurie sources.

A typical installation which was operational at the U.S. Army laboratories in Natick in the 1970s. It consisted of nickel-plated cobalt wafers, which were further encased in stainless steel in groups of 15 wafers each. The source consisting of two radiation "walls" was immersed in a 25-ft-deep storage pool of water when not in use. During irradiation the source would be raised by remote control, and a conveyor carried the material to be irradiated between the walls. The source was capable of processing several thousand kg of material at a dose of 50 kGy. Photographs of the Natick source in the submerged and raised states is shown in Figs. 11.9 and 11.10. The U.S. Army discontinued the use of the source in the 1980s and the source was transferred to the University of Lowell (in Lowell, MA), where it was used in studies on radiation applications. Commercial automatic pallet irradiator have been designed by Atomic Energy of Canada Ltd (Urbain, 1986).

A gamma irradiator with the flux entering the irradiated material from two opposing sides has the advantage of being capable of delivering a fairly uniform dose to the irradiated material. Since the half thickness in water for gamma rays of the energy of the ^{60}Co irradiators is approximately 11 cm, it is possible to obtain a very efficient energy absorption patterns even for fairly large thick packages of food. A number of commercial irradiators processing materials on a contract basis exist in the United States and in Europe. The total production throughputs at this time are limited.



FIGURE 11.9 A cobalt-60 source in raised (operational) position. (Courtesy of U.S. Army Natick Labs.)

An economic analysis of irradiators has been reported—Morrison (1989). She assumed annual throughputs for various applications including irradiation of poultry, fish and fruit ranging from 8 to 416×10^6 lb and estimated the cost of processing at 0.01 to 0.06/lb. The absence of large scale irradiation enterprises makes these values useful only as very approximate estimates.

b. Electron Accelerators and X-ray Generators. Alternative sources of ionizing radiations are electron accelerators and x-ray generators. Machine generation of radiation has several advantages, as well as disadvantages. The machine generated beams have the great advantage that the radiation stops when the machine is turned off, and they do not present the environmental problem of disposing of the radioactive material when it is not longer useful. Electron generators are also capable of high energy outputs and therefore are suitable for high throughput applications.

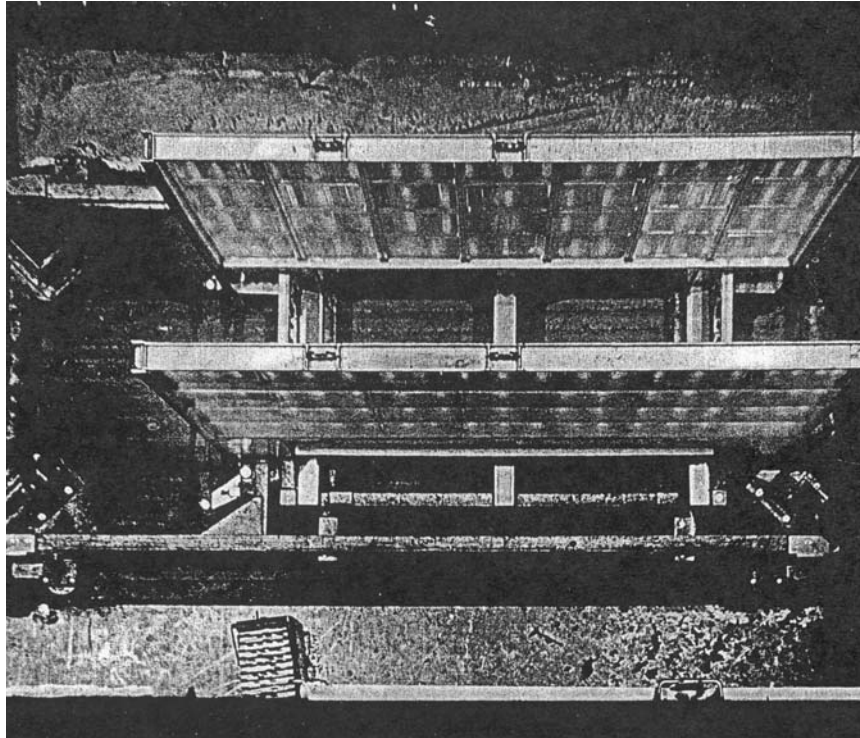


FIGURE 11.10 A cobalt-60 source in submerged position. (Courtesy of U.S. Army Natick Labs.)

Their major disadvantage is the limited penetration by electrons, as shown in Fig. 11.5. The maximum energy allowed by FDA is 10 MeV (above 12 MeV there is the possibility of inducing radioactivity in some atoms which may be present in foods or in packages), and at these energy levels the penetration of electron beams is limited. The acceptable package thickness may be increased by irradiating from two sides, and the lateral dose distribution pattern may be made more uniform by beam scanning. (Figs. 11.11 and 11.12). Even with these improvements the useful package thickness is probably below 3–5 in, depending on product and package characteristics.

Conversion of the electron beams to x rays increases the penetration, but this conversion makes the cost very high because the conversion to x rays is inefficient.

A number of companies produce machines generating high energy electron, and several of them also operate facilities allowing irradiation of products on a contract basis. The North American Suppliers Directory of

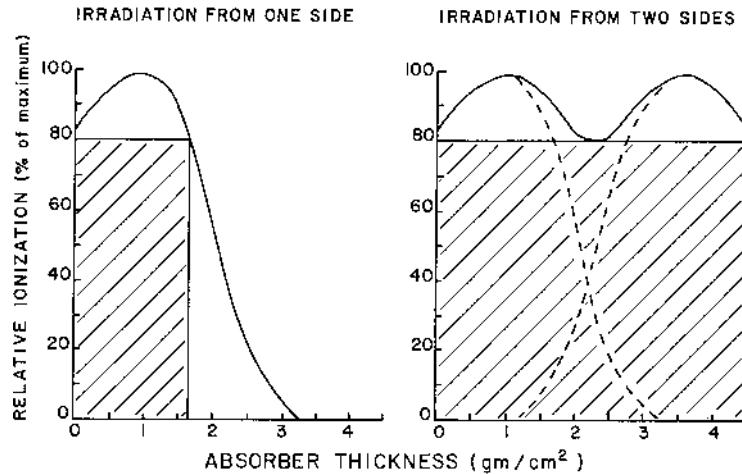


FIGURE 11.11 Relative ionization within a food irradiated with electrons.

Sterilization: Equipment on the web (<http://www.devicelink.com/company98/cat/1267.html>) lists 10 companies.

The listing of European companies includes 18 contract sterilization facilities and 9 manufacturers. The French manufacturer CGR MeV is among the leaders in this field in Europe.

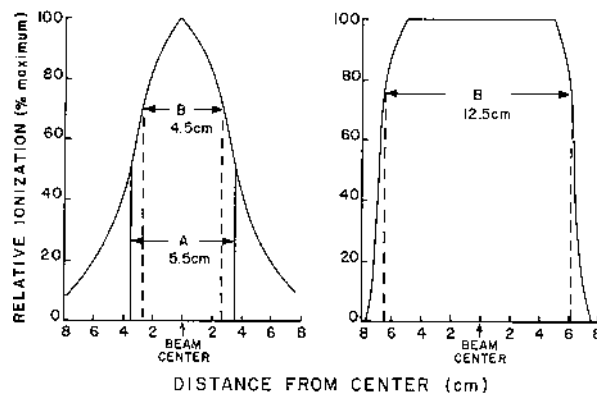


FIGURE 11.12 Schematic representation of effects of scanning an electron beam on lateral distribution of beam density. Left: the situation without scanning. A represents the width receiving at least 50% of maximum dose and B, at least 70%. Right: with scanning. B represents the width receiving at least 75% of the maximum dose.

The overwhelming majority of users of this equipment and contract services are outside the food field. Radiation treatment of industrial material and sterilization of medical supplies are the major applications. The cost of processing by machines was estimated to be in the same order of magnitude as that using cobalt irradiators (Morrison, 1989).

c. Modified Irradiation Processes and Processes Combined with Other Physical Treatments.

Pulsed X-ray Treatment: It has been proposed that new developments in x-ray technology which allow the production of pulses of x-rays may offer unique benefits. The novelty of pulsed application of x-rays lies in the mode of delivery, which results in high dose rates and intermittent application. It is proposed this mode may be useful in minimizing quality defects when delivering a given dose and by maximizing bactericidal effects. Currently available information does not permit to either confirm or deny the existence of such effects, and there is no basis, at this time for assessing the potential for using pulsed x-rays in food preservation.

Combination Treatments: Combining different physical treatments to achieve a given preservation effect, while minimizing the deleterious effect of each of the treatment is a well known paradigm in food technology. It applies to irradiation as well. In the simplest form the effect is simply due to sequential reduction of microbial populations by two methods. Given the assumed first order inactivation kinetics in both irradiation and thermal processing, if an overall reduction of n log cycles is required, then a reduction achieved by process A (e.g., irradiation) of p cycles, means that process B (e.g., heating) needs only be applied to give a reduction of $(n-p)$ log cycles. If the side effects (e.g., flavor defects) of the processes are based on different mechanisms, it can be expected that by reducing the severity of each process the overall effect on flavor is minimized, but the effect on microorganisms remains the same. In fact in many cases a further synergy is observed between processes, if process A not only destroy part of the microbial population, but also further sensitizes the survivors to process B.

G. Organoleptic Acceptability and Safety of Irradiated Foods

The ultimate success of irradiation as a method of food processing depends on its ability to deliver to the public foods that are acceptable, nutritious, and safe, both in fact and in public perception, at an acceptable cost.

The quality factors are therefore of extreme importance, food irradiation can produce changes in texture, flavor, taste and appearance of foods. In this

respect it is no different from the methods of processing, which can also cause these changes, and in fact these changes can and do occur in the absence of any processing. It is essential therefore that each type of processing application be evaluated to determine if the desirable effects produced by the process are not negated by undesirable effects. Since the balance of positive effects varies with type and condition of the food at the time of processing, dose of radiation, conditions of irradiation and subsequent storage and with methodology of handling and preparation after storage, a blanket statement ranking organoleptic effects of different processes is simply not possible. Some food products taste best when eaten fresh, but others actually improve with processing. Similarly the damage to organoleptic properties due to radiation is often considerably less than that resulting from thermal or dehydration processes achieving equivalent storage stability, in other situations irradiated food is less acceptable from an organoleptic point of view.

In the applications that have been proposed by commercial organizations, and by nonprofit research groups with knowledge of industrial food technology, it can be almost taken for granted that organoleptic properties are given adequate consideration. After all they determine if the product will be bought at all.

It is the present author's opinion that for most if not all of the applications currently approved by FDA, or seriously considered for approval, conditions of processing can be developed which result in organoleptically acceptable products.

In the first edition of the present book we posed five questions, the answers to which are central to deciding if the foods produced by irradiation are wholesome. The most recent evaluation papers of FDA (Pauli, 2000) confirm the validity of these question and show that the approvals granted to date are based on adequate answers to these questions:

1. Can the process result in contamination with or induction of radioactivity? The answer to this question is simple. Within the limits of radiation types approved for treatment induction does not occur, and contamination has a probability as near to zero as can be achieved by human foresight.

2. Can a safety program protecting operating personnel be designed and implemented? The answer is again simple. Operations in biomedical and industrial sterilization, as well as in other isotope handling operations have an excellent safety record. The few catastrophic accidents that have occurred in plants handling radioactive materials have been so rare that they are items commanding banner headlines in the World Press.

3. Do the changes in the microbial flora surviving after irradiation create a potential hazard, and in particular, will irradiation preferentially reduce the numbers of spoilage organisms, allowing pathogens to grow undetected without competition? The possibility of such an outcome does exist and has to be

prevented in the relevant process design. The following quote from a recent paper by Dr. Pauli of the FDA shows the present, justifiably conservative FDA attitude.

Before approval FDA requires evidence that the proposed conditions of use achieve the intended microbiological technical effect and that irradiated food is not potentially less safe than nonirradiated food because of the possibility of undetected pathogen outgrowth or toxin production before spoilage is evident. This safety must be demonstrated under all realistic scenarios that may occur in commercial practice. It is worth noting that the microbiological safety question is by no means unique to irradiation but is equally applicable to any food process that reduces the number of microorganisms but which does not eliminate them (Pauli, 2000).

4. Does irradiation result in nutrient losses of public health significance? This subject has been explored extensively and it was concluded that when foods are exposed to ionizing radiation under conditions envisioned for commercial application, no significant impairment in the nutritional quality of protein, lipid, and carbohydrate constituents is observed. Irradiation is no more destructive to vitamins than other food preservation methods (Snyder and Poland, 1995).

5. Does the energy input by radiation cause chemical or biochemical reactions that produce toxic or carcinogenic compounds rendering the food unsafe? It must be noted in this respect that Food and Drug Law of 1958 uniquely considers food irradiation, as a food additive.

The evaluation of the safety of the process has therefore been uniquely rigorous (Josephson et al., 1979).

Acute and chronic toxicity, mutagenicity, and carcinogenicity of irradiated foods were studied more extensively than those of foods processed by any other method by orders of magnitude. This caution was probably justified, because the application of radiation was new, and with respect to the previous methods the population consuming the foods actually served as the test "animals." In addition to various biological tests the studies included thorough reviews of the radiation chemistry of food components using the most modern analytical techniques. The results of the very numerous studies were reviewed not only by U.S. FDA but by international bodies as well.

The Joint FAO/IAEA/WHO Expert Committee in 1981 concluded that irradiated foods are safe and wholesome and that the irradiation of any food commodity up to an overall average dose of 10 kGy presents no toxicological hazard (hence, toxicological testing of foods so treated is no longer required), (Brynjolfson, 1985). The FDA does not grant such a blanket approval but has acted conservatively by approving individual applications on the basis of their specific merits.

H. Status of Commercial Application of Food Irradiation

As mentioned previously the applications radiation preservation of food are very limited. In the United States the essential prerequisite to the commercial use of radiation is the approval of the pertinent federal agencies (FDA or USDA). The approvals for radiation applications have been granted for a number of important applications, including those listed below:

- Control of trichinosis in pork (doses of 0.3 to 1 kGy).
- Delay of maturation of plant materials (up to 1 kGy).
- Insect disinfestation of grains and other materials (up to 1 kGy).
- Sterilization of spices (up to 30 kGy).
- Irradiation of poultry to control pathogens (1.5 to 3 kGy).
- Irradiation of red meats (up to 4.5 kGy for unfrozen, and 7 kGy for frozen meats).
- Most recently FDA approved irradiation of eggs with up to 3 kGy to assist in control of *Salmonella*.
- Approval was also given to sterilization with doses up to 44 kGy of rations to be used in space travel (Karel, 1989).

Two important issues with respect to approval of irradiation application are labeling and post-irradiation identification of irradiated foods. FDA requires labeling if the entire product or major ingredient has been irradiated. The current version of the FDA low-dose irradiation rule requires that the retail label consist of the internationally agreed-upon symbol (International Food Irradiation Symbol), and the phrases “treated with radiation” or “treated by irradiation.” Irradiated spices in foods are considered minor ingredients and do not require labeling in combination products. Chemical and physical methodology for identification of irradiated food has been and continues to be the subject of very substantial research efforts. A perfect method applicable across the board does not exist. It is even more difficult to conceive and implement methodology which would determine post facto the dose of radiation which has been delivered. In a review of control of food irradiation by international and national authorities Ehlerman concluded that “only reliable inspection of records available at the irradiation facility can reveal range and statistical dose distribution and thus render labeling meaningful” (Ehlerman, 1993).

In addition to approval of specific foods for irradiation, the use of specific packaging materials during the irradiation is also subject to regulation, which are based on chemical and physical effects of radiation on these materials. FDA requires that packaging that holds food during irradiation comply with regulations based on appropriate testing. It is important to note, however, that these regulations have been amended only once in recent years. Because of this FDA urges packaging manufacturers and others interested in using a packaging

material for holding food during irradiation to check these regulations early in their planning for commercial development either to ensure that the proposed packaging has been listed in the regulations for packaging to be used during irradiation or to submit a petition (or possibly a notification) for additional packaging materials not raise new issues not considered in the earlier approval (Pauli, 2000). Studies on suitability of irradiated materials were started in the 1950s (Proctor and Karel, 1955) and continued by many organizations.

An extensive review of effects of radiation on plastic packaging materials was published recently (Buchalla et al., 1993).

In spite of the existence of these regulations the actual use of radiation processing in the United States is insignificant. There is a somewhat more significant but still very low volume of irradiation in other countries. France has plants processing mechanically deboned chicken meat and is treating Camembert cheese. Netherlands has commercialized a variety of irradiated products. On the other hand, several commercial ventures outside the United States have failed. These include potato processing in Canada and a fairly extensive grain irradiation program in the former Soviet Union.

The future of radiation processing depends in large measure on consumer attitudes. At the present time there exists a significant and active fraction of the consumers, which has a strong anti-technology bias. This bias is particularly evident in Europe, where consumer groups have lobbied successfully against the use of genetically modified foods and many types of food additives and have a generally negative attitude to food processing. The future of radiation processing and of other technological innovations will depend on the open and truthful discussion of all relevant issues in the public forum (Skerrett, 1997). Almost all measures in the field of public health such as chlorination and fluoridation of water supplies, control of diseases spread by insects by spraying of insecticides, vaccination against diseases, and indeed various food processing measures have potential benefits and risks. Regulation of these measures by regulatory agencies are based on scientific arguments. However the acceptance by the general public is best attained by education of all concerned in the issues relevant to these measures (Karel, 2000).

III. HIGH-PRESSURE PROCESSING

A. Principles

1. General Methodology of Treatment

High-pressure processing (HPP) refers to the application of hydrostatic pressure to foods. Pressures which have been used range from 100 to over 800 MPa equivalent to 1000 to 8000 atm.

The general methodology of HPP is simple in principle. Food packaged in a flexible container is placed in a pressure vessel. The packages do not get deformed because the pressure is uniform. The closed pressure vessel is filled with a pressure transmitting fluid. In most of the present applications the fluid chosen is water. The water is compressed. At room temperature the resulting volume change is 4% at 100 MPa and 15% at 600 MPa. The food remains under pressure for a specified time period, and then the chamber is decompressed and a new batch treated.

2. Interdependence of Temperature and Pressure Effects

It is important to keep in mind an important feature of this process, which distinguishes its characteristic lethal effects from those of ionizing radiation: The lethality of the process is strongly dependent on temperature, and the application of pressure causes significant heating of the media to which it is applied.

The increase in temperature is reported to be approximately 3°C per 100 MPa and varies with the product to which it is applied. Exposure of foods to 800 MPa may therefore increase the temperature by some 24°C. In contrast an ionizing radiation dose of 10kGy, which is typical of high-dose applications, raises the temperature of water by 2.6°C (Davison et al., 1953).

Most significant, however, is the fact that within wide temperature ranges the temperature during irradiation has only relatively minor effects on the lethality of the applied dose, but the effects of applied pressure vary dramatically with relatively small changes in temperature. As an example exposure for 60 min of *B. stearothermophilus* spores to a pressure of 8000 atm (800 MPa) at a temperature of 20°C showed no lethal effect. Treatment at 60°C gave a reduction of 3–4 log cycles at the same pressure and time of exposure (Hayakawa et al., 1994).

B. Physicochemical Effects of Pressure

The principle of Le Chatelier affects the behavior of systems under compression. The principle states that “A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance.” Consider as an example increase in pressure in a gaseous system in which an equilibrium between two molecules A and B exists in the form:



The principle implies that the reaction will adjust to minimize the increase in pressure by reducing number of molecules. The equilibrium will shift in favor of increasing A (Atkins, 1990). Pressure changes the physical properties of materials, and it affects reaction rates. The dependence of reaction rate constants on pressure may be expressed in an equation analogous to the Arrhenius equation, which describes the dependence on temperature: The pressure dependence is

given by

$$-RT \left(\frac{d \ln k}{dP} \right)_T = \Delta V^+ \quad (7)$$

The quantity ΔV^+ is the *activation volume* analogous to the activation energy in the Arrhenius equation. In the range of pressures of interest here the effects of pressure on reaction rates are less dramatic than the effects of temperature in the range of temperatures used in processing. A pressure increase of 100 MPa produces an increase of the order of those produced by temperature increases of 10°C (Tauscher, 1995).

The Le Chatelier principle also implies that increasing pressure will increase the degree of ordering of molecules. It also implies an increase of the melting point with increasing pressure (since the specific volume of a solid is lower than that of liquid). A notable exception to the above rule is water, for which the melting point of the normal ice form (ICE I) decreases with pressure. This is of course due to the well-known unusual volume change in melting of ICE I. Water has a higher density than ice.

At high pressures (several hundred MPa) the freezing point increases with pressure, but the forms of ice created are different from ICE I (Heremans, 1992).

Effect of pressure on food components varies with specific components and other variables. Proteins may be subject to pressure-induced denaturation, and pressure may result in inactivation of some enzymes. Membrane structures (composed of lipid protein complexes) can undergo dramatic changes due to transitions in lipids or changes in protein structure. High pressure is also known to induce changes in structure of gels, but these changes are not well documented (Heremans, 1992).

C. Effects of High Pressure on Living Systems

The fact that high pressure can exert potentially lethal effects on microorganisms has been noted in literature at least 100 years ago, but applications to food processing are recent (Earnshaw, 1995). The proposed mechanisms of microbial inactivation by pressure can be grouped into the following (IFT, 2000b):

1. Effects on membrane
2. Effects on cell biochemistry and physiology
3. Effects on genetic mechanisms

An analysis of the evidence for each of the above effects is beyond the scope of the present book, but it may be noted that membrane damage is considered to have a dominant role by recent reviewers.

The following aspects of the pressure effects, however, require consideration in a book on physical principles of food preservation.

1. Kinetics of inactivation by pressure
2. Sensitivity of different organisms of processing significance
3. Effects of various factors on sensitivity to pressure

1. Kinetics of Inactivation

In order to compare sensitivities of different organisms and to assess the effectiveness of different processes, it is necessary to understand the relations between the intensive and extensive parameters of the process and the lethality effect. In the case of HPP the intensive factor is pressure and the extensive factor is time, in the case of heat processing temperature and time are the corresponding factors. As discussed above in radiation processing it was possible to largely ignore the intensive factor (dose rate) and to base microbial death kinetics on the single (extensive) factor-dose.

The formulation of pressure inactivation kinetics is currently based on very few studies, since most of the work did not include sufficient number of variations of the variables pressure and time to allow development of kinetic equations. Two models have been proposed: (IFT, 2000a,b). Both assume that at constant temperature and pressure the microbial inactivation follows a first order equation:

$$\ln \frac{n}{n_0} = -kt = -2.303 \frac{t}{D_{10}} \quad (8)$$

where k is the reaction rate constant, D_{10} is the decimal reduction time, and n/n_0 is the fraction surviving at any time t .

One model formulated based on work with yeast, assumes that the change of D_{10} with pressure follows the equation

$$\log \frac{D_{10}}{D_{10R}} = \frac{P - P_R}{z(P)} \quad (9)$$

where the subscripts R refer to a reference pressure condition and $z(P)$ is the pressure increase required to accomplish a 1 log cycle reduction in D_{10} .

An alternative model is given below:

$$\ln \frac{k}{k_R} = - \frac{V'(P - P_R)}{RT} \quad (10)$$

where V' is activation volume constant, obtained from the slope of $\ln k$ plotted against P .

2. Sensitivity of Different Organisms

As in the case of thermal resistance nonspore-forming bacteria are the most sensitive to pressure. A compilation of D values for *Campylobacter*, *Salmonella*, *Yersinia*, *Escherichia*, *Listeria*, and *Pseudomonas* species showed D values ranging mostly between 1 and 8 min, for pressure in the range of 300 to 700 MPa, with much higher resistance was reported in one study. The pressure coefficient $z(P)$ could not be calculated from the limited data available in these studies, but sensitivities could be compared on a comparative basis. Among the vegetative pathogens it has been found that *E. coli* O157:H8 was the most pressure-resistant. An important consideration is the apparent nonlogarithmic nature of the lethality curves, and the large differences between the sensitivity to pressure at different temperatures.

Studies on *E. coli* have shown that application of a pressure of 2500 Bar (250 MPa) to *E. coli* for 10 min at 40°C or of 20 min at 50°C, resulted in complete inactivation of suspensions of 10^9 cells/ml. At 25°C, however, a 20-minute exposure resulted in survival of 10^3 cells/ml, and continued exposure for up to 60 min resulted in an additional reduction by only 1 log cycle. Similar deviation from first-order inactivation kinetics (with respect to time) were found with other organisms (Ludwig et al., 1992).

The apparently increased resistance of a surviving fraction of organisms was also observed with *S. carnosus* in nutrient broth exposed to 500 MPa at 20–25°C. A reduction of the concentration by 1 log cycle was achieved in 3 min, but continued exposure failed to achieve further reductions in the count. The above observations underscore the previously mentioned interaction of temperature and pressure in HPP and also the importance of conditions of the populations being exposed. In the example mentioned above, as well as in studies on spores to be discussed below there was evidence that part of the population may have a greater resistance to pressure.

In spite of these potential sources of variability there is a strong indication that HPP in combination with moderate temperatures can achieve sufficient reduction in levels of vegetative organisms to achieve very significant shelf-life extension.

Studies on yeast (*S. cerevisiae*) carried out by Zook et al. (1999) showed D values ranging from 0.2 to 10 depending on temperature, on pressure, and on medium. The value of $z(P)$ was calculated as 113–117 MPa.

Spores are considerably more resistant. Studies on *C. sporogenes* showed D values ranging from 0.695 min at 108°C and 800 MPa to 16.7 min at 90°C and 600 MPa. The values of $z(P)$ were 752 at 108°C and 725 at 90°C.

D values were also obtained for *C. botulinum* Type A-62 inactivation. The D values at 75°C were similar to those for *C. sporogenes*, but $z(P)$ was higher at

1524 MPa. A more recent study on other strains (17 B and Cap9B) showed no inactivation after exposure for 30 min at 75°C and over 800 MPa.

It has been suggested that significant inactivation by pressure can only be achieved with spores if they are caused to germinate, thus changing to a more sensitive vegetative form (Ludwig et al., 1992). The sensitivity of viruses to pressure varies greatly between various types. Most viruses are not readily inactivated, and there is almost no information on parasites.

D. Technological Aspects of HPP

1. Equipment Available for HPP Processing

Equipment for batch HPP processing consists of a pressure vessel, which can be sealed after locating the food material within it, and can then be filled with a compression fluid, which is usually water a small amount of oil or other lubricant. The vessel must be capable of withstanding at least several thousand atmospheres of pressure and have safety features preventing explosions in the event of failure. *Direct compression* may be achieved by compressing the pressure medium with a piston driven by a low pressure pump. This equipment is mainly suitable for small vessels. *Indirect compression* is achieved by pumping additional fluid into the vessel using a high pressure pump -the so-called *intensifier*. Most industrial systems using very high pressures for isostatic pressing and larger scale food equipment use this method. Heat compression may be achieved by hermetically sealing the compression fluid, and then heating it. This method is suitable for high temperature—high pressure processes.

The surfaces exposed to water or food should be made of stainless steel. The additives to the compression fluid (lubricants, anti-corrosion agent, and preservatives must have FDA approval).

Batch equipment is available as laboratory units with volumes of 0.1 to 2 l, and as pilot plant units with capacities of 10 to 25 l. Several pressure vessels may be driven by a single intensifier system. The compression fluid is deaerated to minimize pumping costs due to air compression.

Additional water must be supplied to compensate for the volume reduction due to compression of the fluid. Figure 11.13 shows the fractional decrease in volume of water as a function of imposed pressure, and may be used to estimate the required water addition. The extremely high cost of high-pressure equipment necessitates a high efficiency of utilization. Minimizing batch turnover time is therefore a critical process objective. In this respect batch HPP processes differ from batch thermal processes in which holding time is a much less important contributor to process cost. It has been suggested that hold times of less than 10 min, and a 2-min cycle of loading, sealing, compression, decompression, and unloading may be possible in the future.

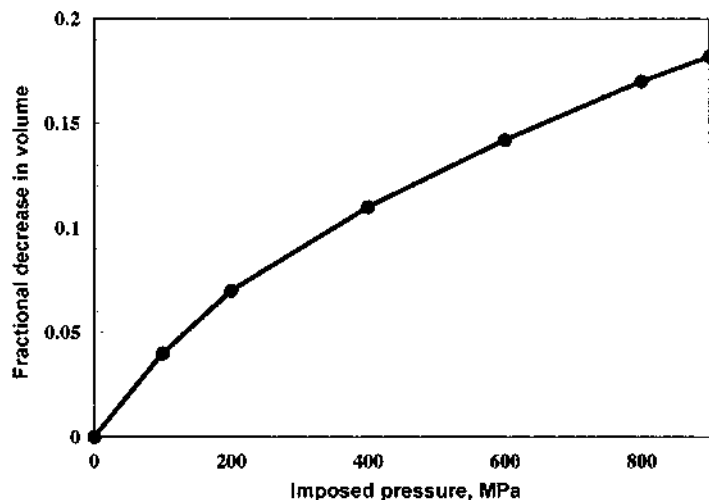


FIGURE 11.13 Effect of imposed pressure on fractional decrease in volume of water.

Semi-continuous operation is feasible with liquid products using a pressure vessel containing a free piston. The vessel is filled with liquid to be processed, displacing the free piston. When filling is complete, the inlet valve is closed and piston used to compress the vessel content. This is achieved by pumping high water under high pressure behind the piston. After the desired holding time the pressure is released, and the processed liquid discharged to a sterile holding tank through a sterile discharge port, and the cycle repeated with a new batch charged into the vessel. The treated liquid can be filled aseptically into appropriate containers.

Continuous operations is not commercially available at this time. Possible application of high-pressure homogenizers has been proposed, but appropriate methodology does not yet exist.

2. Applications of HPP to Preservation of Specific Food Products

Among the early commercial applications of HPP in Japan was the development of jams processed at ~ 300 MPa for 20 min to inactivate yeast. The jams were refrigerated after the process, and their sensory properties and vitamin retention were considered superior.

Orange juice, fresh cut pineapple, and other fruit were treated by several groups with the objective of preventing yeast-initiated spoilage. The inherent low

pH of fruit allows the use of HPP, because of low danger of bacterial pathogens. Blanching to control or post-treatment refrigeration allowed the maintenance of acceptable organoleptic properties in storage. Treatment of tomatoes and lettuce was attempted, but the results were not satisfactory.

HPP was tested as a method of preservation of various meat and fish pastes, including salmon paste, minced meat, liver paste, minced mackerel. Shelf-life extensions were achieved, but various sensory defects limited the ability to maintain high quality.

Development of products with the objective of testing their market acceptance is being carried out in the United States, Europe, Japan, and Canada. Guelph Food Technology Center at Guelph University in Canada reported in their on line newsletter dated September 2000 (<http://www.gftc.ca/newslett/2000-09/highpres.htm>) that the following HPP processed products are currently commercially available, albeit in very small quantities:

- Orange juice under the brand name Ultifruit in France
- Acidified avocado puree from Avomex Co. in Texas
- Salsa from Avomex
- Cooked sliced ham from Espuna Co. Spain
- Shellfish from Motivatt SeaFoods Inc in Louisiana
- Fruit and Vegetable juices from Samantha Inc (USA)
- Orange juice from Ortogel SRL, in Italy

The UK High Pressure Club at the University of Belfast, UK, reported in their on-line bulletin (<http://www.highpressure.org.uk/CommercialProcessing.htm>) that additional companies have some commercial HPP processed products:

- Four Japanese companies producing jams and juices
- Minute Maid in Florida producing HPP orange juice
- Pampryl Corporation in France producing orange juice.

In addition to the use of HPP for preservation and shelf life extension, it has suggested that high-pressure treatments may have specific beneficial effects on food properties. Among applications suggested are:

- Tenderization of pre-rigor beef to minimize need for aging.
- Alteration of structure of starch and of proteins in rice to reduce the time needed for cooking rice.
- Inducing gel formation of proteins. Claims have been made for better texture of pressure induced protein gels.

3. Modification of HPP Processing

The apparently limited effectiveness of HPP in achieving consistent sterilization or even pasteurization in a range of products has led to consideration of modifications in the process, including:

1. Pulsed application of high pressure. It is reported that pressure pulsing or oscillatory pressure treatment is more effective than equivalent single pulse or continuous treatment (IFT, 2000).
2. Rapid decompression after static treatment. It has been suggested that rapid decompression may cause cavitation in the cells and increase process lethality.
3. Combination of HPP with ultrasound, irradiation, and chemical treatments are potential ways of improving HPP effectiveness. It should be obvious from previous discussion that combination with thermal treatment is inherently a feature of HPP.

At the time of this writing the feasibility of these modifications is yet to be proven. The increased costs of pulsed application or decompression operation may prove too high to be counterbalanced by the potential benefit. Combination processes have considerable merit, but it must be proven that the relatively costly HPP contributes significantly to the effectiveness of the combination treatment. In designing “hurdle” preservation processes in which each treatment contributes a part of the additive or synergistic total effect, it is necessary to consider the cost–benefit ratio of each treatment. Given the high cost of HPP its benefits would need to be considerable to include in a hurdle process.

IV. HIGH-INTENSITY PULSED ELECTRIC FIELDS (PEF)

A. Principles

High-intensity pulsed electric field (PEF) treatment is the application of pulses of high voltage to materials placed between two electrodes. Studies on exposure of microorganisms to electric fields have shown that electric field can cause profound changes to cell membranes. This knowledge led to a laboratory technique known as *electroporation*. Electroporation is the use of a transmembrane electric field pulse to induce microscopic pores (“electropores.”) in a membrane. Their presence allows molecules, ions, and water to pass from one side of the membrane to the other. Under some conditions the electroporated cells can recover (the electropores reseal spontaneously) and cells will continue to grow and express their genetic material. Throughout the 1980s the use of electroporation became very popular because it was found to be an exceptionally practical way to place drugs, genetic material (e.g., DNA), or other molecules into cells. Under appropriate conditions

(calcium ions play an important role in creating such conditions) fusion of two adjacent cells can be accomplished, known as *electrofusion*.

Studies on survival of microorganisms in electric fields demonstrated that inactivation could be achieved by pulsed application of electric fields of 20 kV or more. It was established that the effects were nonthermal, and probably due to cell membrane disruption. A patent claiming the application of PEF to preservation of fluid foods was issued in 1987 to Maxwell Laboratories, which continued development of methodology of such treatments (Dunn and Pearlman, 1987). The Krupp Corporation in Germany and several academic institutions, including notably Washington State University, have continued the investigation of the process. The justification for exploration of PEF for food processing is the proposed potential for extension of shelf life of fluid foods without the organoleptic changes associated with some thermal treatments.

Maxwell Technologies of San Diego developed equipment for production of very short intense electric pulses. The principal components of the equipment have been used not only in the development of PEF but also in the proposed food processing of pulsed light and of oscillating magnetic fields.

The principle of the PEF process as currently practiced is the storage of a large amount of energy from a DC power supply in a series of capacitors and discharging that energy in the form of high voltage pulses in a chamber containing the food. The time course of the pulse may be exponential, or square. Figure 11.14 shows a generator producing an exponential discharge, the time course of which is indicated schematically in Fig. 11.15. Figure 11.16 shows a generator of a square pulse, and Fig. 11.17 shows the time course of the pulse produced by such generators. It is also possible to produce systems in which the charge is reversed rapidly to produce instant-charge-reversal charges, which are reported to be more energy efficient. A flow diagram for processing fluids continuously is shown in Fig. 11.18.

The proper design of the treatment chamber is critical to the achievement of the process objectives. Some commercial equipment developed for water treatment is available from PurePulse Technologies (<http://www.purepulse.com/technology/tech.html>) and various laboratory and pilot plant scale designs were developed by researchers in the field. The equipment may be operated in batch or continuous modes.

A detailed description of chambers developed at Washington State University is provided by Qin et al. (1996). In all designs fluid food is exposed to a high intensity voltage pulse by being located between two electrodes, but the geometric features, including chamber volume, and distance between electrodes vary.

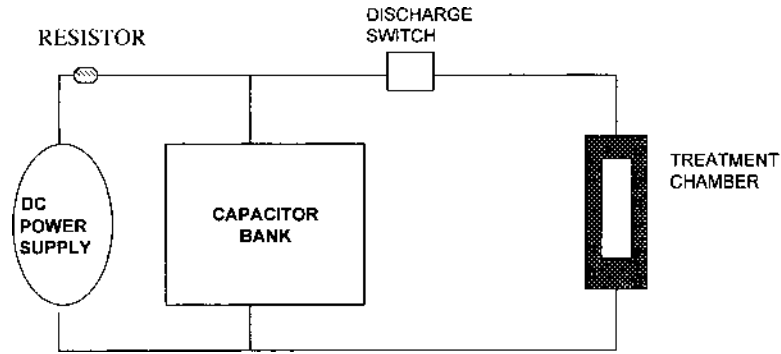


FIGURE 11.14 Schematic representation of equipment for generation of pulsed high-intensity electric fields, with exponential voltage decay.

B. Effects of PEF on Microorganisms

As discussed above the lethal effects on microorganisms are attributed to membrane damage. The extent of that damage depends on pulse intensity as well as on number of pulses, each with defined time duration.

The lethal effects of any physical process depend on an intensive factor and an extensive factor. In thermal processes the intensive factor is temperature and the extensive factor is time. In PEF the intensive factor is the electric field intensity, and the extensive factor is time (the number of pulses multiplied by duration of each pulse). As in other processes the extensive factor may be complicated by whether pulse width (time per pulse) has effects additional to those of total treatment time.

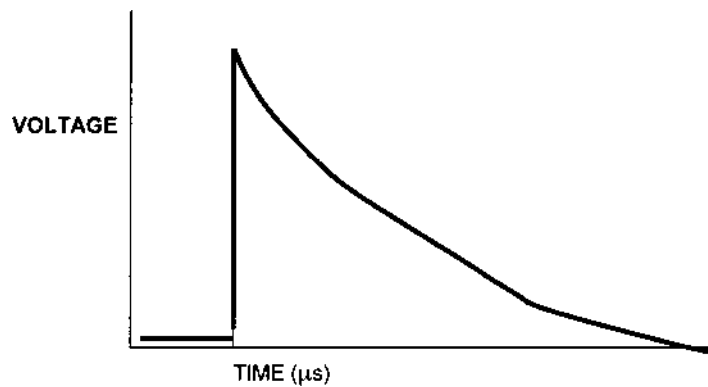


FIGURE 11.15 Exponential voltage decay.

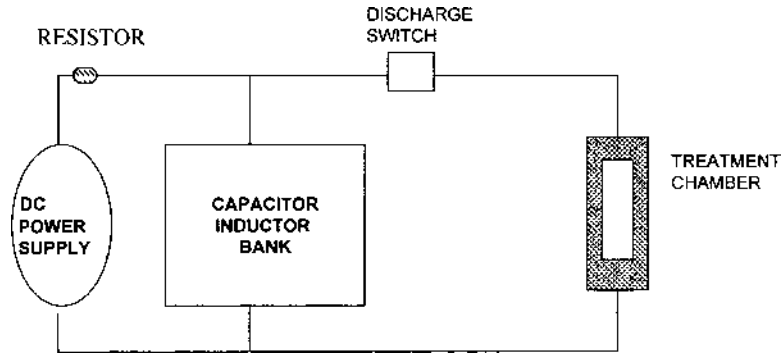


FIGURE 11.16 Schematic representation of equipment for generation of high intensity electric fields, with square wave pulses.

Various models have been developed, two of which were used by IFT in its report on kinetics of microbial inactivation in alternate preservation technologies (IFT, 2000b). The first model was based on work of Hulshegger (Hulshegger et al., 1983) and others and is shown below:

$$\frac{n}{n_0} = \frac{t}{t_c} \exp\left(-\frac{(E - E_c)}{K}\right) \quad (11)$$

where

n/n_0 is the fraction of organisms surviving.

t is the treatment time.

E is the applied electric field. The subscript c refers to “critical” (or “reference”) values of t and E .

K is a kinetic constant.

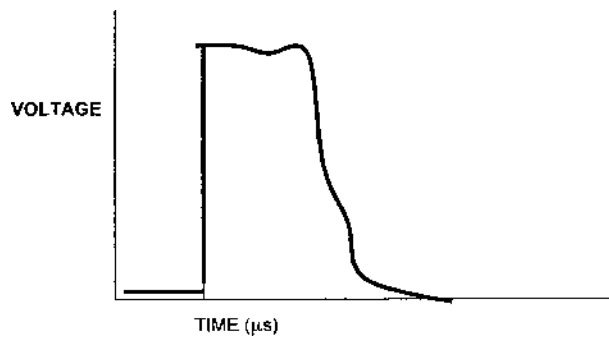


FIGURE 11.17 Square wave pulse voltage decay.

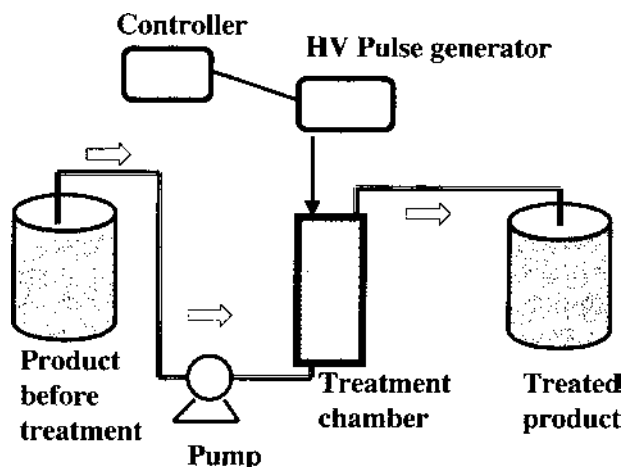


FIGURE 11.18 Schematic representation of food flow in a PEF process.

Higher values of K and lower values of E_c correspond to increasing sensitivity of microorganism to inactivation of PEF. Treatments of several vegetative microorganisms suspended in buffer at pH 7.0 were analyzed. The values of E used were between 4 and 20 kV/cm, and the calculations yielded values of K between 2.2 and 8.1 kV/cm, with values of E_c ranging from 0.7 to 13 kV/cm. Of the seven microbial populations studied *S. aureus* and the yeast *C. albicans* were most resistant and *E. coli* the most sensitive. However, the generality of these results was questioned. One of complicating factors in the analysis was the fact that a count of the *E. coli* survivors after 30 h of incubation indicated a much higher resistance than the resistance calculated on the basis of a 4-h incubation, suggesting at least the possibility of reversible effects.

A second model was proposed by Peleg (Peleg, 1995) and is shown in

$$\frac{n}{n_0} = \frac{1}{1 + \exp\{[E - E(n)]/K(n)\}} \quad (12)$$

$E(n)$ and $K(n)$ are algebraic functions of the number of pulses (n) or treatment time. The equation may be simplified by substituting constants $E(50)$ and K for the functions $E(n)$ and $K(n)$. As in the case of Eq. (11), higher values of K and lower values of $E(50)$ indicate increasing sensitivity. An analysis using the Eq. (12) gave values of K between 1.2 and 3.1 kV/cm, and $E(50)$ values, between 6.7 and 21.2 kV/cm. *C. albicans*, and the resistance was dependent on number of pulses.

It has also been proposed that the dependence of the process effectiveness on electrical field intensity could be expressed in terms similar to those used for

thermal and pressure processing using

$$\log \frac{D_{10}}{D_R} = \frac{-(E - E_R)}{z(E)}$$

where D_{10} is decimal reduction time at a given intensity E , D_R is decimal reduction time at reference intensity E_R and $z(E)$ is the increase in E to achieve a tenfold decrease in D_{10} .

The data available in literature at present does not allow the calculation of above constant, and much additional research is required to allow process design based on quantitative relationships.

The data does allow one to conclude, however, that vegetative bacteria suspended in fluids (including buffer, milk, liquid egg, and soup) could be treated by PEF to reduce the bacterial populations by several log cycles. Similar results could be obtained with yeast in buffer and in juices. Ho et al. reported some enzyme inactivation (30 to 85%) in buffer.

C. Applications to Food Products

The applications reported to date indicate potential for extending shelf life of foods by reducing microbial populations. It has been reported that this can be achieved without affecting adversely the organoleptic acceptability.

The extension of shelf life depends on product, treatment parameters, and storage conditions. A shelf life of several months was reported for refrigerated orange juice, and apple juice was apparently stable for over a month at room temperature. Raw milk was stable for up to 2 weeks after PEF treatments.

These reports of some PEF successes must be considered in need of confirmation.

The limitations of current PEF are in part due to the following issues (IFT, 2000b):

1. Lack of standardized commercial equipment.
2. Effect of physical properties of the treated product. As an example it is reported that presence of air bubbles adversely affects the process.
3. Best results are obtained with homogeneous liquid with low electric conductivity. Salt containing products are therefore difficult to process. Presence of particles in the liquid may adversely affect. Processing with PEF, and large particle may make the processing impossible.
4. Absence of quantitative methodology for measuring the treatment severity.
5. Lack of adequate models to express inactivation kinetics.

V. HIGH-VOLTAGE ARC DISCHARGE

An application suggested for food preservation is based on rapid discharge of high voltage through an electrode gap below the surface of aqueous suspensions of microorganisms. The discharge causes several effects, including creation of a hydraulic shock wave and chemical effects including production of highly reactive free radicals. Lethal effects on microorganisms may be due to membrane disruption and to chemical reactions involved oxygenated free radicals.

The effectiveness of this method as a method of food preservation remains to be investigated in detail (IFT, 2000b).

VI. ULTRAVIOLET LIGHT

A. Effects of Ultraviolet Light on Biological Systems

Ultraviolet (UV) light has biological and biochemical effects and has been used in food processing for various applications. Ultraviolet is part of the electromagnetic spectrum shown in Fig. 11.4. The energy UV photons is below that of x rays, and its biological effects derive from excitation rather than ionization of molecules. Processing applications may use UV light in the following ranges:

UVA 315 to 400 nm (long wavelengths effective in tanning of human skin)

UVB 280 to 315 (may cause skin burn, and may lead to skin cancer)

UVC 200 to 280 (which is considered the germicidal spectrum)

Shorter wavelengths of UV light are known as vacuum UV range, since these wavelengths are absorbed by almost all substances, and the transmission requires the medium of vacuum. Germicidal effects of UV are considered to be due to absorption of the photons by DNA molecules leading to lethal mutations. The effects on DNA are dependent on total energy absorbed, and below a certain level of absorbed energy may be reversible. It has been observed that a photoreactivation mechanism is operative with some bacteria which is enhanced by visible light.

Enhanced lethality may be observed due various photochemical effects in particular in presence of oxidizing agents, and photosensitizers. The absorption of UV light in matter is given by Eq. (4) introduced earlier in connection with absorption of ionizing radiation. Preservation application include primarily disinfection of food contact surfaces and of water supplies. However more recently there has been an increased interest in processing of juices, and this application was recently approved by FDA (IFT, 2000a).

The survival curve of microorganisms exposed to UV light and plotted as fraction surviving versus time of exposure to a given intensity of light is sigmoidal. Low doses of energy result in part in sublethal injury; additional UV energy results in rapid decline in numbers. A tailing phase is then observed which may be due to several factors including existence of a resistant fraction of the

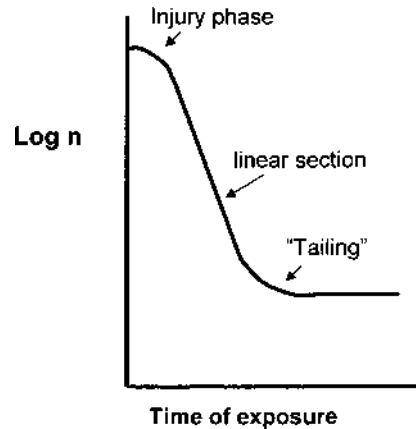


FIGURE 11.19 Typical survival curve for microorganisms exposed to UV light. n = number of viable organisms.

population or shielding by suspended solids of part of the irradiated volume. A schematic representation of a sigmoid survival curve is shown in Fig. 11.19. The data on kinetics of inactivation is sparse, but there is an indication that in the logarithmic “linear” section the lethality is related to the *fluence*, defined as the total radiant energy passing through unit cross-sectional area of an infinitesimally small sphere. It is expressed in J/m^2 . It is often termed *UV dose* in literature reporting germicidal effects. It is equal to *fluence rate* in W/m^2 multiplied by time of exposure. Experiments by Hoyer showed that 4 log cycle reduction of a number of bacteria and two viruses could be achieved with exposures of 50 to 380 J/m^2 . Of the organisms studied *Mycobacterium smegmatis*, a phage and the two viruses (Poliovirus, and Rotavirus SA 11) were the most resistant requiring a dose of 200 to 380 J/m^2 . *E. coli* ATC 23958 and *Vibrio cholerae* required only 50 J/m^2 . However, the bacteria were made much more resistant by photoreactivation. In the case of post-irradiation reactivation the strain of *E. coli* required 200 J/m^2 for the same lethality effect, and the *Vibrio* strain 210. The more resistant organisms also increased their resistance further. With photoreactivation all of the organisms studied required doses of 200 J/m^2 or more for the 4 log cycle reduction.

B. Applications and Considerations in Process Control and Validation

In view of the relative novelty of applications in processing of fluid foods, much work remains to be done to allow design of processes on a sound scientific and

engineering basis. The experience with applications in control of pathogens in water provide some guidance. To eliminate pathogens in water a radiant exposure of at least 400 J/m^2 of UV at 254 nm is required to reduce pathogens by 4 log cycles. The dose must be delivered to every volume element of the water. Thus homogeneity of the product flow, and of the radiation field, as well as constancy of the absorption characteristics of the fluid have a critical impact on process design criteria. If the above parameters vary significantly the dose must be greatly increased to provide an adequate safety factor. While such a measure may have only cost implications in water processing, an increase in exposure to UV of food products is potentially a source of organoleptic defects. In the case of foods containing particulate solids, total reliance on UV inactivation of pathogens may be difficult to achieve, and the UV treatment may have to be combined with hurdles to microbial growth such as lowered water activity and pH.

The most recent review available at this writing is a report prepared by IFT under FDA contract. (IFT, 2000b). The report lists the following research needs in the area of UV processing.

1. Effects of composition parameters and in particular of suspended and dissolved solid concentrations
2. Identification of most resistant pathogens
3. Development of methods for process validation
4. Development and evaluation of kinetic models of lethality
5. Studies to optimize critical process factors

VII. PULSED-LIGHT TECHNOLOGY

The application of light pulses has been developed and promoted by PurePulse of Maxwell Technologies of San Diego. It is based on application of very short intense flashes of light. The equipment used consists of a high-energy electrical energy capacitor that discharges pulses of electrical energy to “flash lamps,” which produce flashes of broad spectrum light as shown schematically in Fig. 11.20. The spectrum of emitted light is in the range of 200 nm to 1 μm . It covers the span therefore from UV light to infrared radiation (Fig. 11.4). Forty-five percent, of the energy is in the visible light range, 25% in the UV range and 30% in the IR range. The flashes are very intense (20,000 times the intensity of sunlight at Earth’s surface), but have an extremely short duration (less than 1 millisecond). The energy penetrating the surface of the treated material is absorbed in accordance with the Beer Lambert Law [Eq. (4)]. (Part of the energy is reflected and does not penetrate the surface). The absorbed energy is converted primarily into heat, but some is also used for excitation of various molecules. For satisfactory disinfection the UV component is especially important, with lethal effects discussed in the preceding section. In water and

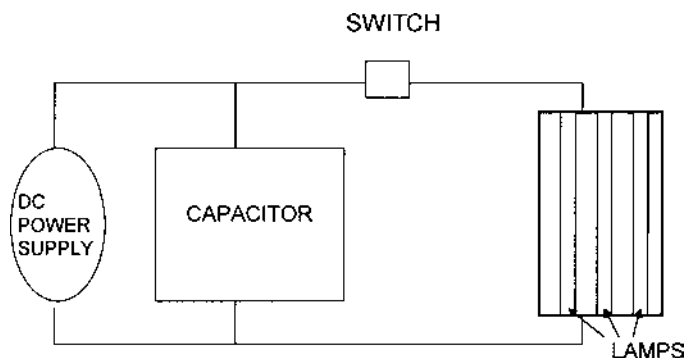


FIGURE 11.20 Schematic representation of equipment for generation of pulsed high-intensity broad spectrum light.

some transparent fluids a penetration of a sufficient intensity of the UV component to depths of 0.25 cm is possible, however, most food materials are opaque and the penetration is below 1 mm. The major applications of this technology lie in treatment of surfaces and of transparent fluids (e.g., water and dilute solutions) exposed to the light in very thin films.

Kinetic data on inactivation of various microorganisms are extremely limited. Most of the tests were testing the effectiveness of the pulses in disinfecting surfaces of food and of packaging materials and are too limited to allow the development of quantitative models of inactivation.

The tests were reported primarily by Dunn and co-workers at Maxwell Laboratories who were the developers of these applications. (Dunn et al., 1995). The concentration of mold spores (*Aspergillus niger*) on surface was reduced by 7 log cycles with several flashes with an intensity of 1 J/m^2 . Several organisms including *E. coli*, *S. aureus*, *B. subtilis*, and *S. cerevisiae* were inactivated by using 1 to 35 pulses of 1 to 2 J/m^2 .

In application to surfaces of foods the inventors' success with curds of commercial dry cottage cheese in reducing the concentration of an inoculum of *Ps. aeruginosa* by 1.5 log cycles was achieved by applying two flashes with an energy density of 16 J/m^2 . The surface temperature of the treated cheese was increased by only 5°C , and the sensory quality was reported to be unimpaired. Successful disinfection of surfaces was reported for fish and shrimp.

Another application for which the treatment was reported to be effective was the elimination of microbial contamination of surfaces of eggshells and of surfaces of packaging materials.

In addition to the broad spectrum light pulse technology a system of UV pulses has been patented for insect control (Lagunas-Solar, 1997). It uses

a wavelength of 247 nm, and is reported to be in commercial production in Chile, and used to disinfect surfaces of grapes exported from that country to the United States (IFT, 2000b).

The development of pulsed light technology must be considered to be in its early stages, and requires much further research. An IFT report to the FDA concludes that needed research includes the following:

1. Identification of critical process factors
2. Suitability for processing of solids and opaque liquids
3. Assessment of potential for formation of toxic an/or unpalatable compounds
4. Assessment of resistance of organisms and of the mechanisms of inactivation
5. Evaluation of advantages of the process compared to the more conventional UV processes

VIII. OSCILLATING MAGNETIC FIELDS (OMF)

The company which introduced the pulsed electric field, as well as the pulsed broad spectrum light equipment (Maxwell Technologies of San Diego) has also suggested the use of oscillating magnetic field for food preservation. The equipment, shown schematically in Fig. 11.21, is based on the capacitor discharge principle and also used in the two above-mentioned technologies. Effects of magnetic fields on organisms have been suggested previously.

Magnetic fields may be static or oscillating, and may be homogeneous or heterogeneous. In the OMF technology food is treated with magnetic pulses of with pulse duration in the millisecond range. One to 100 pulses may be delivered with a total exposure time of 25 to over 100 ms. In the patent application a frequency of 5 to 50 kHz, and intensity of 5 to 50 Tesla was specified for preservation. Inactivation of several microorganisms was reported.

However a critical review by IFT reported the following:

A review of literature shows that inconsistent results have been obtained on the effect of OMF on microbial growth. In some cases OMF stimulated or inhibited microbial growth and, in others, it had no effect on microbial growth. The results show that, although not well understood, the effect of magnetic fields on the microbial population of foods may depend the magnetic field density, number of pulses, frequency and the properties of food (resistivity, electrical conductivity and thickness).

The underlying mechanisms of potential inactivation are also uncertain. The report (IFT, 2000b) concluded that additional research is required to assess the potential of this technology. Research is still required to determine:

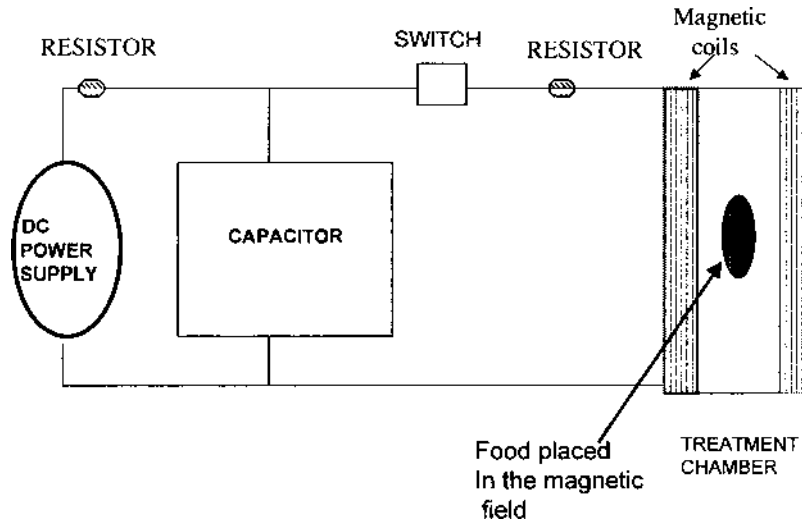


FIGURE 11.21 Schematic representation of equipment for treatment oscillating high-intensity magnetic fields.

1. Key resistant pathogens.
2. Establish effects of magnetic fields on inactivation.
3. Elucidate destruction kinetics.
4. Determine the mechanism of action of magnetic fields.
5. Determine critical process factors.
6. Validate the process using indicator organisms or surrogates.

IX. ULTRASOUND

A. Applications of Ultrasound in Food Technology

Ultrasound is defined as energy generated by sound waves of over 20,000 vibrations per second. It has very extensive applications in food and pharmaceutical industries as well as in chemical and biological research laboratories. The application of ultrasound in medical diagnostics is wide-spread and well known. It has also been used in therapeutic applications. It has also widespread uses in food technology. It has been used in testing various quality attributes including presence of internal defects in fruits, texture, and composition. It has been widely applied in process monitoring of processes. It has applications in cleaning of surfaces, in degassing of liquids, and in a variety of processes in which it promotes diffusion, including dewatering, filtration, extraction and various heat transfer operations.

Its applications to food preservation have been preceded by wide-spread use in laboratories for cell disruption, and extraction of cell-free enzyme preparations. These operations deal with small volumes however and are thus relatively easy to control, and to conduct under defined conditions.

Application to inactivation of microorganisms in foods is more difficult. Studies on inactivation of salmonellae have shown mixed results, producing a 4-log cycle reduction in broth, but little effect in chocolate milk. More successful was the application of ultrasound disinfection of surfaces of poultry in chilled chlorinated water baths.

The most successful applications have been those combining ultrasound with thermal treatments (Earnshaw, 1995). It has been shown that these treatments are synergistic, and their use can reduce undesirable effects of heating.

B. Mechanism of Inactivation of Microorganisms by Ultrasound

Ultrasonic waves passing through a liquid produce alternate compression and "rarefaction." At high wave amplitudes a process known as *cavitation* results in production of bubbles, or cavities. In liquids containing small gas bubbles a condition known as *stable cavitation* may occur in which these bubbles grow in size, and their vibration produces eddies in the surrounding liquid. This eddy effect, known as *microstreaming* produces strong forces, without bursting the bubbles. However the resulting shear is effective in disrupting microbial cell membranes with lethal effects.

In *transient cavitation* the bubble sizes change very rapidly, and the bubbles collapse, producing on a microscopic level very high pressures (up to 100 MPa) and high temperatures (up to 5000K). These conditions result in disruption of cell walls and death.

The extreme local conditions can have important chemical effects, including *sonolysis* of water with ions and free radicals similar those produced by ionizing radiation. These may have direct effects on microbial DNA but also have the potential for initiating undesirable chemical reaction especially in presence of oxygen.

The nature and intensity of ultrasound effects depends on conditions of application, in particular on temperature, the properties of the sonic radiation, and viscosity of the substrate. It is also known that different organisms have different sensitivities. As in other lethal processes gram positive organisms are more effective than gram negative bacteria. Spores are much more resistant than vegetative cells.

TABLE 11.7 Effect on Ultrasound and Heating on Inactivation of *L. cytogenes* and of *Z. bailii* (D_{10} values of specified treatments in minutes)

| Product | Heat only | Presonation | | Simultaneous treatment | |
|-----------------------------|-----------|-------------|---------|------------------------|---------|
| | | 20 KHz | 800 KHz | 20 KHz | 800 KHz |
| <i>L. cytogenes</i> at 60°C | | | | | |
| UHT milk | 2.1 | 0.4 | >10 | 0.3 | 1.4 |
| Rice pudding | 2.4 | | 0.3 | | 4.5 |
| <i>Z. bailii</i> at 55°C | | | | | |
| Orange juice | 10.5 | 2.4 | 1.4 | 3.9 | >10 |
| Rice pudding | 11.0 | 2.3 | | 1.0 | >10 |

C. Application of Ultrasound in Combination with Heating

Combined treatment utilizing ultrasound and moderate temperatures has considerable advantages. Sonicated cells become sensitized to thermal effects, and the raising of temperature results in lowering of viscosity which assists in ultrasound penetration.

Table 11.7 based on data reported by Earnshaw (1995) shows the effectiveness of the combined treatment in inactivating *Listeria monocytogenes*.

Combination treatments have considerable potential, but results can be complicated and individual applications must be investigated on their own merit. Temperatures above the boiling point there is loss of the cavitation effect. In those situations combinations of ultrasound, heating, and high pressure can be used to enhance effectiveness. Inactivation of spores of several bacilli was reported with ultrasound combined with heating at 112°C and 300 KPa.

X. STATUS AND PROSPECTS OF NONTHERMAL FOOD PRESERVATION PROCESSES

It may be appropriate to briefly present here the author's assessment of the current status and future prospects of the nonthermal preservation processes described above. At present none of them has very extensive application in food preservation. (UV irradiation is important in surface disinfection, and ultrasound is an important technique in processing aspects outside of preservation.)

Food irradiation is technically highly developed, its effectiveness as well as its limitations well established, and regulatory approval is available for its application to a number of important food preservation needs. Its commercialization on a large scale will depend entirely on public acceptance, and on its cost.

It has the potential for contributing to the solution of some extremely important global food preservation problems including control of some very dangerous pathogens and the minimization of losses due to insect infestation. In the age of almost unlimited global trade it can assist in minimizing spread of plant and animal diseases without recourse to chemical treatments. It seems likely therefore that it will become important, and the half a century of research will pay off.

HPP is a technology that is currently under intense investigation by research institutes and industry. It is inherently expensive and at present it does not offer unique solutions to major global problems. Its applications seem likely to remain limited. Broader applications will be realized if research into scientific and engineering aspects produces breakthroughs. Continuous processes, if proven effective, may reduce costs substantially.

UV irradiation will continue to be applied to disinfection of surfaces and water supplies, especially in view of declining popularity of chemical disinfecting treatments. Pulsed light with a broad wavelength spectrum may offer some additional advantages, but these remain unproven.

PEF and Oscillating Magnetic Fields are at present only potential technologies of preservation. Research is continuing and progress may change the situation. At present however the outlook for extensive applications is very uncertain.

SYMBOLS

| | |
|-----------|--|
| C | speed of light |
| c_I | Curie, unit of radioactivity |
| D | dose of radiation |
| D_{10} | decimal reduction time, or decimal reduction dose |
| D_o | dose reducing population by 1 natural log cycle |
| E | applied electric field |
| E | energy of electron or photon |
| Gy | Gray, unit of radiation |
| h | Planck constant |
| I | intensity of radiation at a given point |
| I_o | intensity of radiation entering the surface of absorber |
| k, K | constants |
| n | number of organisms in specified volume, or mass at given time |
| n_o | number of organisms in specified volume or mass before treatment |
| R | gas constant |
| R_{MAX} | maximum penetration distance of electrons |
| T | temperature |
| t | time |
| V | activation volume constant |

| | |
|--------------|--|
| X | distance within the absorber |
| $z(E)$ | increase in E to achieve a tenfold decrease in D_{10} |
| $z(P)$ | imposed pressure required to decrease D_{10} by a factor of 10 |
| ΔV^+ | activation volume |
| λ | wavelength |
| μ | absorption constant |
| ν | frequency of radiation |
| ρ | density |

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12

Protective Packaging

I. PROTECTION OF PRODUCT AS A MAJOR FUNCTION OF PACKAGING

A. Functions of Packaging

Most food is consumed far removed in time and space from the point of its production; hence the need for the preservation processes discussed in this book. A necessary aid for the storage and distribution of food is packaging. The functions of packaging are several.

Packaging serves as a material handling tool containing the desired unit amount of food within a single container and may facilitate the assembly of several such units into aggregates. For example, some fluids are packaged in bottles which may be placed in boxes, and these boxes in turn can be assembled into easily handled pallets.

The package may also serve as a processing aid. For instance, the metal can be used in heat sterilization of many food items serves not only a protective function but, by its dimensional stability, assures that when fully packed the food maintains a certain shape and location for which heat penetrations can be calculated. In the case of flexible heat-processable pouches, which do not provide such dimensional permanence, it is necessary to introduce guiding racks or separators, which in a sense constitute temporary packages.

The package is a convenience item for the consumer. The examples one could choose here are very numerous. A beer can, for instance, serves as the drinking utensil as well as a process, storage, and distribution container. A variety of packages aid in handling, preparation, and consumption of foods by the consumer. Unfortunately, numerous examples also exist of poorly designed containers providing a barrier to efficient utilization of foods.

The package is a marketing tool. The sales appeal and product identification aspects of packaging are particularly important to the sales and marketing branches of food companies, and since these branches often have a dominant role in business decisions it is these aspects that often dominate package design. A trip to any supermarket can provide any reader with literally thousands of examples of packaging directed at marketing. These include such obvious product identification aspects as keeping a constant shape and labeling pattern for a container (consider Campbell Soup cans and the Coca Cola bottle). Various advertizing-oriented features are also used (for instance, bottles of products advertized as delicate often have "hourglass" shapes, and "robust" products often are packaged in squarish, husky-appearing bottles). This aspect of packaging often has been the target of consumer protection associations and advocates and has also encouraged the formulation of regulations to prevent deceptive packaging.

Packaging, when properly used, can be a cost-saving device. This aspect is very complicated, however, because it requires the simultaneous consideration of numerous interactions. Certain packages have obvious economic benefits, such as prevention of spills, ease of transporting, prevention of contamination, reduction of labor cost, and so on. There are also the obvious inherent costs: the packaging material itself, the packaging machinery, shipping weight of the package, and so on. In addition, there may be social costs hidden from immediate view: cost of disposal, cost of avoiding ecological disturbances due to accumulation of wastes (e.g., pollution), and costs associated with changes in energy consumption patterns. With respect to the last point, modern packaging systems have tended to evolve to minimize consumption of muscle power at the expense of electrical power. These hidden costs and benefits sometimes favor one kind of packaging, whereas the immediately visible balance is in favor of another. Unfortunately, thorough cost-benefit analyses of food packaging systems have not yet appeared.

Protection of the product is the most important aspect of packaging and the only one we shall consider in this chapter. It should be remembered, however, that the other functions cannot be ignored by the food technologist.

B. Protective Packaging

In considering the protective function of packaging we have to consider what aspects of quality are being protected. The quality of products as they reach the consumer depends on the condition of the raw material, on method and severity

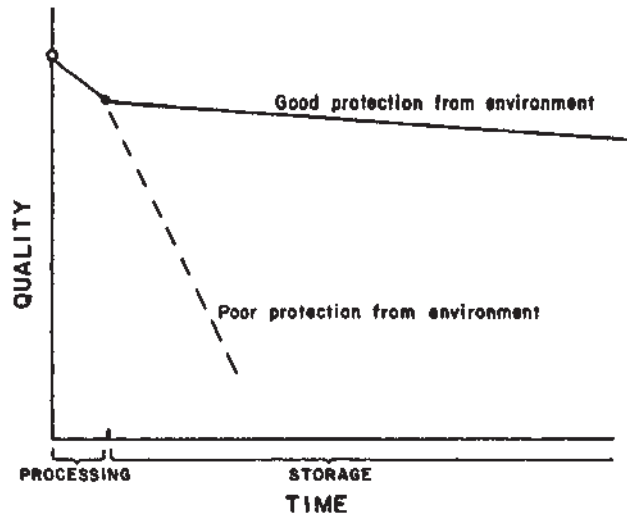
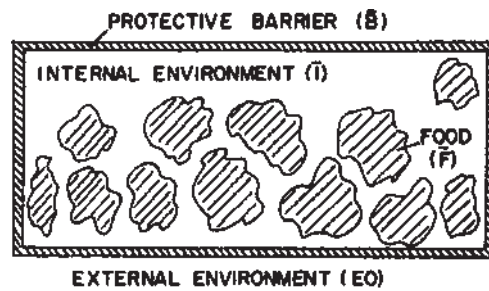


FIGURE 12.1 Schematic representation of quality loss during processing and storage.



\bar{T}_0, \bar{F}_0 = initial conditions
 t = time
 $\bar{F} = f(\bar{T}, \bar{F}_0, t)$
 $\bar{T} = f(\bar{T}_0, \bar{F}, EO, B, t)$
 $\bar{B} = f(\bar{T}, EO)$

FIGURE 12.2 Schematic representation of interaction between packaged food and the environment.

TABLE 12.1 Package–Environment Interactions

| Environmental factors | Pertinent package properties |
|--|------------------------------|
| Mechanical shocks | Strength |
| Pressure of oxygen, water vapor, etc. | Permeability |
| Light intensity | Light transmission |
| Temperature | Thermal conductivity |
| | Porosity |
| | Reflectivity |
| Biological agents | Penetrability |

of processing, and on conditions of storage. Figure 12.1 demonstrates this point graphically. In this figure we show quality (by which we mean the totality of desirable attributes, including eating quality, and absence of undesirable ones, such as toxic factors) decreasing in storage. (There are, of course, exceptions to this pattern, e.g., aging of wines and beef.) The rate and extent of this decrease depends on the conditions of the environment in which the food is stored (Fig. 12.2). This internal environment, \bar{I} may be maintained at conditions different from the external environment, EO (and preferably more favorable than EO), by interposing a protective barrier, B .

The chemical, physical, and biological mechanisms of food deterioration are sensitive to various environmental factors, and the most pertinent barrier property of the package varies with each product. Some of the environmental factors and the corresponding pertinent packaging properties are listed in Table 12.1.

II. NATURE OF PACKAGING MATERIALS

The protection offered by a package is determined by the nature of the packaging materials and by the type of package construction. A great variety of materials is used in packaging, as shown in Table 12.2.

A. Glass

Glass containers have been used for many centuries and still are among the important packaging media. Physically, glass is a supercooled liquid of very high viscosity. Chemically, it is a mixture of inorganic oxides of varying composition. Most container glass is of the soda-lime–silica type.

Container glass usually consists of 70–75% sodium and calcium silicate, 6–12% calcium and magnesium oxide, and small amounts of aluminum, barium, and other metallic oxides. The materials are mixed with “cullet,” or crushed glass

TABLE 12.2 Approximate Value of Packaging Materials Shipped Annually in the United States

| Material | Value (billions of dollars) |
|----------------------------------|--------------------------------|
| Paper containers (includes bags) | 40 |
| Aluminum cans | 14 |
| Steel cans | 6 |
| Flexible plastic films | 10 |
| Rigid plastic containers | 8 |
| Glass containers | 15 |

Source: Brody (2001).

from broken or defective containers, and the mix is melted in a furnace at temperatures in excess of 2700°F.

Bottles are formed in two steps. An exact amount of molten glass is metered into a mold, smaller than the final bottle, and compressed gas or a mechanical plunger presses the glass against the walls of the mold. The partially formed bottle is transferred to a second mold, where it is blown by compressed air into its final shape. The mouths of the container are fire polished and the bottles are annealed at high temperature. All containers are inspected; in most modern installations they are subjected to mechanical tests (squeezing by automatic equipment), and defective containers are rejected and used for cullet.

The most important packaging properties of glass, such as moldability, inertness, transparency, and strength, can be modified by relatively minor changes in the glass composition. Color, for instance, can be controlled by inclusion of small amounts of oxides of various metals, such as chromium, cobalt, and iron, and semiopacity can be imparted by addition of fluorine compounds.

The major packaging design problems involving glass arise from its mechanical properties. Glass is brittle and its tensile strength depends greatly on the condition of the surface. Commercial glass containers have only a small fraction of the potentially possible tensile strength because the surface conditions cannot be maintained at the perfect level required for maximum strength. As a consequence the containers must be made of fairly thick glass, and they therefore have substantial weight. Recent developments in glass packaging have included use of treatments and compositions which improve optical, mechanical, and thermal properties of glasses (Robertson, 1993).

A recent development is the use of very thin glass encased in a plastic exterior. The resultant bottle has the advantage of inertness of interior surface with resistance to abrasion by the exterior surface.

The properties of containers also depend on type of construction. Types of containers commonly used include bottles, jars, jugs, and tumblers. A variety of closures is available, and the recent trend toward maximum convenience for the consumer has resulted in substantial efforts toward development of easily opened closures. Convenience as well as esthetic considerations are often paramount in package design, and satisfying these requirements demands substantial ingenuity by the design engineer.

Glass containers possessing the proper type of closure can be used for practically all types of packaging applications, including heat processing, gas packaging, and other types of preservation requiring hermetically closed containers. For more detailed discussion of glass in packaging the reader is referred to specialized publications (Brody and Marsh, 1987).

B. Metals

1. Rigid Metal Containers

The most common container for packaging of foods other than beer and carbonated beverages is the so-called tin can. It is traditionally used for heat-sterilized products and is made of tinplate, which consists of a base sheet of steel with a coating of tin applied to it by "hot dipping" or by the electrolytic process. The amount of tin coating depends on the process and the type of can. A typical tinplate may be 0.01 in thick, with the tin coating contribution only about 0.00005 in to this thickness. To make the can more suitable for specific packaging applications enamels and linings can be applied to the tin or to the tinless steel sheets. The composition of these linings varies with intended use. Plastics, shellacs, resins, glass, and inorganic oxides are among materials used for this purpose.

Three different types of base steel are common:

1. Type L. This steel is very corrosion resistant and therefore most suited to canning of acid products.
2. Type MR. This steel is less restricted than L in contents of C, S, P, M, and Si and is suitable for mildly corrosive products.
3. Type MC. This is least restricted in composition and is used for noncorrosive products.
4. Type N is used when exceptional strength is required.

In recent years very substantial changes have occurred in the can industry, and a great variety of cans different from the can made of standard tinplate has been developed. In particular, these developments have been aimed at beer and carbonated beverage applications but may have additional applications in other foods. Tin-free steel, utilizing direct chromium-containing coatings or such very thin thermoplastic coatings as nylon, has been used. The other innovation is the utilization of cans with cemented, or welded, rather than soldered side seams.

This development is in part connected with the utilization of tin-free steel. However, in recent years there also has been increasing concern with the potential contamination of foods by lead from soldered side seams.

Coatings for cans can be of the following types: oleoresin, vinyl, epoxy, hydrocarbon, acrylic, phenolic, and wax. The industry refers to all of these, except for waxes, as lacquers or enamels.

The C and R enamels are of the oleoresin type and are most common in food industry. The C enamel contains zinc oxide, designed to react with sulfides evolved during heat processing. The sulfides otherwise tend to react with iron. Iron sulfide is of course black and is objectionable from an esthetic point of view. The R enamels contain no zinc oxide. The other enamels are used in specific applications, since each type has specific advantages and restrictions.

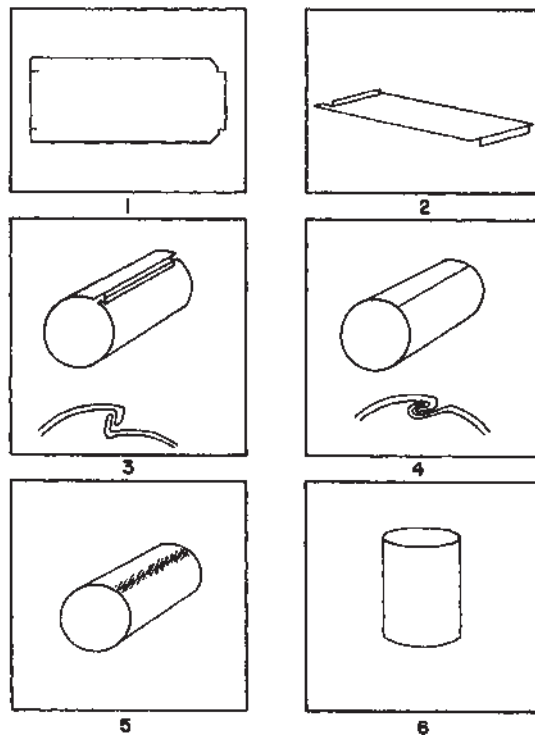


FIGURE 12.3 Steps in formation of a can. (1) Body blank with notched corners; (2) body blank hooked; (3) cylinder formed; (4) hooks flattened; (5) side seam formed; (6) completed cylindrical body.

Tin cans are fabricated as follows (Figs. 12.3, 12.4). Sheets of tin plate with or without an enamel coating are cut into pieces of a size sufficient to form the body (sides) of a can. Each such piece or "body blank" is notched at the corners, hooked or turned back at the edges to be joined, formed into a cylinder, and joined by means of the hooks. The hooks are then flattened and soldered to form the side seam. The side seam consists of four layers of tin plate except for the portion that engages the ends (top and bottom) of the cans. At these two intersections the body blanks are notched so that a two-layer lap seam is formed. The lap seam, being less bulky, folds more easily and securely into the seam which is formed when the ends are attached. Cutouts, tabs, or small incisions are sometimes incorporated in the side seam design. These modifications serve to increase the surface area of the soldered joint, which in turn strengthens the can.

A small flange is next formed on each rim of the cylindrical body to facilitate sealing the can ends. The can ends are formed by stamping metal disks from strips of tin plate. The various contours necessary for strengthening the can ends are formed during this operation. The edges of the can ends are curled and a rubberlike sealing compound is flowed into the curl to form a gasket. The bottom end of the can is attached by means of a double seam (Fig. 12.4). The double seam consists of five layers of tinplate plus the gasket. No solder is used for making the end seals (double seams).

The cans are tested individually to insure the absence of leaks, after which they are shipped to the canner. Generally, the canner can expect to find no more

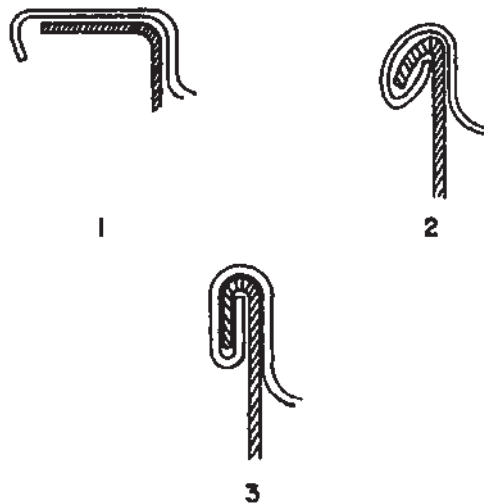


FIGURE 12.4 Steps in formation of a double seam.

than one defective can in each 10,000. After the can is filled, the canner applies the top end, again by means of a double seam. The double-seaming operation can be accomplished at speeds approaching 800 cans per minute per machine.

A simple convention is used by the canning industry to identify the size of a can. Such numbers as 211×300 , 303×406 , and 307×409 are common designations. In each case the first three-digit number indicates the diameter of a can and the second three-digit number indicates the height. The first digit of the number indicates inches and the last two digits indicate sixteenths of inches. For example, 211×400 indicates the can is $2\text{--}11/16$ in in diameter and exactly 4 in tall. In addition to this dimensional system, most sizes of cans have simple number designations. For example, a 307×409 can is also known as a No. 2 can.

Sanitary cans made of aluminum have in recent years moved into a position of commercial importance. Although cans fabricated from aluminum are presently more expensive than cans fabricated from tin plate, there are certain applications where the initial cost disadvantage is offset by a functional advantage or by a saving in shipping cost resulting from the lightness of aluminum.

Recognized advantages of the aluminum can as compared to the tin plate can are lighter weight (lower shipping cost), ease of salvageability, absence of sulfide discoloration, increased resistance to certain types of corrosion, and ease of opening (pull tab). On the other hand, aluminum cans possess two major disadvantages as compared to tin plate cans: less strength and higher cost. Pure aluminum is quite weak. It can be strengthened by the addition of small quantities of magnesium, but this has an adverse effect on its resistance to corrosion. Even the magnesium–aluminum alloys possess less strength than tin plate of the same thickness. As a consequence, aluminum must be of heavier gage than tin plate in order to achieve cans of equal durability.

Cans made of aluminum have made a very substantial impact on the beverage market but have not been used extensively for heat-sterilized food products. It is known, however, that successful sterilization and a satisfactory shelf life can be attained with properly coated all-aluminum cans.

2. Metal Foils

The most important food-packaging foils consist essentially of pure aluminum. They are used in thicknesses ranging from 4 to $150\ \mu\text{m}$. The thickness of uncoated aluminum foil largely determines its protective properties. Foils of low thickness have microscopic discontinuities (pinholes) and allow limited diffusion of gases and vapors. Foil 0.0015 in thick or thicker is likely to have essentially zero water-vapor permeability, indicating a complete absence of pinholes. The properties of thinner foils can be improved by combination with one or more plastics in the form of coatings or laminations.

The use of foils made of metals other than aluminum is very limited. Lead, tin, and zinc foils are mainly of historic interest, and the recently developed steel foils have yet to find major packaging uses.

C. Paper

A very considerable proportion of packaged foods is stored and distributed in packages made of paper or paper-based materials. Because of its low cost, ready availability, and great versatility paper is likely to retain its predominant packaging position for some time to come.

The packaging properties of paper vary considerably depending on the manufacturing processes and on additional treatments to which the finished paper sheet can be subjected. Its strength and mechanical properties depend on mechanical treatment of the fibers and on the inclusion of fillers and binding materials. The physicochemical properties of paper, such as permeability to liquids, vapors, and gases, can be modified by impregnating, coating, or laminating. The materials used for this purpose include waxes, plastics, resins, gums, adhesives, asphalt, and other substances.

The quality of materials made by the above converting processes varies considerably. Some laminated, waxed, and coated papers deserve the designation of protective materials. Certain grades of converted papers, however, offer little more than protection from light and mechanical damage.

Papers can be used as flexible packaging materials or as materials for constructing rigid paper containers. Flexible packaging applications include the use of papers for wrapping materials as well as for manufacture of bags, envelopes, liners, and overwraps. Some of the more important types of paper used for these purposes include Kraft paper, greaseproof papers, glassines, and waxed papers, as well as papers prepared by conversion of these basic types.

Rigid paper containers include a great variety of types, varying in materials and methods of construction. They may include cartons, boxes, fiber cans, drums, liquid-tight cups, tetrahedral packs, and many others. They can be constructed from paperboard, laminated papers, corrugated board, and the various types of specially treated boards and papers. Frequently, paper containers have liners or overwraps, made usually of protective grades of paper, plastics, or metal foil.

D. Plastics

Plastics are organic polymers of varying structure, chemical composition, and physical properties. A brief review of the types of plastics used in food packaging is given below.

1. Cellophanes

Cellophanes are frequently classified as plastics, and this usage is followed here, in spite of the fact that the major constituent of cellophanes—cellulose—is a natural rather than a synthetic polymer. In addition to cellulose, all cellophanes contain a plasticizer, such as glycerol or ethylene glycol. (Plasticizers are materials, usually solvents of low volatility, added to plastics to reduce the attractive forces between the polymer chains. This results in plastics of better flexibility.) Plasticized cellulose, called plain cellophane, offers no protection to the diffusion of water vapor. It is usually coated with protective agents, such as nitrocellulose, waxes, resins, and synthetic polymers. The packaging properties of cellophanes are determined primarily by the nature of these coatings.

2. Cellulosics

Cellophane provides the base material for the production of cellulose acetate, ethyl cellulose, and cellulose nitrate. The cellulosics have properties similar to those of cellophanes but have fewer applications in the packaging of foods.

3. Polyolefins

Polyethylene is one of the most important packaging materials of the present time. It is a hydrocarbon polymer with the nominal formula $-(\text{CH}_2-\text{CH}_2)_n-$. Commercial polyethylenes are produced with a variable amount of branching within this nominally linear polymer. High-density polyethylene has the least branching and as a result the greatest thermal stability and the lowest permeability. High-density polyethylene is used in film form as well as for production of rigid plastic containers, including milk bottles. Low-density polyethylene has the advantage of maximum flexibility and low cost and is widely used for packaging of foods in bags or as an overwrap. Polyethylenes are also widely used in laminations, where they provide the inner layer requiring good heat sealability. Polypropylene is closely related to polyethylene and its properties and uses are similar. Polybutene and poly (methyl pentene) are also used as package components.

4. Vinyl Derivatives

Vinyl derivatives have the general formula $-(\text{CH}_2-\text{CXY})_n-$, where X and Y are either hydrogen atoms or other substituents, such as chlorine, benzene, methyl and hydroxyl. The properties of vinyl polymers are dependent on the nature of substituents, on molecular weight, on the spatial arrangement of groups within the chains, and especially on orientation and crystallinity.

The following generalizations about the effects of polymer structure on functional properties are of particular importance in packaging.

1. Strength, resistance to high temperatures, resistance to action of solvents, and resistance to diffusion increase with increasing degree of crystallization.
2. The presence of polar groups decreases resistance to diffusion of polar molecules.
3. Linearity of chains and orientation of crystallites improve strength and impermeability.
4. Addition of plasticizers increases permeability and solubility.

Some important food-packaging materials based on vinyl polymers and their chemical formulas are listed below.

Saran, copolymer of vinyl chloride $-(\text{CH}_2-\text{CHCl})_n-$ and vinylidene chloride, $-(\text{CH}_2-\text{CCl}_2)_n-$
 Polyvinyl alcohol $-(\text{CH}_2-\text{CHOH})_n-$
 Polyvinyl acetate $-(\text{CH}_2-\text{CHOCOCH}_3)_n-$
 Polystyrene $-(\text{CH}_2-\text{CH}-\text{C}_6\text{H}_5)_n-$
 Polyvinyl chloride $-(\text{CHCl}-\text{CH}_2)_n-$

5. Polyesters

The polyester of most importance in food packaging is polyethylene terephthalate, a condensation product of ethylene glycol and terephthalic acid, which is better known in the United States under the Du Pont trade name Mylar. Mylar is a crystalline linear polymer of excellent strength and inertness. Mylar has been widely used in lamination in particular as the outer, abrasion-resistant layer of laminations to be used for food pouches requiring good protective properties. Polycarbonates are polyesters of carbonic acid and have carbonate ($-\text{O}-\text{CO}-\text{O}-$) linkages. They have outstanding mechanical properties over a wide range of temperatures.

6. Polyfluorocarbons

Several polymers with the backbone composed of carbon and fluorine, or of hydrogen and chlorine atoms in addition to C and F, form the basis for several packaging films with remarkable properties. These materials are very costly but have unique properties. Teflon and other fluorinated hydrocarbons which are the equivalents of polyethylenes with hydrogen replaced by fluorine have remarkable inertness and high permeability to oxygen. In contrast, trifluorochloroethylene has an extremely low permeability to all gases and is in particular effective as a water vapor barrier. Polyvinyl fluoride is intermediate in permeability but has excellent resistance to sunlight.

7. Polyamides

A number of polyamide films, which are condensation polymers of diamines with diacids, are available on the market and have found extensive applications. Nylons, as these polymers are usually called in the trade, are inert and heat resistant and have excellent mechanical properties. They are usually coated or used in combination with other materials to produce packaging materials of food inertness as well as low permeability.

8. Polyacrylonitriles

Polymers derived from acrylonitrile ($\text{CH}_2=\text{CH}-\text{CN}$) are widely used in packaging applications. Copolymers of acrylonitrile and styrene are particularly useful in beverage packaging. Bottles made of the copolymer have outstanding barrier properties with respect to water and to oxygen. Concerns about potential extraction of residual, potentially toxic acrylonitrile led to extensive study and reviews. Under current FDA regulations the bottles made of the copolymer must contain less than 0.1 ppm of the residual acrylonitrile.

E. Biodegradable and Edible Films and Coatings

Recent interest in sustainable and environment friendly technologies has generated very considerable research and development activity directed toward production and use of biodegradable, in particular edible, packaging materials. Biodegradability is the focus of a report by Weber (2000) which surveyed the activities in the European Community. According to this report, 30,000 tons of biodegradable materials were used in food packaging in 2000, and this amount is expected to increase several fold in 2002. The factors slowing the development are the lack of cost advantages, and the absence of major packaging concerns among the promoters of the concept. The benefits lie in decreased damage to environment. According to Weber (2000) biodegradable materials available currently, including those based on proteins, cellulose derivatives, starch, and synthetic biodegradable polymers are degraded within 6 months of placing into composting.

Edible materials studied as packaging components include hydrophilic polymers, lipid-based material and their combinations. Beyond biodegradability edible materials have additional potential advantages. They may enhance the value of the food by carrying added nutrients or flavors, they may be used in “active” packaging applications as carriers of agents enhancing food stability, and they may provide the convenience of prepackaging individual food portions within an overall package. Components potentially useful as packaging films and coatings can also be extremely useful in providing internal barrier functions, preventing undesirable mass transfer within the food. The research in this field in

Europe and in the United States has been the subject of several reviews (Guilbert, 1986; Guilbert et al., 1991; Krochta and Mulder Johnson, 1987; Wu et al., 2002; Morillon et al., 2002).

Among the hydrophilic polymers studied were a number of proteins including casein, whey proteins, collagen, gelatin, egg albumen, wheat gluten, soy protein, and corn zein. Among the polysaccharides studied were cellulose derivatives, starch and its derivatives, algal polysaccharides including alginates and carrageenan, chitosan derived primarily from crustaceans, and polymers derived from microorganisms, including pullulan. The lipid-based materials include oils and fats of plant and animal origin, as well as their derivatives (e.g., mono- and di-glycerides), waxes of plant and animal origin, lacs from plant sources, as well as resins derived from plants.

The hydrophilic polymers potentially useful in edible food packaging have in general good mechanical properties, are relatively easy to process, and at low relative humidities have good barrier properties with respect to oxygen. Their water vapor permeability, however, is high and at elevated relative humidity both the oxygen and water vapor permeability become excessive. On the other hand the lipid-derived materials do provide good resistance to water, but it is often difficult to obtain strong and continuous films from them, especially when thin films rather than thick coating are needed.

The approach of developing packaging materials combining both types of materials has been tried in a number of research and development studies. Among the early studies proving the usefulness of a polymer–lipid bilayer were those of the Wisconsin group headed by Owen Fennema (Kamper and Fennema, 1984). Excellent barrier properties have been obtained when continuous films of the hydrophobic material can be combined with continuous films of the hydrophilic polymers (bilayer or multilayer systems). The technical difficulties of obtaining such “laminates” has led to the application of materials prepared from emulsions of the lipid in a continuous phase containing the hydrophilic polymer. Such materials represent essentially continuous hydrophilic films with hydrophobic inclusions or “fillers.” The extent to which barrier properties of such systems is improved depend of fractional volume of the lipid-derived phase, and the size, shape and orientation of the dispersed lipid particles.

F. Combinations

For many packaging applications it is necessary to combine two or more different materials in order to obtain a package with satisfactory properties. Some of the combinations used in food packaging have been mentioned in the preceding sections. The following list is intended to show the great variety of materials that can be used for this purpose:

1. Plastic combinations containing two or more plastic films laminated with various types of synthetic and natural adhesives
2. Plastic, silicone, and wax coatings on packages made of metals, paper, wood, and other materials
3. Rigid cans made of paper, with metal bottoms and tops
4. Plastic films with thin metallic coatings
5. Metal foils with thin plastic coatings
6. Barrier materials constructed of as many as six or seven materials including paper, textiles, metals, plastics, waxes, and resins.

III. EFFECT OF ENVIRONMENT ON FOOD STABILITY AND THE NEED FOR PROTECTIVE PACKAGING

The package affects the quality of foods by controlling the degree to which factors connected with processing, storage, and handling can act on components of foods. The processing and storage factors amenable to control by packaging include light, oxygen concentration, moisture concentration, heat transfer, contamination, and attack by biological agents.

A. Light

Food can be adversely affected by prolonged exposure to light. The chemistry of light-catalyzed changes can be quite complex. For instance, light promotes the following chemical reactions in food: oxidation of fats and oils to produce the complex of changes known as oxidative rancidity; oxidation of milk leading to formation of volatile and unpleasant mercaptans; and changes in various pigments, including the pink pigment astaxanthin (in salmon and shrimp) and the green, yellow, and red pigments of plant products, as well as the red pigment of meats (myoglobin). Riboflavin is especially photosensitive and when exposed to sunlight it loses its vitamin value and also activates or sensitizes other components to photodegradation. Ascorbic acid, or vitamin C, is also quite sensitive to light and it interacts with other components during light exposure.

The catalytic effects of light are most pronounced with light of the highest quantum energy, i.e., light in the lower wavelengths of the visible spectrum and in the ultraviolet spectrum. Specific reactions involved in deterioration of foods, however, may have specific wavelength optima; in particular the presence of sensitizers may shift the effective spectrum very substantially. Sensitizers present in food include riboflavin, β -carotene, vitamin A, and peroxidized fatty acids.

Sensitivity of a given class of foods to various wavelengths of light can vary with the method of processing. Fresh meats are known to discolor rapidly when exposed to ultraviolet light but are resistant to visible light. Meats preserved with nitrite, however, undergo discoloration due to visible as well as ultraviolet light.

In addition to wavelength the intensity of light and duration of exposure are important. In this respect we again must distinguish between the sensitivity of different products. As in the case of ionizing radiation, the penetration of light into food follows an exponential equation:

$$I_x = I_o e^{-\mu X} \quad (1)$$

where I_x is the intensity of light at depth X in food, I_o is the intensity of light at the surface of food, and μ is a characteristic constant (absorbance) for the given wavelength of light and a given food material.

The most penetrating quanta of light are those with wavelengths which are least effective per quantum of energy. Thus, ultraviolet rays penetrate less deeply into food than the red light components. In some cases the relatively shallow penetration of light into food products is an adequate protection in itself. Consider, for instance, the potential for loss of riboflavin in bread. In breads with well-developed crusts, 95% of the short-wavelength light is absorbed in the outer 2-mm layer of bread. If we make an unrealistically harsh assumption that all of the vitamin in this layer is destroyed and that the bread is exposed to light from all sides; then the volume in which the riboflavin is lost (V_i) is equal to the surface area of bread (A_i) multiplied by 2 mm. Assume a brick-shaped loaf of 10 cm \times 20 cm. A_i is then equal to $2(10 \times 10) + 4(10 \times 20) = 1000 \text{ cm}^2$, and $V_i = 1000 \text{ cm}^2 \times 0.2 \text{ cm} = 200 \text{ cm}^3$. Since total volume of the loaf is $10 \times 10 \times 20 \text{ cm}^3 = 2000 \text{ cm}^3$, the maximum loss under these exaggerated conditions is only 10%.

The loss of riboflavin in a similarly shaped bottle of milk during exposure to light cannot be dismissed so lightly. This is true even when it assumed light penetration in milk and bread are identical. The reason is that while the light cannot reach the vitamin located in the depth of the bottle, a diffusion process can occur in this liquid product, and an exchange can occur between riboflavin in the surface and riboflavin in the interior, thus continuously supplying some more vitamin to the irradiation surface. Similarly, free radicals produced by light at the surface of the liquid can migrate inward and react to damage the vitamin molecules in the interior. Even in a solid product with limited diffusion, surface reactions often suffice to produce damage resulting in unsaleability of the product. This is obviously the case with sensitive colors or when small amounts of potent off flavors or toxic compounds are produced.

B. Oxygen

Oxidation reactions are often the cause of undesirable changes in foods. One such reaction has already been mentioned, namely oxidative rancidity due to peroxidation of fats and oils in various foods. In addition, many vitamins, pigments, and some amino acids and proteins are oxygen sensitive. Packaging can control two variables with respect to oxygen, and these have different effects

on rates of oxidation reactions in foods. The first variable is the total amount of oxygen available. For instance, by packaging in a hermetically closed container which is constructed of an impermeable material, it can be assured that the total amount of oxygen available to react with food is finite. Under these circumstances, no matter how fast the rate of reaction, the extent of the reaction cannot exceed that which corresponds to complete depletion of oxygen. If the extent of reaction is of no consequence from the point of view of food quality, then the rate of reaction is irrelevant to shelf life.

On the other hand, situations do exist where the above is not true, either because the amount of oxygen in a sealed container is in fact significant with respect to deterioration potential or because the container allows some permeation. In these instances another variable is important, namely, the concentration of oxygen in the food, and this in turn depends on oxygen pressure.

In many cases, for the purposes of assessing the influence of packaging measures on oxidation-caused deterioration in foods we can proceed by establishing relations between the rates of reaction in the food and the oxygen pressure in the space surrounding the food, without worrying about diffusion effects in food. Where the food itself is very resistant to diffusion of oxygen this correlation is not useful, unless the size and surface area of the material for which the correlation has been determined is specified.

Quast and Karel (1971) have studied the diffusion of oxygen in foods under conditions that can occur during processing, handling, packaging, and storage. They have found that oxygen diffusion can affect rates of oxidation in two types of situations (Table 12.3): (1) when oxidation occurs very rapidly (such as in fish meal during curing in bulk bins) and (2) in a very dense product (such as butter). Oxygen diffusion also strongly influences meat color.

TABLE 12.3 Effect of Diffusion on Oxidation of Some Food Products in Air

| Product | Temperature (°C) | Effective oxygen diffusivity (cm ² /s) | Product thickness (cm) | Reduction of oxidation due to diffusion resistance (%) |
|-------------------------------|------------------|---|------------------------|--|
| Potato chips (past induction) | 37 | 2×10^{-1} | 100 | 0 |
| Fish meal | 37 | 8×10^{-2} | 10 | 0 |
| Fish meal | 37 | 8×10^{-2} | 100 | 50 |
| Butter | ~5 | 1.6×10^{-8} | 10 | 60 |

Source: Quast and Karel (1971).

The relation between rate of oxidation and oxygen pressures varies with type of reaction, type of product, and temperature. The relationship is nonlinear and above some level oxygen pressure has no effect on oxidation rate. This behavior is typical for oxidizing fats and oils in products with large surface to volume ratios and little internal diffusion resistance. When the surface to volume ratio decreases, oxidation of lipids can approach a linear dependence on oxygen pressure (Fig. 12.5).

Oxidation of meat pigment to an undesirable brown color has a complicated response to oxygen pressure. In fresh meats discoloration rates show a maximum at about 24 mm oxygen pressure corresponding to about 2–3% oxygen at atmospheric pressure (Fig. 12.6). The discoloration of cured meat pigments is almost directly proportional to oxygen pressure. Of course these differences in discoloration behavior dictate different requirements for package properties.

Another complicated oxygen permeation requirement is that of fresh fruits and vegetables. The respiration of these commodities continues after harvest and, as shown in Table 12.4, some vegetables and fruits have very high demands for oxygen and produce an essentially equimolar amount of carbon dioxide. The rate of respiration can be reduced by reducing the partial pressure of oxygen, as shown in Fig. 12.7. As can be seen in the same figure, however, a reduction of

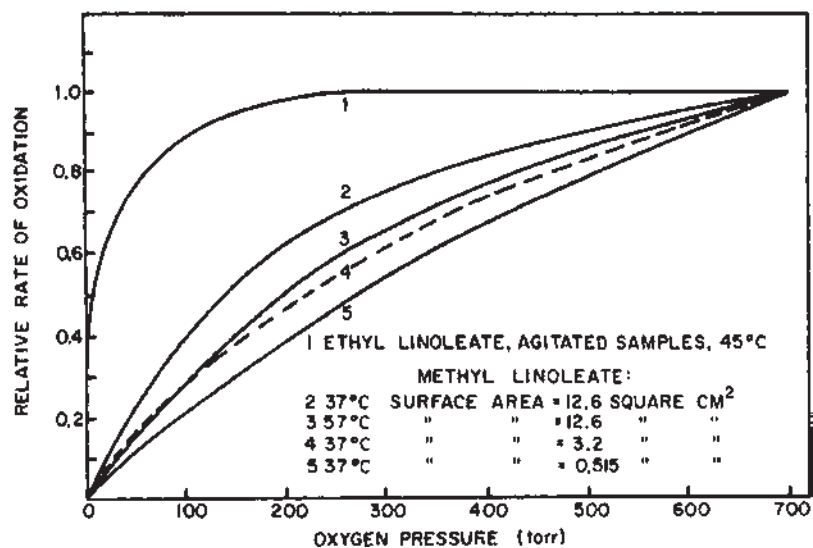


FIGURE 12.5 Dependence of oxidation of lipids on oxygen pressure for different surface areas per unit volume.

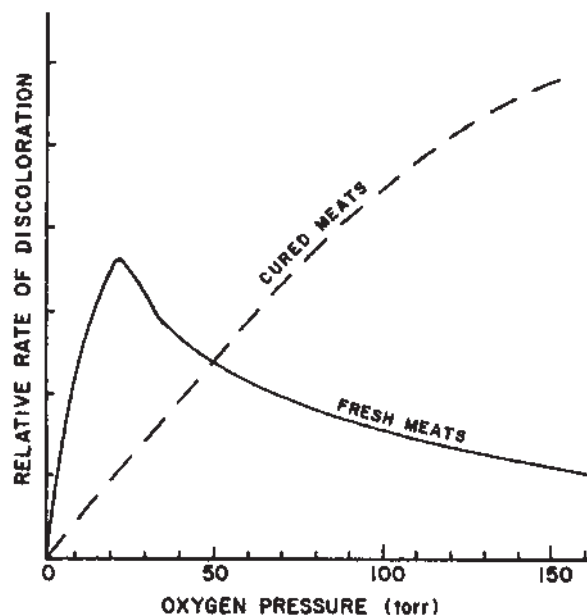


FIGURE 12.6 Rates of discoloration of meats as a function of oxygen pressure.

oxygen concentration to a very low level produces a sharp rise in the respiratory quotient, defined as the ratio of carbon dioxide evolved to oxygen consumed. This is due to the fact that there exists a critical oxygen value which varies with the commodity and with temperature and is often called the *extinction point of aerobic respiration*. Below this value the plant tissues produce alcohol and carbon dioxide without absorbing oxygen (anaerobic respiration). If anaerobic

TABLE 12.4 Rates of Respiration of Some Fruits and Vegetables

| Fruit or vegetable | CO ₂ production (mg/kg h) at | | |
|--------------------|---|------|------|
| | 5°C | 15°C | 20°C |
| Peas | 100 | 300 | 400 |
| Asparagus | 50 | 200 | 300 |
| Banana | — | 60 | 120 |
| Tomato | 20 | 30 | 40 |
| Grapefruit | 5 | 10 | 15 |

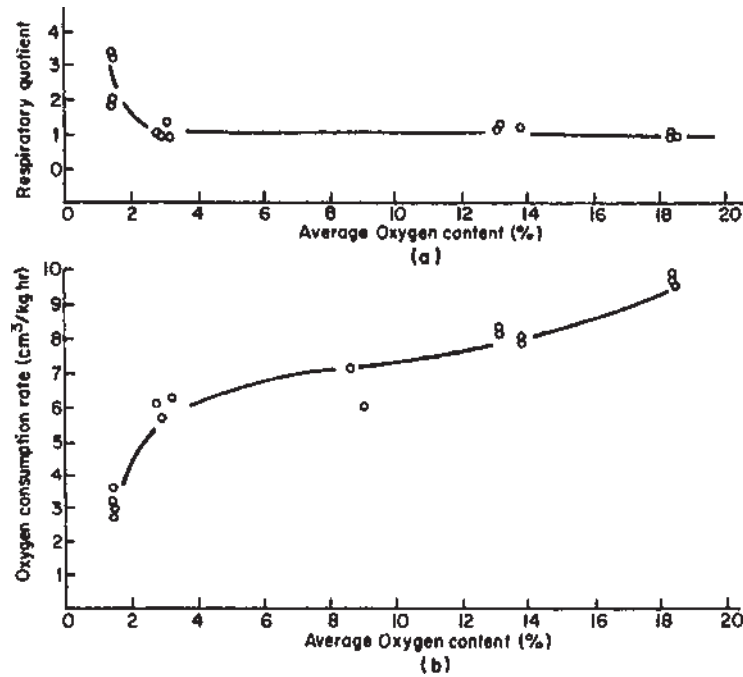


FIGURE 12.7 Respiratory quotient (a) and respiration rate (b) for apples, as a function of oxygen concentration.

respiration continues the fruit or vegetable spoils rapidly. Although it is desirable to slow rates of aerobic respiration of fruits and vegetables by lowering oxygen pressure, the oxygen level must be maintained above the critical value at which anaerobic respiration starts. A more detailed discussion is presented in Sec. V.D.

The above examples show that the oxygen response of foods is varied and must be known before package selection is undertaken.

C. Water

The water content of foods is dependent on the relative humidity of the immediate environment. In Chapter 5, we have reviewed in considerable detail the water relations of foods and need only to reemphasize here that these relations strongly affect packaging requirements.

D. Temperature

In practically every preceding chapter we have had occasion to mention the effects of temperature on rates of biological, chemical, and physical events in foods. Some degree of temperature control can be attained by packaging measures, but other control measures are often more feasible.

E. Sensitivity to Mechanical Damage

One of the functions of the package is to protect the food from various mechanical disturbances, such as spillage, or various mechanical deformations, such as breakage, abrasion, compression, or bending. A complete discussion of food rheology would be necessary to assess the differences in sensitivity among different products. Conversion of laboratory tests on food rheology to specification of requirements for mechanical properties of containers is in any case still quite primitive. For present purposes, it is sufficient to say that most if not all containers require adequate strength to maintain their own integrity (and therefore maintain separation between the food and the external environment). As additional requirement for cushioning (or protection of food from mechanical shocks) may also arise.

F. Sensitivity to Attack by Biological Agents

All food is subject to attack by some biological agents. The sensitivities of foods to microorganisms and viruses vary greatly with environmental conditions, and the corresponding requirements for packaging protection vary accordingly. Thus, foods relying on destruction of microorganisms prior to or immediately after packaging (sterilized products) require absolute package protection from recontamination. Other kinds of products, for instance those preserved by addition of chemicals, are much less sensitive and may tolerate some contamination.

Similar considerations apply, albeit to a lesser degree, to attack by insects, a potential danger for practically all types of foods. Other biological agents, such as rodents, can be more effectively controlled by proper warehouse and truck sanitation and by proper design of shipping containers than by packages that protect individual consumer portions of the product.

IV. PROPERTIES OF MATERIALS THAT DETERMINE THE DEGREE OF PROTECTION AGAINST ENVIRONMENTAL FACTORS

A. Light-Protection Characteristics

The total amount of light absorbed by the food is given by the following formula:

$$I_{\text{abs}} = I_o \text{Tr}_p \frac{1 - R_f}{(1 - R_f)R_p} \quad (2)$$

where

I_{abs} is the intensity of light absorbed by the food.

I_o is the intensity of incident light.

Tr_p is the fractional transmission by the packaging material.

R_p is the fraction reflected by the packaging material.

R_f is the fraction reflected by the food.

The fraction of the incident light transmitted by any given material can be considered to follow the Beer–Lambert law:

$$I_x = I_o e^{-\mu x} \quad (1)$$

The absorbance, μ varies not only with the nature of the material but also with the wavelength. The light transmitted through a given material therefore gives a characteristic spectrum of transmitted light dependent on incident light and the properties of the package. Figure 12.8 shows light-transmission curves for several food-packaging materials. It is readily apparent that several of the plastics, while transmitting similar amounts of light in the visible range, offer varying degrees of protection against the damaging ultraviolet wavelengths. The protection against uv light by different packaging materials often can be characterized by a “cutoff” wavelength below which transmission of light becomes negligible, and these wavelengths are sometimes listed in compilation of package properties.

The barrier properties with respect to light of a packaging material can be improved by special treatments. Glass is frequently modified by inclusion of color-producing agents or by application of coatings. Figure 12.9 shows the differences in light transmission between transparent and colored bottle glass. The light transmission curve of window glass of comparable thickness is included for comparison.

Modification of plastic materials may be achieved by incorporation of dyes or by application of coatings. Figure 12.10 shows the effect of such treatments on cellophanes.

As a consequence of the successive absorption of light in both the packaging material and in the food, the total energy delivered to different points

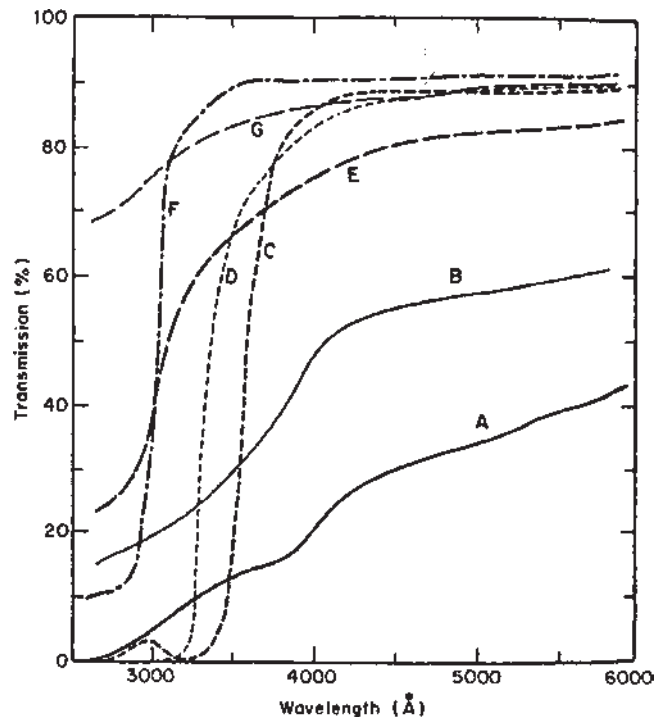


FIGURE 12.8 Light transmission through various flexible packaging materials: (A) low-density polyethylene, 3.5 mil thick; (B) translucent wax paper, 3.5 mil thick; (C) Saran, 1.1 mil thick; (D) Pliofilm, 1.4 mil thick; (E) Pliofilm, 1.4 mil thick; (F) cellulose acetate, 1 mil thick; (G) low-density polyethylene, 1.5 mil thick.

in the food varies and the spectral characteristics of the light vary as well. Figure 12.11 shows schematically how relative intensity of light at all wavelengths and the relative intensity of short wavelengths may vary in a packaged product. Consider the situation as indicated in Fig. 12.11 with the thickness of the packaging material being X_p and its absorbance for any one wavelength μ_p . If a food has absorbance μ , then we can calculate the intensity of light of a given wavelength at plane X in the food as follows (assuming that reflection can be ignored):

$$I_i = I_o e^{-\mu_p X_p} \quad (3)$$

$$I_X = I_i e^{-\mu X} \quad (4)$$

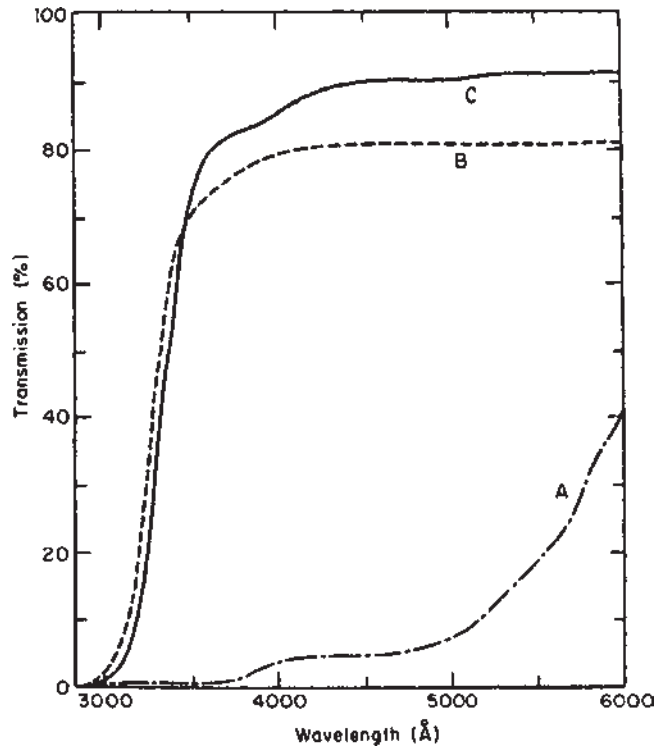


FIGURE 12.9 Transmission of light through three types of glass: (A) Amber bottle glass, 11.8 mil thick; (B) transparent milk bottle glass, 11.6 mil thick; (C) window glass, 11.9 mil thick.

where I_i refers to intensity at the surface of the food and I_x refer to intensity at plane X in the food. Combining Eqs. (3) and (4), we obtain

$$I_x = I_o e^{-(\mu_p X_p + \mu X)} \quad (5)$$

and therefore

$$\ln \frac{I_o}{I_x} = \mu_p X_p + \mu X \quad (6)$$

B. Permeability to Gases and Vapors

1. Definitions

The protection of foods from gas and vapor exchange with the environment depends on the integrity of packages, including the seals and closures, and on

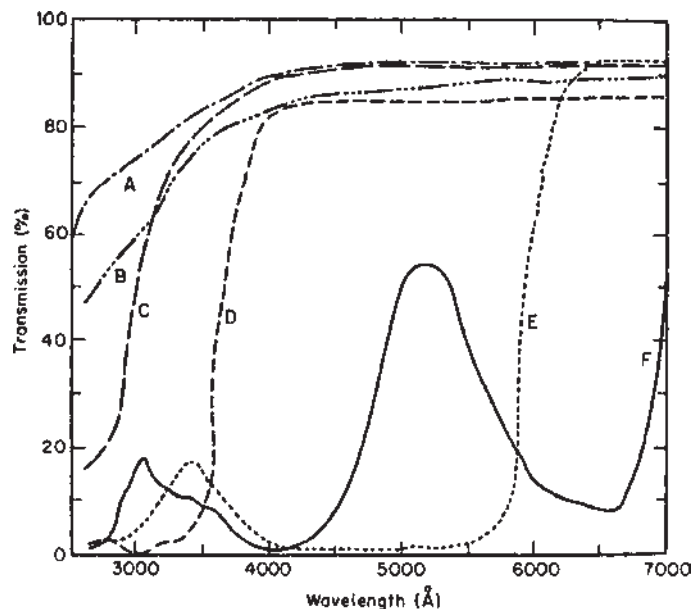


FIGURE 12.10 Transmission of light through various types of cellophane: (A) Plain cellophane, 0.9 mil thick; (B) Sara-coated cellophane, 1.5 mil thick; (C) nitrocellulose-coated cellophane, 1 mil thick; (D) cellophane with special UV absorbing coating, 1 mil thick; (E) dyed cellophane (red), 1 mil thick; (F) dyed cellophane (dark green), 1 mil thick.

the permeability of the packaging materials themselves. Gases and vapors can permeate through materials by macroscopic or microscopic pores and pinholes or they may diffuse by a molecular mechanism, known as *activated diffusion*. In activated diffusion the gas is considered to dissolve in the packaging material at one surface, to diffuse through the packaging material by virtue of a concentration gradient, and to re-evaporate at the other surface of the packaging material. The equilibrium and kinetic considerations governing mass transfer have been discussed in Chapter 4 and found applicable to dehydration and freeze drying. They apply here as well.

In particular, for the case of gas transport in one direction (from the atmosphere into a package) the diffusion law applies:

$$J = -DA \frac{dc}{dX} \quad (7)$$

where

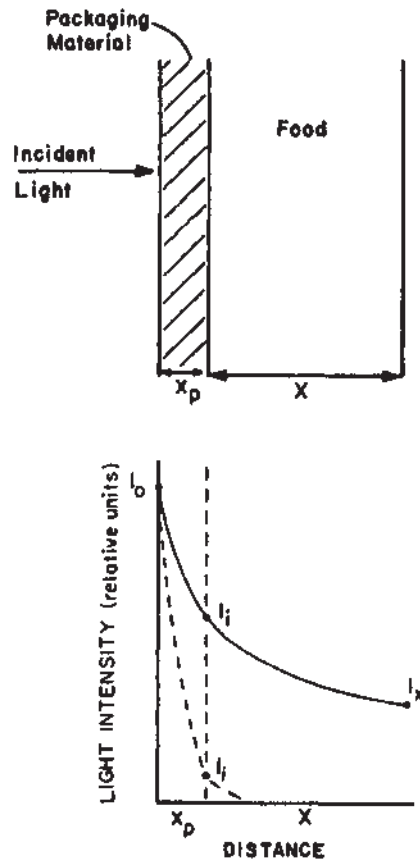


FIGURE 12.11 Schematic representation of light absorption in a packaged food product.

J is the flux of gas in appropriate units (e.g., mol/s)

A is the area (cm^2)

D is the diffusion coefficient for the gas in the membrane (cm^2/s)

c is concentration of the gas in the membrane (mol/cm^3)

X is distance in membrane measured in direction of flow (cm)

If D is a constant and steady-state conditions exist, then (as shown in Fig. 12.12):

$$J = DA \frac{c_1 - c_2}{\Delta X} \quad (8)$$

However, c_1 and c_2 are difficult to measure within the membrane. If Henry's law applies, we have

$$c = S_p \quad (9)$$

where S is solubility ($\text{mol}/\text{cm}^3/\text{atm}$) and p is partial pressure of gas (atm).

Then we can combine Eqs. (8) and (9) and obtain

$$J = DSA \frac{p_1 - p_2}{\Delta X} \quad (10)$$

The quantity DS is known as the permeability constant. We shall use for it the symbols B or b . The permeability constant is defined in terms of quantities defined below:

$$B \equiv \frac{\text{amount of gas} \times \text{thickness}}{\text{area} \times \text{time} \times \text{pressure difference}}$$

There is no single convention as to units to be used for the permeability constant and Table 12.5 shows that many different units are in fact being used in the literature. In addition to permeability coefficients as defined above, some authors use permeance which is not corrected to unit thickness. Furthermore permeance to water vapor is sometimes reported in units which are neither corrected to unit thickness nor to unit pressure, but this value always must be reported with specified thickness, humidity, and temperature. Such a unit is WVP (water-vapor permeability), used extensively in practical packaging technology and usually defined as grams of water per day per 100 in^2 of package surface, for a specified thickness and temperature and for a relative humidity on one side of approximately 0% and on the other side of 95%.

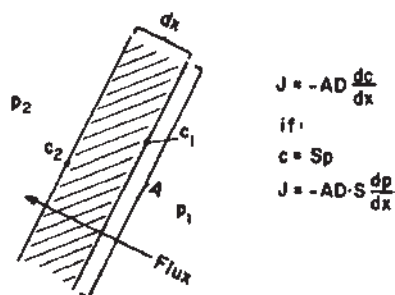


FIGURE 12.12 Schematic representation of steady-state activated diffusion across a packaging film.

TABLE 12.5 Some Units Used in Reporting Permeability

| Amount of gas | Thickness | Area | Time | Pressure difference |
|-----------------------|-----------|---------------------|-------|---------------------|
| cm (STP) | mm | cm ² | s | cm Hg |
| mol | cm | cm ² | s | cm Hg |
| cm ³ (STP) | cm | cm ² | s | cm Hg |
| g | cm | cm ² | s | mm Hg |
| cm ³ (STP) | mil | 100 in ² | 24 h | atm |
| g | cm | cm ² | 24 h | 0.21 atm |
| cm ³ (STP) | mil | m ² | 24 h | atm |
| cm ³ (STP) | cm | cm ² | min | atm |
| cm ³ (STP) | 100 μm | 100 cm ² | 24 h | atm |
| g | mil | 100 m ² | h | atm |
| cm ³ (STP) | mil | 100 in ² | 100 h | atm |

1. In preparing the present edition we reviewed the practice in the most recent reviews and research papers on the subject, and found that the units used are still not uniform, and no single convention has been universally adopted. In the present chapter we shall use, whenever feasible the following units: For permeability of so-called fixed gases (including nitrogen, oxygen and carbon dioxide) the *barrer*. This unit was named after Richard Barrer, a pioneer in the study of diffusion through membranes. It is defined as follows: 1 barrer = 10^{-10} mL cm cm⁻² (cm Hg)⁻¹ s⁻¹. In SI units 1 barrer is equal to 7.5×10^{-18} m² s⁻¹ Pa⁻¹ (Rogers, 1986; Rowlett, 2000).
2. For water vapor we shall continue our practice of reporting permeation rate per unit area, corrected for thickness of membrane the units we will use will be (g mm m⁻²)/dw with specification of temperature and humidity of measurement.

This unit of water vapor transmission is in conformance with the practice in the recent treatise on packaging by Robertson (1993). The permeability unit in Robertson (1993) is 10^{-11} mL cm cm⁻² cm Hg⁻¹ s⁻¹ and is therefore equal to 0.1 barrers.

2. Measuring Permeability

There are many methods for measuring permeability and it is not possible to review them in detail here. Two major types of measurement are shown schematically in

Fig. 12.13. In the pressure-increase method a membrane is mounted between the high-pressure and the low-pressure sides of a permeability cell. Both sides are evacuated and the membrane is degassed. Then, at "zero" time a known constant pressure p_H of the test gas is introduced on the high side, and p_L (low-side pressure) is measured as a function of time. If the measurement is continued only as long as p_H remains much larger than p_L , the Δp remains essentially constant, and the permeability constant can be calculated as shown in Fig. 12.14.

In the concentration-increase method, both sides are at the same total pressure, but a partial pressure difference is maintained by sweeping one side continuously with the test gas and by maintaining on the other side an inert gas into which the test gas is diffusing. Figure 12.15 shows an experimental arrangement for measuring gas permeability by concentration increase using gas chromatographic analysis for oxygen or carbon dioxide (Karel et al., 1963). Modern instrumental methods allow continuous direct recording of oxygen permeation using an oxygen electrode.

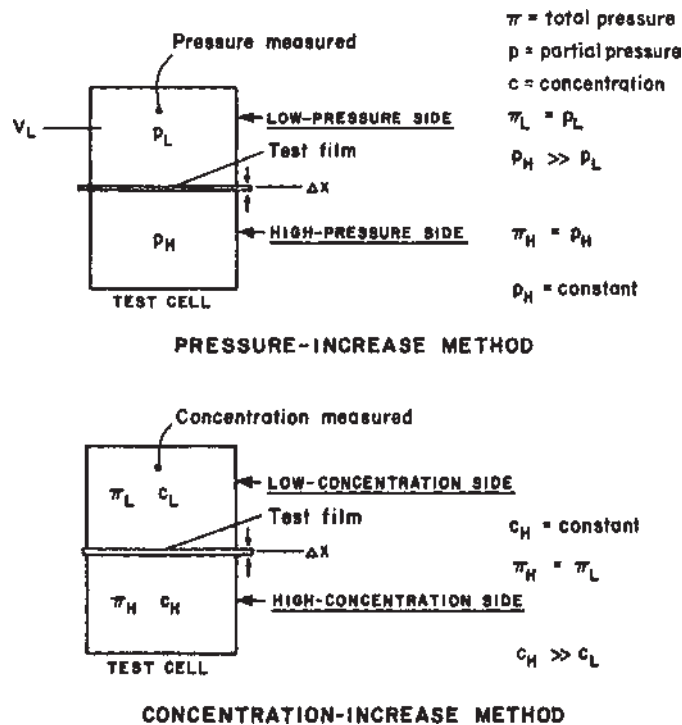


FIGURE 12.13 Principles of two types of permeability measurement.

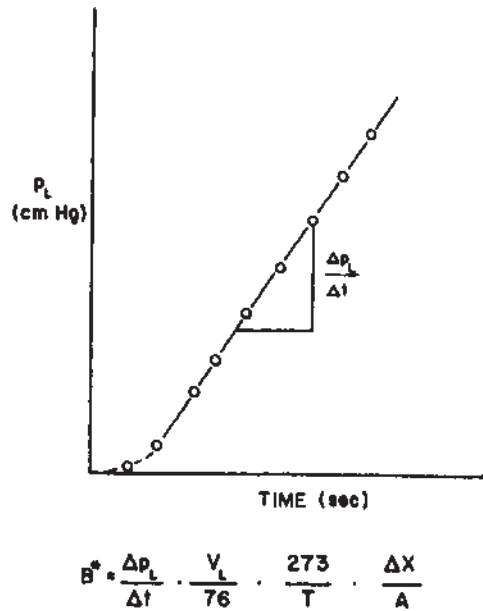


FIGURE 12.14 Calculation of permeability from the slope of the pressure-increase curve.

Water vapor permeability is usually measured gravimetrically. A desiccant maintaining a low water-vapor pressure is sealed in an aluminum cup (WVP cup) by a film sample as shown in Fig. 12.16. The cup is placed in a cabinet at constant temperature and constant humidity and the permeability is determined from the rate of weight increase due to water adsorbed by the desiccant. The desiccant must be of a type maintaining a low vapor pressure of water in spite of water sorption. Calcium sulfate, magnesium perchlorate, and calcium chloride have been used for the purpose. Silica gel also can be used for comparative tests but the partial pressure of water sorbed on it increases with coverage. Sometimes it is advantageous to conduct such permeability tests in sealed pouches rather than in the WVP cups.

Another way of measuring water-vapor permeability is to measure relative humidity in a compartment separated by the test sample from a source of water. A simple arrangement for this purpose, involving an electric hygrometer has been designed by the author and his co-workers and is shown in Fig. 12.17. More elaborate and expensive instrumentation for the same purpose, based on the same principle, is also available commercially.

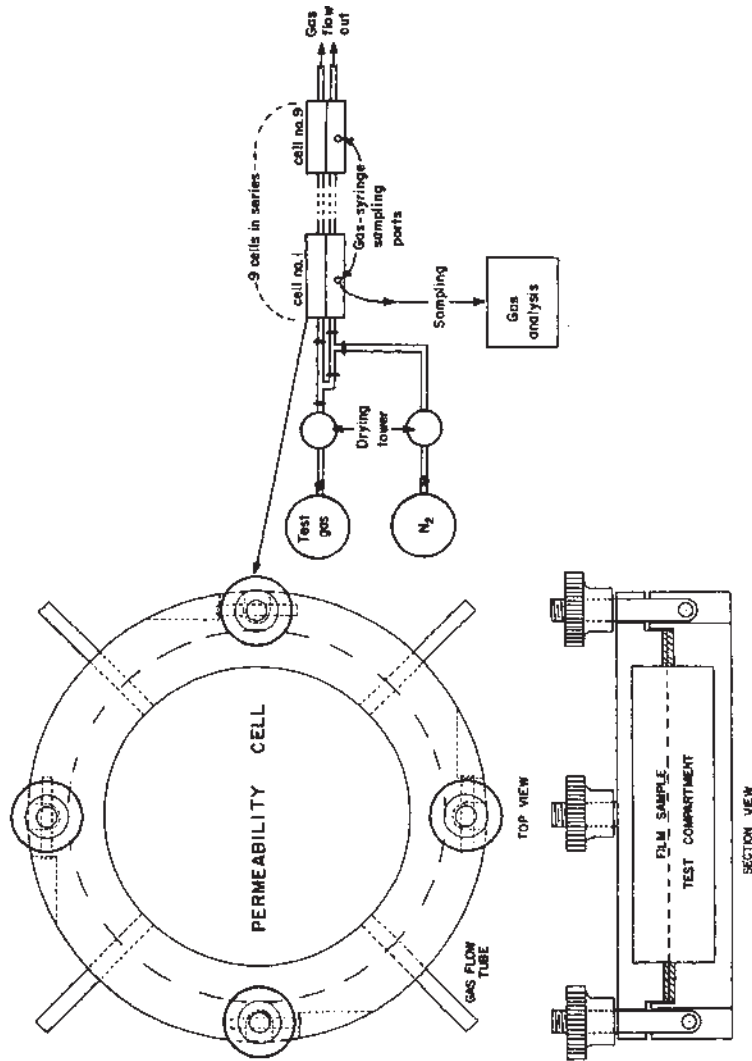


FIGURE 12.15 System for permeability measurement using a concentration-increase method.

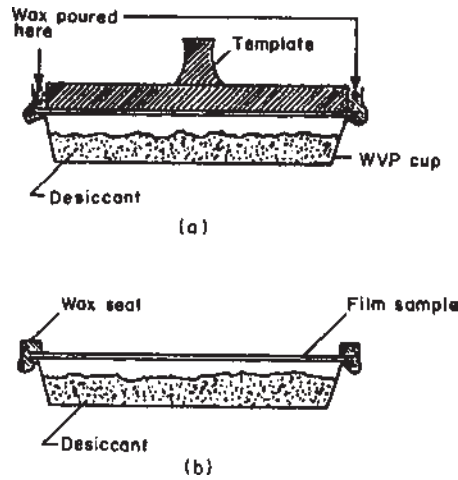


FIGURE 12.16 Cup used for gravimetric measurement of water-vapor permeability: (a) formation of wax seal and (b) cup with wax seal in place.

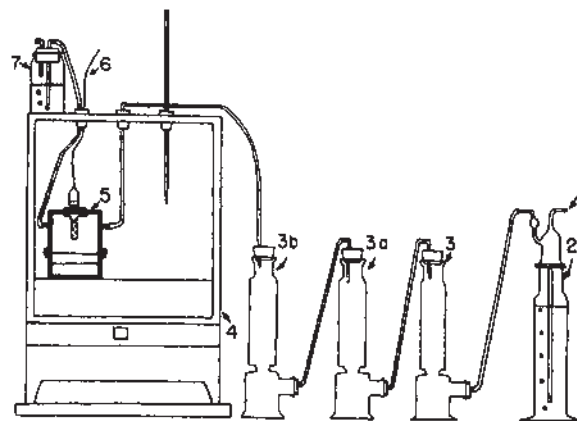


FIGURE 12.17 System for water vapor permeability measurement using an electric hygrometer: (1) connection with compressed air line, (2) gas washing bottle, (3, 3a, 3b) the three gas-drying towers, (4) constant temperature cabinet, (5) the permeability cell, (6) connection with the electric indicator, and (7) the backpressure bottle.

TABLE 12.6 Permeability of Some Materials to Hydrogen and Helium

| Material | Gas | Temperature (°C) | Permeability (barrers) |
|-------------|----------------|------------------|------------------------|
| Quartz | H ₂ | 300 | 5 |
| | H ₂ | 700 | 40 |
| | He | 300 | 0.1 |
| | He | 700 | 25 |
| Pyrex glass | He | 0 | 0.04 |
| | He | 300 | 4 |
| Palladium | H ₂ | 350 | 6.5×10^5 |
| Rubber | H ₂ | 18 | 80 |
| | H ₂ | 60 | 500 |

3. Permeabilities of Packaging Materials to “Fixed Gases”

Oxygen, nitrogen, hydrogen, carbon dioxide, and other gases with low boiling points are known as *fixed gases*. We group them together because they show similar “ideal” behavior with respect to permeability through packaging materials. Table 12.6 shows the permeability of helium and hydrogen through several materials. Metals and glass in thicknesses used in packaging have permeabilities too low to be significant, so that only polymeric materials need be considered. Table 12.7 shows permeabilities of a number of packaging materials to O₂, CO₂, and N₂ at room temperature. Table 12.8 shows some oxygen permeability values. Table 12.9 shows typical ratios for several materials.

These values illustrate the following points:

First, for any given gas there exist materials with widely differing permeabilities. Thus polyvinylidene chloride (saran) is 100,000 times less permeable to oxygen than is silicone rubber.

Second, there are regularities in transmission of different gases through the same material. Normally, carbon dioxide permeates four to six times faster than oxygen, and oxygen four to six times faster than nitrogen. Since carbon dioxide is the largest of the three gas molecules, one expects its diffusion coefficient to be the lowest, and so it is. Its permeability coefficient, however, is the highest, because its solubility, *S*, in polymers is much greater than that for other gases.

Fixed gases also show the following ideal behaviors: (1) the permeabilities can be considered independent of concentration and (2) the permeabilities change

TABLE 12.7 Typical Permeability Values of Plastic Films at 25°C

| Film | Permeability barriers | | |
|-------------------|-----------------------|--------|----------------|
| | Nitrogen | Oxygen | Carbon dioxide |
| LDPE ^a | 2.0 | 5.0 | 30 |
| HDPE ^b | 0.3 | 0.9 | 3.7 |
| PVDC ^c | 0.001 | 0.004 | 0.03 |
| Polyamide | 0.01 | 0.04 | 0.16 |
| PET ^d | 0.005 | 0.02 | 0.12 |
| Cellulose acetate | 0.3 | 0.8 | 6.8 |
| Silicon rubber | | >200 | >2000 |

^a LDPE = Low density polyethylene.

^b HDPE = High density polyethylene.

^c PVDC = Polyvinylidene chloride (e.g., saran).

^d PET = Polyethylene terephthalate (e.g., Mylar).

TABLE 12.8 Permeability to Oxygen of Various Packaging Materials at 25–30°C

| Material | Permeability range (barrers) |
|-------------------------------|------------------------------|
| Conventional polyethylene | 3–6 |
| High-density polyethylene | 0.6–1 |
| Plioilm | 0.1–2 ^a |
| Saran | 0.004–0.1 |
| Plain cellophane | 0.1–2 ^b |
| Polyvinyl fluoride | 0.01–0.04 |
| Mylar (polyester) | 0.02–0.04 |
| (Poly)trifluorochloroethylene | 0.02–0.4 ^a |
| Cellulose acetate | 0.4–1.2 ^b |
| Silicone rubber | over 100 |
| Coated and waxed papers | 0.04–5 ^c |
| Foil laminations | 0 ^d |

^a Depends on type and amount of plasticizer.

^b Depends on humidity.

^c Depends on type, quality, and amount of coating; humidity; conditioning; and other factors.

^d For undamaged samples.

TABLE 12.9 Typical Permeability Ratio Values of Plastic Films at 25°C

| Film | Permeability ratios (molar units) | |
|--|-----------------------------------|--------------------------|
| | Water vapor/oxygen | Carbon dioxide/oxygen |
| Perforated films | | 1 |
| Polystyrene | 100 | 5 |
| Polyamide | 10 | 4 |
| Polyester | 5,000 | 3 |
| Cellulose acetate | 10,000 | 6 |
| Silicon rubber | 20 | 6 |
| Polypropylene | 30 | 4 |
| Various protein films | | 4 to 30 (varies with RH) |
| Various films based on polysaccharides | | 7 to 40 (varies with RH) |

with temperature in accordance with the following relation:

$$B = B_0 e^{-E_p/RT} \quad (11)$$

where E_p is the activation energy for permeability (kcal/mol) and B_0 is a constant.

Table 12.10 shows some values of E_p and Fig. 12.18 shows how permeability varies with the reciprocal of absolute temperature. For some materials there is a definite break in the permeability–temperature curve and above a critical temperature (or temperature range) the material is much more permeable. Such effects (for instance, in polyvinyl acetate around 30°C and in polystyrene around 80°C) are due to a glass transition at a temperature, T_g . Below T_g , the material is “glassy” and above it, “rubbery.”

At this point some discussion of structure and morphology of polymeric packaging materials is necessary. Polymeric solids can be crystalline, amorphous, or semicrystalline. Packaging materials are either semicrystalline or amorphous. In semicrystalline materials part of the volume is occupied by ordered aggregates of polymer chains, *crystallites*. These crystallites are considered impermeable to gases and vapors. The rest of the volume is occupied by amorphous regions, i.e., polymer chains in a substantially disordered state. Amorphous polymers exist almost totally in a disordered state. Below T_g the holes, pores, and other voids between chains remain fixed because the mobility of the disordered chains is severely limited. Above T_g the chains have greater

TABLE 12.10 Activation Energies (E_A) for Permeation of Gases

| Film | (E_A) for O ₂ (kJ/mol) | (E_A) for CO ₂ (kJ/mol) |
|-------------------|---------------------------------------|--|
| LDPE ^a | 30 | 33 |
| HDPE ^b | 35 | 35 |
| PET ^c | 27 | 25 |
| Polyamide | 41 | 38 |
| Natural rubber | 41 | 38 |
| PVDC ^d | 58 | 50 |
| Perforated films | 4 | 4 |

^a LDPE = Low density polyethylene.

^b HDPE = High-density polyethylene.

^c PET = Polyethylene terephthalate (e.g., Mylar).

^d PVDC = Polyvinylidene chloride (e.g., Saran).

freedom of motion and the voids between them assume an amoebalike quality of constantly changing shape, and location. Obviously these changes have an important effect on the ability of molecules to diffuse through the material, especially fairly large molecules.

The differences in the ability of different polymer films to transmit gases arise in part from differences in crystallinity, in part from mobility differences between different types of polymeric chains, and finally from specific influences of functional groups of the polymers on the solubility of gases and vapors in the amorphous portion of the polymer. (The crystalline portions are considered nonsorbing.) The crystalline content of a polymer is of primary importance in determining its permeability. Ideally one expects the permeability to increase linearly with the square of the noncrystalline volume fraction. This relation, however, holds only for such small molecules as hydrogen and it deviates very substantially for very large molecules, such as sulfur hexafluoride. These deviations occur because the presence of crystalline regions exerts some restraining influence on the mobility of polymer chains in noncrystalline regions, and such restrictions are particularly impeding to the flow of large molecules.

The permeability of polymers also can be modified by cross-linking polymers (for instance, vulcanizing, which is a process of cross-linking natural rubber). Cross-linking restricts mobility of chains and reduces permeability, provided that crystallinity is not impaired. Orientation of polymer chains by stretching the films increases crystallinity and decreases permeability.

Ideal behavior (D independent of concentration, $\log B$ proportional to $1/T$) of films does not occur (1) when polar gases, especially water, diffuse through a hydrophilic polymer and (2) when low boiling organic compounds, including

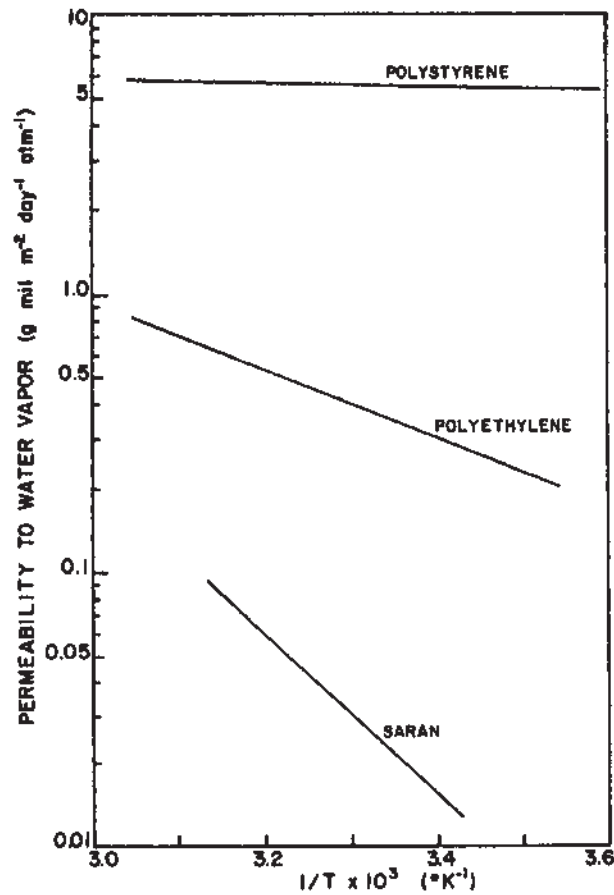


FIGURE 12.18 Dependence of permeability of absolute temperature.

solvents and flavors, diffuse through any polymer. Effects of water content on permeability are particularly important in food packaging, and are reviewed in the next section.

4. Permeability to Water

As indicated above, with water vapor and hydrophilic polymers we encounter deviations from ideality. The permeability constant varies with water concentration as well as with temperature, and the temperature dependence may not be as

simple as that shown in Eq. (11). Most data are reported for 100°F and for a humidity (at the high-pressure side) of 95% RH. Some data are shown in Table 12.11.

The permeability of films to water vapor usually increases rapidly at high relative humidities due to sorption of water and concomitant swelling of the material. Figure 12.19 shows how the rate of water transfer through a nylon film varies with water activity at the surface of the high-pressure side of the film. Table 12.12 shows how the permeability constant varies when the high-pressure side is at 100% RH and the humidity at the low-pressure side is varied.

The calculation of water transport through such materials as nylon, cellulose, polyvinyl alcohol, and most of edible films based on biopolymers, which show a humidity-dependent permeability, can be made only if this dependence can be characterized by a suitable mathematical function. A number of approaches to obtaining such information are possible and techniques have been reported for this purpose (Comyn, 1986).

Temperature is another factor that has a bearing on permeability. For the system water-polar polymers, Eq. (11) can be used only over narrow temperature ranges.

TABLE 12.11 Typical Water-Vapor Transmission Rates (WVTR) of Plastic Films

| Film | Range of WVTR ^a (at 38°C and 95 vs 0% RH) |
|----------------------------|---|
| Cellophane | 8–40 |
| Coated cellophanes | 0.08–0.8 |
| Low-density polyethylene | 0.3–0.6 |
| High-density polyethylene | 0.1–0.2 |
| Polyvinylidene chloride | 0.04–0.2 |
| Polyethylene terephthalate | 0.01–0.1 |
| Silicon rubber | > 50 |
| Polypropylene | 0.08–0.16 |
| Waxed papers | 0.08–6 |
| Coated papers | 0.08–2 |
| Polystyrene | 2.8–4 |
| Polyamide (Nylon 6) | 6–9 |
| EVAL ^b | 5–6 |

^a WVTR in $\text{g mm}^{-2} \text{d}^{-1}$.

^b EVAL = Ethylene vinyl alcohol copolymers.

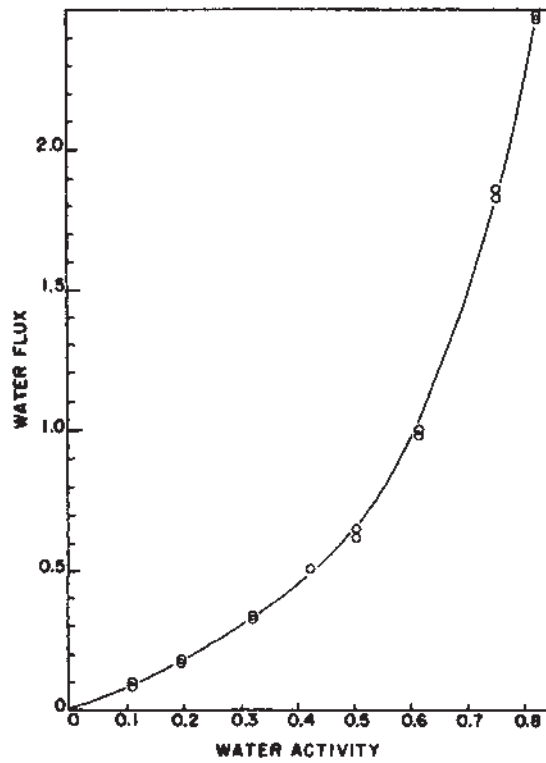


FIGURE 12.19 Dependence of water-vapor transfer rate through nylon films on water activity at the high humidity side of the film.

TABLE 12.12 Permeability (b)^a of Several Films to Water Vapor when High-Pressure Side is at 100% RH and the Other Side is at Various RHs

| Material | RH | | |
|-------------------|------|------|------|
| | 31% | 56% | 80% |
| Polyethylene | 0.18 | 0.19 | 0.17 |
| Polyvinyl alcohol | 48.5 | 67 | 97 |
| Cellulose acetate | 39 | 48.5 | 73 |
| Nylon | 7.3 | 12.1 | 21 |

^a $b = \text{g mil m}^{-2} \text{ day}^{-1} \text{ torr}^{-1}$

Source: From Hauser and McLaren (1948).

5. Permeability to Humidified Gases

Exposure of hydrophilic films to high humidity results in sorption of water, swelling, and greatly increased mobility of polymer chains. Water has effects similar to other plasticizers or solvents of relatively low volatility which enhance flexibility of polymer chains. Plasticizers tend to increase the permeability to all gases, and sorbed water is no exception. The increase in permeability is particularly dramatic for transport of gases through materials which are excellent gas barriers when dry. This situation is illustrated in Table 12.13, which shows the permeabilities of (1) cellophane, (2) polyethylene, and (3) a laminate of polyethylene and cellophane. The cellophane permeability depends on humidity, and when it is kept dry or protected from high humidity by a layer of polyethylene it is a good barrier to carbon dioxide.

The dependence of permeability on water content of the packaging materials, which in turn is controlled by the relative humidity, is particularly significant in hydrophilic biopolymers, including those proposed for biodegradable and edible packaging. For instance the permeability of wheat gluten films to oxygen at 90% RH is 25 times greater than at 0% RH. Given similar RH condition differences chitosan permeability to oxygen increases 500-fold and that to carbon dioxide by a factor of 150. Similar increases in permeability to water vapor are noted for most edible biopolymers.

The increase gas and vapor permeability is due to plasticization of the polymers by water. An important consequence of this plasticization is a decrease in the glass transition temperature (T_g). Arvanitoyannis et al. (1994)

TABLE 12.13 Effect of Relative Humidity on Transmission of CO₂ Through Polyethylene and Cellophane

| Material ^a | Position | RH of high-humidity side (%) | CO ₂ transmission barrers |
|-----------------------|-----------------|------------------------------|--------------------------------------|
| C | — | 0 | 0.004 |
| C | — | 100 | 1.0 |
| P | — | 0 | 20 |
| P | — | 100 | 20 |
| C + P | P faces high RH | 0 | 0.01 |
| C + P | P faces high RH | 100 | 0.01 |
| C + P | C faces high RH | 0 | 0.01 |
| C + P | C faces high RH | 100 | 1.2 |

^aP = 1 mil polyethylene, C = 1 mil cellophane.

studied the properties of rice starch, and potato starch films equilibrated at different humidities. The resulting water contents ranged from 6 to 19%, and these differences in water content affected T_g to a considerable extent. Potato starch had a T_g at 410K at water content of 6.6%, which dropped to 324 at 15.6% water, and to 314K at 19% water. The corresponding values for rice starch were: T_g at 393K at 6.5% water; 327K at 15.2% water and 308K at 18.6% water. Diffusion coefficients for various gases in amorphous polymers typically depend on temperature as shown in Fig. 12.20, the relationship follows the Arrhenius equation, but the activation energy for diffusion (E_D in kJ/mol) changes at T_g . Since the permeability coefficient is a product of D and S , it is not surprising that the activation energy for permeability (E_P in kJ/mol) also shows a break at T_g . Arvanitoyannis et al. (1994) found this to be the case for potato starch films. Rice starch films below T_g show the following E_D values for nitrogen, 2.6; oxygen, 2.3; and carbon dioxide, 2.8. Above T_g the corresponding values increase to 3.8, 3.4, and 3.9 for nitrogen, oxygen, and carbon dioxide, respectively. The values of E_P show similar behavior. They are between 2.8 and 3.3 below T_g and between 4.1 and 5 above T_g . Arvanitoyannis and Biliaderis (1998) conducted a similar study on plasticized edible films made from sodium caseinate and soluble starch. They observed that E_P for nitrogen was 18 below T_g , and 43 above T_g . For oxygen the corresponding values were 25 below T_g and 46 above T_g .

In contrast to hydrophilic polymers lipid films do not swell at high humidity, and ambient RH does not significantly affect their permeability.

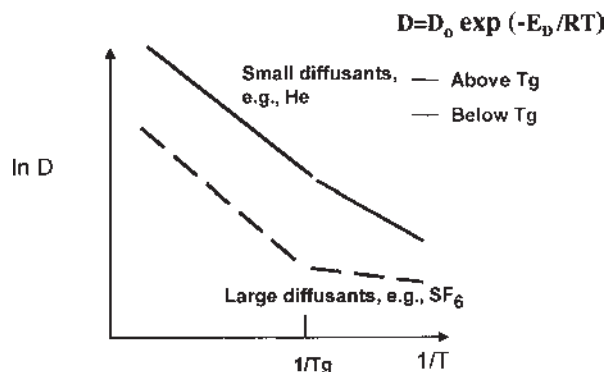


FIGURE 12.20 Effects of temperature on diffusion of gases in amorphous polymers.

Coatings made of chocolate are excellent barriers to water vapor as demonstrated by Biquet and Labuza (1988). Lipid coatings do show drastic changes in their barrier behavior at critical values of temperature, but these are due to melting (a first order transition) and not to a glass transition. Composite films made of hydrophilic and hydrophobic materials show a complex dependence on water content which depends on geometry of the composite films. We shall discuss the effect of geometry in the next section.

A problem combining effects of film geometry and moisture sensitivity exists in the use of certain laminates in heat sterilization in flexible pouches. Among the important requirements for stability of heat-processed foods is protection from atmospheric oxygen. According to Koros (1990) canned meats, baby foods, and canned vegetables require oxygen protection permitting at maximum oxygen ingress of 1 to 5 ppm. This is a much stricter requirement than that for dried foods (5–15 ppm) or oils and fats (50–200 ppm). Among the most effective oxygen barriers, which is suitable for retort processing is ethylene vinyl alcohol (EvOH). The problem with its utilization is its hydrophilicity, as a result of which its water content at high relative humidities increases to 10% at 25°C and to 30% at 120°C, which is in the range of temperatures used for sterilization. The oxygen permeability of the material increases drastically with increasing water content. At 5% water the permeability is 10 times that of the dry material, at 10% water it increases a hundredfold, and at 20% or higher it is 1000 times the permeability in the dry state (Alger et al., 1990). The water absorbed by the material during steam sterilization increases the permeability during storage, because desorption of the water subsequent to removal from the retort and cooling is slow. Tsai and Wachtel (1990) studied (EvOH) based multilayer containers, and found that upon retorting in steam at 115°C the oxygen permeability increased by a factor of 25. Furthermore upon subsequent cooling and storage at ambient temperature the permeability was still 10 times greater than the value prior to retorting. Furthermore, oxygen penetrating the package during a transient high permeability phase provides oxidizes sensitive food components and provides initiators of subsequent oxidation reactions.

The solution to the problem has been achieved by producing multilayer structures in which the oxygen barrier (EvOH) layer is protected by layers with superior water barrier and mechanical resistance properties. Two such laminates are:

Polypropylene/EvOH/Polypropylene
Polypropylene/EvOH/Polycarbonate

In both of the above arrangements polypropylene is the layer adjacent to the food (Alger et al., 1990).

6. Permeability of Multilayer Materials

The following relationship applies to the flux of gas or vapor through several materials arranged in series (steady state is assumed; see the hypothetical three-layer material shown in Fig. 12.21.

$$J_1 = J_2 = J_n \quad (12)$$

$$J_1 = \frac{B_1 A_1}{\Delta X_1} (p_1 - p_2) \quad (13a)$$

$$J_2 = \frac{B_2 A_2}{\Delta X_2} (p_2 - p_3) \quad (13b)$$

$$J_3 = \frac{B_3 A_3}{\Delta X_3} (p_3 - p_4) \quad (13c)$$

$$J_T = \frac{B_T A_T}{\Delta X_T} (p_1 - p_4) \quad (14)$$

Since

$$A_1 = A_2 = A_3 = A_T \quad (15)$$

$$\frac{\Delta X_T}{B_T} = \frac{\Delta X_1}{B_1} + \frac{\Delta X_2}{B_2} + \frac{\Delta X_3}{B_3} \quad (16)$$

$$B_T = \frac{\Delta X_T}{\Delta X_1/B_1 + \Delta X_2/B_2 + \Delta X_3/B_3} \quad (17)$$

If all the permeabilities are independent of concentration, then Eq. (17) can be used to calculate the permeability constant for any multilayer material. Knowledge of the individual thickness and permeabilities is needed, of course. In some situations, Eq. (17) is not useful. We have already encountered such a situation in Table 12.13. Films or papers with a high permeability are often coated with resistant coatings. Usually the permeability of such coated materials cannot be readily calculated using Eq. (17). This is because the permeability constant for coatings is often a function of coating thickness. Furthermore, coated materials often have permeabilities which vary with water vapor concentration. Calculation of water-vapor fluxes through such composite materials, however, can be achieved using slightly more sophisticated mathematical techniques (Karel et al., 1971).

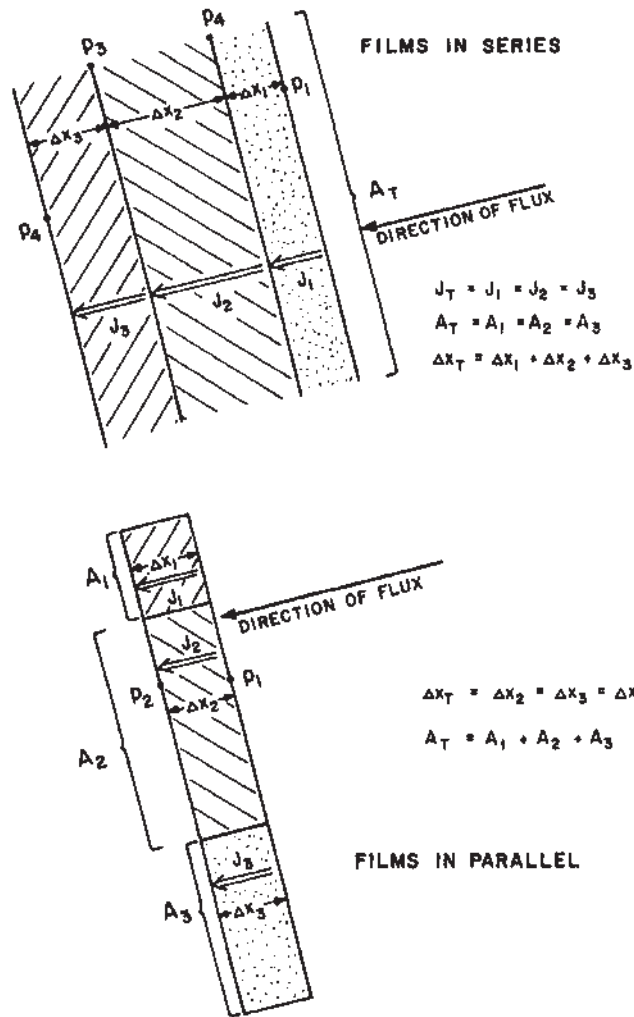


FIGURE 12.21 Schematic representation of permeation through several materials in series and in parallel.

The above relations for films in series hold only for flat membranes. When cylinders, spheres, or other shapes are considered one must consider changes in cross-sectional area for flow. Under these conditions one uses approximations or exact solutions of the type we have considered for flow of heat in paths with changing cross-sectional area (mean transfer areas).

When several materials are arranged in parallel the following equations hold given equal thicknesses (Fig. 12.21):

$$J_T = J_1 + J_2 + J_3 \quad (18)$$

$$B_T A_T = B_1 A_1 + B_2 A_2 + B_n A_n \quad (19)$$

$$B_T = \frac{\sum B_i A_i}{A_T} \quad (20)$$

Composite films made of two or more materials with significantly different permeability show a more complicated behavior when neither of the two geometric arrangements discussed above (parallel or in series) describes the situation. Figure 12.22 presents schematically the permeation paths in a situation in which a film contains “obstacles,” that is, inclusions, which have a much lower permeability than the continuous phase of the film. The figure compares the situation with films in series.

The inclusion of fillers is widely practiced in development of effective barriers. Bissot (1990) reported the use of fine mica platelets inside an EvOH film, which increased the resistance to oxygen permeation by a factor of 3. This corresponds to the schematic representation in Fig. 12.22b.

The inclusion of barriers in dispersed form is also one of the methods of producing composite barriers of hydrophilic polymers and lipids. This may be accomplished by producing layers of the two components, or by preparing the barrier from an emulsion in which case the lipid exists in the composite barrier in the form of droplets or deformed droplets as shown in Fig. 12.22a. It is probably

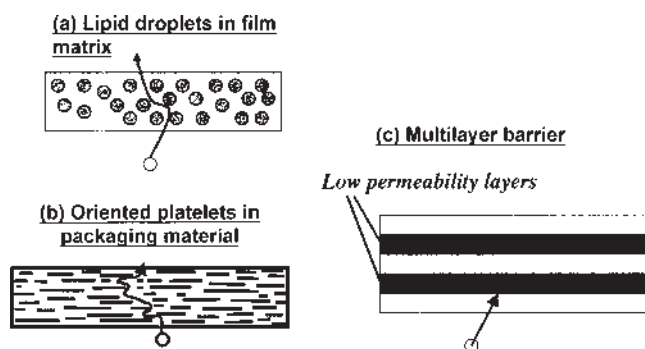


FIGURE 12.22 Schematic representation of permeation paths in the presence of obstacles.

obvious from inspection of the droplet obstacle paths compared to the multilayer situation shown in Fig. 12.22c that the layers in series are more effective. Debeaufort et al. (1993) and Gontard et al. (1994) compared the effectiveness as water vapor barriers of bilayers and emulsion-generated films for two edible hydrophilic polymer plus wax systems. When wax was used to form a bilayer, the permeability of gluten films to water was reduced by a factor of 200; but when a wax emulsion was used to obtain a gluten–wax barrier system, the permeability was reduced only by a factor of 5. In the case of similar methyl cellulose–wax systems the bilayer system was 30 times more effective than the emulsion system.

Many mathematical models have been proposed for describing the permeability of the obstacle systems. The permeability reduction is due to at least two factors:

1. Increase in path length for the diffusing molecules, which depends on the volume fraction of the obstacles, and on tortuosity of the path, which is a strong function of the shape of the obstacles.
2. Changes in the structure of the continuous phase due to the presence of the inclusions. This is particularly important in swellable polymers which where the inclusions may impede swelling and the resulting increase in permeability.

A model proposed by Michaels and Bixler for semicrystalline polymers is shown in Fig. 12.23. In this model the crystalline polymer region are the obstacles and are assumed to have D and S values of zero. The diffusion coefficient is considered to be inversely proportional to tortuosity, and to the chain immobilization factor β , and directly proportional to the amorphous volume fraction (Michaels et al., 1963; Weinkauff and Paul, 1990). Similar models would be applicable to other bi-phasic barrier systems.

7. Flow-Through Pinholes, Cracks, and Seal Imperfections (Convective Flow)

In cases where pores or pinholes provide the major means of transport, molecular interactions between the packaging material and the gas or vapor become unimportant and the flow depends on properties of the gas and on size and shape of the pores. Depending on the total pressure at which the transport occurs we can have: (1) molecular diffusion, (2) laminar flow, (3) slip flow, or (4) surface flow.

The flow of gases through fine pores and capillaries occurs by one of these four regimes. *Molecular flow* occurs at very low pressures when intermolecular collisions are relatively infrequent and the flow is affected mainly by molecules colliding with walls of the capillaries. *Laminar flow* occurs when pressure is sufficiently high so that intermolecular collisions predominate. *Slip flow* occurs at pressures intermediate between the two extremes. *Surface flow* occurs when

$$D = D_A / (\tau \beta)$$

$$S = S_A V_A$$

$$B = S D = S_A D_A V_A^2 / (\xi \beta)$$

D = diffusion coefficient in the semicrystalline polymer
 D_A = diffusion coefficient in amorphous polymer
 V_A = volume fraction of amorphous polymer
 S = solubility of diffusant
 β = chain immobilization factor
 ξ = tortuosity
 τ = geometric impedance factor = ξ / V_A
 B = permeability

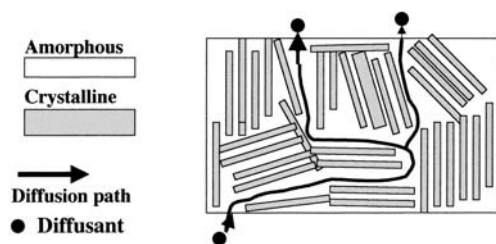


FIGURE 12.23 Permeability in semicrystalline polymers (model of Michaels and Bixler).

molecules adsorbed onto the surface of the walls of the capillaries can migrate from one localized adsorption site to another.

For the present purposes it is sufficient to characterize any material in terms of an overall convective flow constant, β

$$J = \beta A \frac{dp}{dx} \quad (21)$$

where β has the same dimensions as B . The major differences between behavior of β and B are as follows.

a. Effect of Different Packaging Materials. B depends primarily on molecular structure of the packaging material, β on pore size distribution. Hence a paper sieve and one made of a metal give similar values of β when their pore sizes are similar.

b. Effect of Gas Properties. The important properties of a gas in activated diffusion are molecular size and solubility in the polymer. In convective flow the important properties are molecular size and viscosity. As a consequence, B usually varies as follows:

$$\text{CO}_2 > \text{O}_2 > \text{N}_2$$

On the other hand β for different gases varies only slightly and larger molecules tend to permeate less readily. Yam and Lee (1995) reported a permeability ratio for $\text{CO}_2:\text{O}_2$ equal to 1.0 for microporous films and to 0.8 for perforated films, (microporous films have very small perforations).

c. Effect of Total Pressure. Total pressure as well as total pressure difference have a very significant effect on β since they determine which of the several flow regimes is controlling. B on the other hand, is ideally completely independent of total pressure.

d. Effect of Temperature. There is a drastic difference in the effects of temperature on B and β . Gas viscosity increases with increasing temperature, hence one of the factors controlling β causes a decrease in β as temperature increases. On the other hand, B is a product of D and S , both of which increase exponentially with temperature. In general, therefore, B increases rapidly with increasing T but β either increases slightly, stays constant, or actually decreases (depending on packaging material, pore size distribution, and pressure).

For most packaging materials there is also a large difference in magnitude of the fluxes involved. A pinhole in a metal can or an imperfection in the seal of a saran pouch usually transmits gas orders of magnitude faster than the intact surface of these containers.

C. Temperature Control by Packaging

Packaging affects the rate of heat transfer to and from the enclosed food products. The heat transfer may take place by conduction, convection, or radiation and is accordingly affected by the packaging material thickness and thermal conductivity, its porosity, and its reflectivity. These properties collectively determine the insulating value of the package.

The temperature rise in refrigerated food products exposed for a short period of time to elevated temperatures can be greatly retarded by the use of insulating containers.

The insulating properties of packages are of even greater importance in the handling and distribution of frozen foods. Thawing rates of frozen food depend on the type of container. Single containers of food defrost more rapidly than containers packaged in shipping cases. Other packaging factors of importance are size of package and location to the transporting vehicle.

An interesting problem in insulative packaging is the control of temperature changes in food packages placed in refrigerated display cabinets. In this instance, most of the cooling takes place by conduction and convection, while simultaneously there is heat input by radiation from fluorescent lamps used for lighting. Under these conditions the high reflectivity and high conductivity of aluminum foil offers advantages, particularly with such products as ice cream.

D. Control of Biological Attack by Packaging

1. Microorganisms

The protection of package content from attack by microorganisms depends on mechanical integrity of the package (absence of breaks and seal imperfections) and on resistance of the package to penetration by microorganisms. Mechanical integrity is treated in Sec. IV.E.

Extensive studies on a variety of plastic films and metal sheets have shown that microorganisms, including molds, yeast, and bacteria cannot penetrate these sheets in the absence of pinholes. However, in practice, thin sheets of packaging materials, including aluminum foil and plastic, do contain pinholes. Fortunately there are several safeguards against the passage of microorganisms through pinholes in films:

1. Because of surface tension effects, microorganisms cannot pass through very small pinholes unless the microorganisms are suspended in solutions containing wetting agents and the pressure outside the package is greater than within.
2. Materials of packaging are generally used in thicknesses such that pinholes are very infrequent and small.
3. For applications in which package integrity is essential (such as sterilization of food in pouches) adequate test methods are available to assure freedom from bacterial recontamination.

The potential for growth of microorganisms, in particular molds, on package surfaces is greatest when the surfaces are subjected to very high humidities. Under tropical conditions this danger becomes very significant and may require the treatment of package surfaces with antimicrobial agents.

Under more moderate conditions packages remain free of mold growth without such measures provided recommended practices with respect to sanitation and housekeeping are followed.

2. Resistance to Insect Infestation

In order to avoid insect infestation one must assure that the package contents are free of viable insect eggs or larvae, and that the package cannot be penetrated from the outside by adults or larvae. (Eggs and pupae of insects obviously have no penetration power of their own but can penetrate by virtue of gross contamination with dust and soil.) In storage and distribution the most desirable condition is one in which the environment external to the packages (truck interiors, warehouses, railroad cars) is insect free. Such conditions are not always possible and the package is expected to provide a defense against insect penetration. The following are some of the decisive factors in such a defense:

a. Condition of Package Surface. Highly polished and slippery surfaces, free of debris and dust, are most desirable. In order to bore into the package the insects require a “foothold” on the surface. It is believed that wax-dipped packages used in World War II to distribute rations in insect-infected areas were effective partly because of surface conditioning rather than because of increased package barrier properties.

b. Resistance to Emission of Odors. Insects do not read labels; they rely on chemical senses in their quest for food. A perfect odor barrier combined with cleanliness of surfaces helps avoid insect attack.

c. Paper Package Construction. Packaging materials that are resistant to insect penetration and have well-formed seals and closures aid greatly in assuring protection.

d. Use of Repellants. The surfaces of packaging materials can be further protected against insect attack by incorporation of insect repellants. In such cases it is essential to assure that these chemicals do not enter the food supply in levels presenting potential health or esthetic problems. Various chemicals have been proposed for this purpose, including pyrethrin, malathion, DDT, and Lindane, and these can be applied in waxes, coatings, or surface sprays. A particularly suitable method of application appears to be to incorporate such coatings in multiwall packages, since under these conditions the danger of transfer of the chemicals to the food is minimized.

Different insects have different penetrating powers and also different sensitivities to various environmental conditions. Beetles and moths present most problems. Table 12.14 shows the main foods attacked and the environmental requirements of several insects attacking stored food products. Table 12.15 shows the ability of insects to penetrate different types of packaging materials.

E. Protection from Mechanical Damage

1. Strength of Packaging Materials

Maintenance of the integrity of the package depends first of all on the mechanical properties of the packaging materials. The strength of materials is a complicated matter and we present here only a generalized picture intended to acquaint the reader with fundamentals. There are different types of tests which are usually conducted on materials and they measure strength and deformability under various controlled conditions. Figure 12.24 shows schematically how force is applied to sheets of materials in five such tests: tensile, compression, impact, tear, and bursting strength. In all five tests one measures the force (or energy) required to achieve the specific failure. The tensile test is capable of providing additional information about the mechanical properties of the material tested, i.e., tensile

TABLE 12.14 Characteristics of Some Insects Attacking Stored Food Products

| Insect name | | Main food attacked | Comments |
|--------------------------|---------------------------------|-----------------------------------|--|
| Common | Scientific | | |
| Confused flour beetle | <i>Tribolium confusum</i> | Cereals, flour, dried fruit | Optimum 20–30°C |
| Cadelle | <i>Tenebroides mauritanicus</i> | Grains, cereals | Very cold resistant, very penetrating |
| Mediterranean flour moth | <i>Ephestia kuhniella</i> | Most cereal products, dried fruit | |
| Lesser grain borer | <i>Rhyzopertha dominica</i> | Grain | Requires warm climate, optimum over 30°C |
| Yellow meal worm | <i>Tenebrio molitor</i> | Cereal products, meat scraps | Requires high humidity, prefers dampness |

strength, modulus of elasticity, maximum elongation, and resilience. Figure 12.25 show graphically what each of these represents in the stress vs strain diagram. Each test must be conducted under controlled conditions of temperature, material precondition, sample preparation, and rate of application of force (rate of loading).

Mechanical properties of some packaging materials as measured in such standardized tests are shown in Table 12.16. The significance of values obtained in such standardized tests to practical package performance must be assessed by packaging engineers in accordance with intended use. Tests of bursting strength are routinely performed on paperboards which are designed to contain heavy

TABLE 12.15 Penetration of Packages by Insects

| Material | Average number of weeks before penetration by a mixed population of insects |
|--------------------------------|---|
| Paper and jute bags | < 1 |
| Polyethylene | 3–4 |
| Mylar | 6–8 |
| Laminates of plastic and paper | 6–8 |
| Aluminum-containing laminates | > 12 |

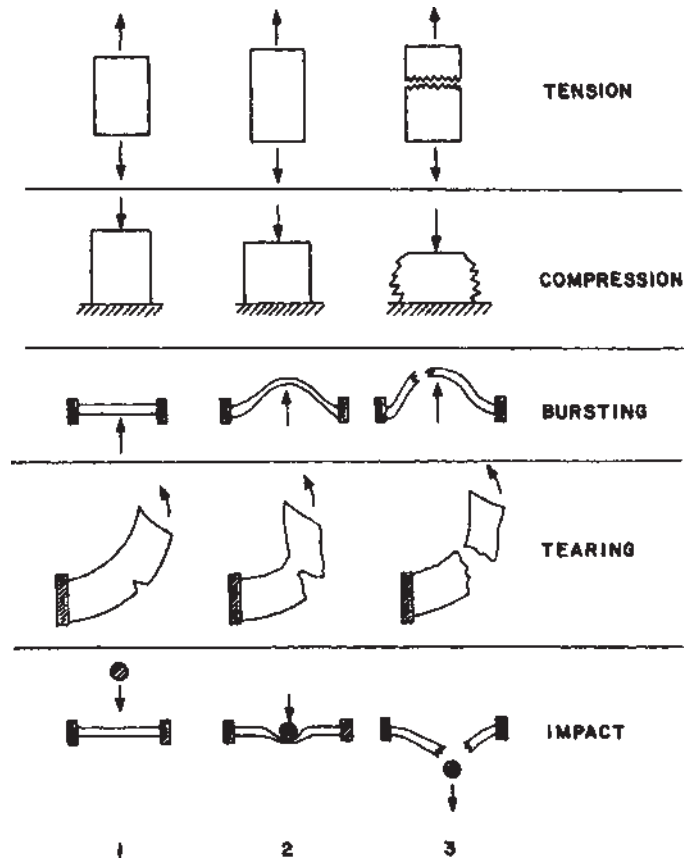


FIGURE 12.24 Schematic representation of forces applied to materials in tests of mechanical properties. Arrows represent direction of applied forces. Three states are shown: (1) material at beginning of test, (2) deformation due to applied forces, (3) failure of material.

loads. High tensile strength is clearly required for applications in which tension exists in the plane of the package wall, e.g., in shopping bags.

Additional specialized tests can be performed. Among these are folding endurance for carton materials, puncture resistance, abrasion resistance, and wet strength. In many situations, however, results of mechanical tests on packaging materials are difficult to relate to package performance and additional tests on completed containers, with or without contents, may be necessary. It may also be necessary to conduct accelerated aging tests to determine whether mechanical strength of the materials changes during storage in a given environment.

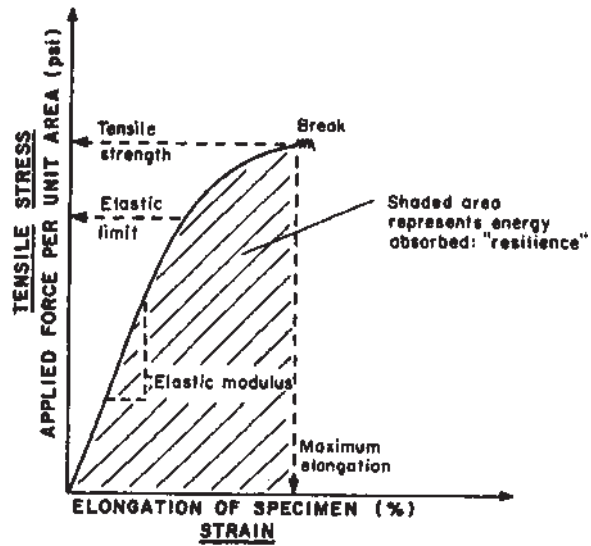


FIGURE 12.25 Stress-strain diagram for a hypothetical material.

TABLE 12.16 Mechanical Properties of Selected Packaging Materials^a

| Material | Tensile strength (Pa × 10 ⁻⁷) | Elongation (%) |
|-------------------------------|--|--------------------|
| Cellophanes | 5 | 5-50 |
| Cellulose acetate | 5 | 5-50 |
| Polyethylene (LD) | 15 | 100-800 |
| Mylar | 15 | 40-100 |
| Saran | 4 | 20-150 |
| Aluminum foil | 50 | 20-50 ^a |
| Packaging papers ^b | 50 | 2-50 |
| Aluminum-plastic laminations | 100 | 10-40 |
| Steel foil | 300 | 1-15 |

^a Depends strongly on temperature.

^b Depends strongly on additives to paper and on relative humidity.

“Wet” strength of paper and paperboard is particularly important, since cellulose-based materials tend to have a much reduced strength when they are plasticized by water. Organic plasticizers have similar effects on nonpolar polymers and are often added to increase flexibility, provided the associated decrease in ultimate strength is not detrimental.

2. Tests on Packages to Determine Adequacy of Mechanical Strength and Integrity

These test procedures vary with the container and the intended use.

Metal cans are used often for sterilized foods and require testing to assure absence of leaks. Freedom from pinholes is tested for by manufacturers, before lids are sealed on, by applying overpressure. Correct sealing procedures for lids are checked by the processors. Processors also conduct checks on sealed cans containing no products or on cans from which the product has been removed. This test is usually done by attaching a tube to the side of the can away from the seam, submerging the can in water, and applying gas pressure through the tube. Rising gas bubbles are indicative of a leak. Similar internal pressures also can be generated by sealing in the can an amount of dry ice (solid CO_2) calculated to give the desired test pressure (1.5–2 atm) upon sublimation.

In addition, it is possible to check for inadequate vacuum (whether due to leaks, poor gas exhaustion, or microbial growth) by checking the sound made when the lid is tapped or by any mechanical or optical method capable of detecting the deviation of the can lid from the shape assumed when the can is sealed under proper vacuum. Some of these methods can be used effectively and automatically for 100% inspection on the line. Internal pressure of a can can be readily and nondestructively measured by any of several contact gages which depend on measuring can lid deflection when vacuum is applied to the top surface of the can lid.

Glass containers require close control of such dimensions as height and mouth diameter because of demands of automatic filling and capping equipment. Another test conducted routinely on the line is that for resistance to temperature fluctuations. This done by subjecting glass containers to temperature drops under controlled conditions. Because glass strength is extremely dependent on surface conditions of the container, visual inspection of the surface is an important part of testing. Some manufacturers also routinely test glass containers for resistance to internal pressure and compression.

Plastic pouches and laminated pouches require tests on strength and integrity of heat seals. Tests similar to tensile strength tests on flat sheets can be

used to measure strength of heat seals, and the internal pressure tests mentioned above for cans can also be applied to pouches.

Shipping containers and other containers undergoing hazards of mechanical shocks during distribution should be subjected to tests simulating such mechanical abuses. Two major types of test are usually employed: (1) impact tests and (2) compression tests. Impact tests usually take the form of drop tests of various types. Drop-testing equipment has been designed to simulate various types of hazards in shipping. Compression tests also simulate shipping hazards as well as the behavior of containers stacked or palletized in warehouses.

3. Cushioning

Cushioning means protecting the product from shock. Mechanical shock is usually caused by rapid deceleration, a quantity usually measured in multiples of gravitational acceleration, g , and the sensitivity of articles to mechanical shocks is called the G factor. Thus an item with a G factor of 5 means that it will withstand deceleration five times greater than g , or $5 \times 32 \text{ ft/s}^2$. Cushioning acts by damping the shock imparted to the articles which are in the package. A simple model of this action is shown in Fig. 12.26, which considers the cushion as a compressible spring that on impact temporarily absorbs energy which otherwise can be imparted to the product over a short period of time with potentially damaging effects. Pertinent characteristics of the cushioning materials are indicated in Fig. 12.27. The packaged articles undergo maximum deceleration at the time the cushion is compressed to the "stopping distance," and this maximum deceleration is defined as follows:

$$\text{Maximum deceleration} = \frac{\text{energy absorbed by cushioning}}{\text{stopping distance} \times \text{mass of product}}$$

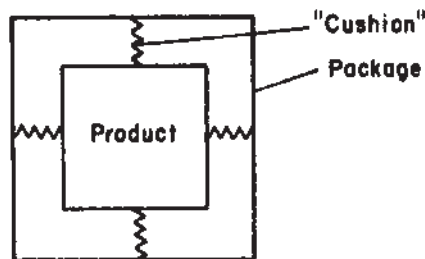


FIGURE 12.26 Schematic representation of cushioning of packaged foods.

Cushioning design, however, is complicated by the differences in load absorption characteristics of different materials. These characteristics are shown schematically in Fig. 12.28, from which it is evident that cushion response is often time dependent. Thus, two cushioning materials with the same load-compression curves under static loads applied relatively slowly may have different responses in dynamic testing in which the vibrations or shocks are applied very rapidly.

Most of the work on cushioning of packaged articles has been done on nonfood items, such as electronic components. This kind of information is applicable to some items that are brittle, such as eggs, freeze-dried foods, and some bakery items (biscuits and cookies). In freeze-dried foods the amount of damage is often measured in terms of total weight of "fines." The amount of fines can be reduced in such products by packaging them in skin-tight pouches, which are then spot glued to the interior of paperboard cartons. The skin-tight pouch prevents piece-to-piece impacts and the carton minimizes the effect of impacts from outside.

Other types of foods have their own internal cushioning (mainly water-swollen tissues, such as fresh meats or fruit; fatty tissues; or air entrapping structures, such as in lettuce or broccoli), and in these instances the problem is not with breakage but with surface bruising. The analysis of damage sensitivity in such items is usually done on a statistical basis, from consideration of total bruise area or similar quality defects.

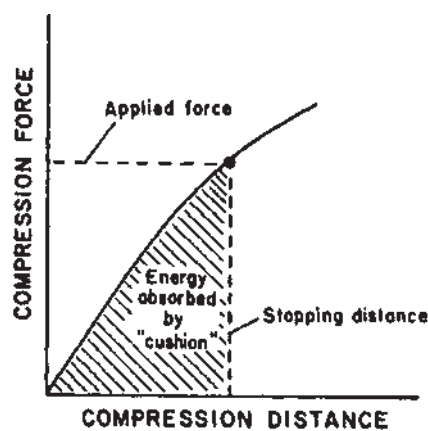


FIGURE 12.27 Schematic representation of properties of a hypothetical cushioning material.

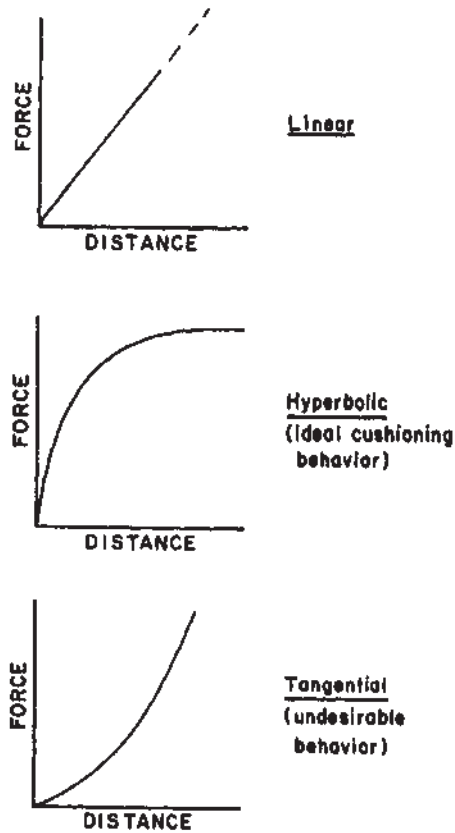


FIGURE 12.28 Mechanical behavior of three types of cushioning materials.

V. CALCULATION OF SHELF LIFE AND REQUIREMENTS FOR PACKAGING

A. General Approach

Given the great complexity of factors involved in package-product interactions, the choice of proper packaging methods for a given product and the prediction of effectiveness of a given packaging system have been determined either by extended storage tests or by judicious guessing. This approach, however, has substantial economic penalties and severely limits freedom of choice, resulting usually in overpackaging. This is not only wasteful but severely impedes the development of entirely new packaging concepts which are currently needed to reduce problems of environmental pollution.

Recently it has become possible to apply knowledge of mechanisms of nutrient degradation to predict shelf life of a particular food–package combination or, conversely, to determine protective packaging requirements for a given food if the needed shelf life is known. These techniques are based on kinetic parameters of reactions causing deterioration of foods and on mass-transfer properties of the packaging materials. Analytical or numerical solutions useful for predicting the desired quantities can be obtained either with or without computer assistance.

The work on prediction of storage life as a function of efficiency of packaging measures and of environmental storage conditions was initiated on a large scale following World War II. Initial work was stymied by the complexity of the factors involved in this problem. The general opinion often voiced was that the complexity of these factors precluded laboratory prediction of shelf life. Initial laboratory evaluation of packaging problems can, however, greatly simplify the overall task of eliminating obvious failures and pinpointing likely successes. Such an evaluation should answer the following questions.

1. What are the optimal conditions for storage of the particular food product in terms of the important environmental factors?
2. What are the external environmental conditions to which the package is likely to be exposed?
3. What barrier properties are required in order to maintain an optimal internal environment?

In a series of studies reviewed by Karel (1983), an approach was taken based on the following five assumptions (Fig. 12.2):

First, properties of food which determine quality, \bar{F} , depend on the initial condition of the food, \bar{F}_0 , and on reactions which change these properties with time t . These reactions, in turn, depend on the internal environment of the package I .

It is assumed that deteriorative mechanisms limiting shelf life and their dependence on environmental parameters (oxygen pressure, water activity, temperature) can be described by a mathematical, although not necessarily analytical, function. As an example consider Eq. (22), which describes a deterioration dependent on the three above-mentioned parameters.

$$\frac{d\bar{D}}{dt} = f(\text{RH}, PO_2, T) \quad (22)$$

where

\bar{D} is the deteriorative index.

t is time.

RH is equilibrium relative humidity.

PO_2 is oxygen pressure.

T is temperature.

Second, maximum acceptable deterioration level \bar{D}_{\max} can be determined by correlating objective tests of deterioration with organoleptic or toxicological parameters.

Third, the internal environment, I , depends on the conditions of the food, F ; on package properties, B ; and on external environment, EO. It is assumed that changes in environmental parameters can be related to food and package properties. For instance,

$$a = f(a_0, t, \text{RH}, k_1, \dots, k_n, T, \dots) \quad (23)$$

where a is water activity in the food at any time, a_0 is initial a , and k_1, \dots, k_n are constants characterizing sorptive and diffusional properties of the food and package.

Fourth, barrier properties of the package can in turn be related to internal and external environments (I and EO).

Fifth, the various equations can be combined and solved with or without the aid of a digital computer. The solutions predict storage life or required package properties for a given storage.

B. Analysis of Storage Requirement of Moisture-Sensitive Foods

Many of the reactions which cause quality deterioration depend on moisture content. As mentioned in Chapter 5, we can distinguish two types of dependence: (1) those reactions for which a definite critical moisture content exists and below which the rate of spoilage is insignificant and (2) reactions that proceed at all moisture contents, at rates which depend strongly on moisture content. The prediction of moisture protection required for the first case (that of a single critical moisture content) is relatively easy if some simplifying assumptions are accepted.

1. Moisture Increase in a Simplified Situation

Consider, for instance, the case of a product requiring a shelf life of t_c and in which the water activity should never exceed 0.7. Let us assume that the average storage conditions are 90°F and 85% RH, and that the sorption isotherm of the food is linear as represented by Eq. (24)

$$m = \sigma a \quad (24)$$

where m is moisture content (g H₂O/g solids), a is water activity, and, σ is a constant.

Since $a = p/P^\circ$ (where P° is vapor pressure of water at 90°F), we have

$$p = \frac{m}{\sigma} P^\circ \quad (25)$$

Since $RH = (p/P^\circ)100$, we also have

$$P_{\text{outside}} = 0.85P^\circ$$

The increase in moisture content (m) of the food in the package is equal to the amount of water diffusing in, divided by the weight of solids (assuming no internal resistance to diffusion in the food) and is given by

$$\frac{dm}{dt} = \frac{bA}{\Delta X s} (0.85P^\circ - p) \quad (26)$$

where

t is time (days).

b is permeability ($\text{g mil m}^{-2} \text{ day}^{-1} \text{ torr}^{-1}$).

ΔX is thickness of the packaging material (mil).

A is package area (m^2).

s is weight of solids (g).

$0.85P^\circ$ is the constant partial pressure of water outside the package.

Combining Eqs. (26) and (25)

$$\frac{dm}{dt} = \frac{bAP^\circ}{\Delta X s \sigma} (m_e - m) \quad (27)$$

where m_e is the moisture content in equilibrium with outside RH, in our case, $= 85\sigma/100$. Integrating, we obtain

$$\ln \frac{m_e - m_i}{m_e - m_c} = \frac{bAP^\circ}{\Delta X s \sigma} t_c \quad (28)$$

where m_i is initial moisture and $m_c = 0.7\sigma$. We can now calculate the required permeability:

$$b = \left(\ln \frac{m_e - m_i}{m_e - m_c} \right) \frac{\Delta X s \sigma}{AP^\circ t_c} \quad (29)$$

2. Loss of Vitamin C During In-Package Desiccation

Another situation in which it is relatively easy to determine package requirements is one in which a deteriorative reaction depends only on moisture content and time. (Temperature is assumed to be constant at the expected average level.) In many cases, for instance, in dehydrated powders, vitamin C loss can be approximated by:

$$-\frac{dC}{dt} = km \quad (30)$$

where C is vitamin C content.

Let us now assume that the powder is placed in a hermetically closed can containing a package desiccant in order to achieve slow drying to the desired moisture content. A question that may be asked is what must be the minimum area of the internal package of desiccant to assure that no more than, say, 5% of the vitamin is lost before the moisture content is brought down to a very low level (when $m = 0.05$, assume that the rate of vitamin C loss is negligible). If we assume that the partial pressure of water at the desiccant surface is close to zero, we have $m_e = 0$ and the loss of water from the food is given by

$$-\frac{dm}{dt} = \frac{-AbP^\circ}{\sigma\Delta X_s} m \quad (31)$$

Combining Eqs. (31) and (30), we obtain

$$-\frac{dm}{dt} = \frac{-AbP^\circ}{\sigma\Delta X_s k} \frac{dC}{dt} \quad (32)$$

Hence, in this very simple case, loss of the vitamin is proportional to loss of water, and the required area for our specific example is given by

$$A = \frac{(m_i - 0.05)(\sigma\Delta X_s k)}{bP^\circ(C_i - 0.95C_i)} \quad (33)$$

where C_i is the initial vitamin C content.

3. Nonenzymatic Browning in a Dehydrated Product

A more complicated but very common situation is one in which a dehydrated product is limited in shelf life by nonenzymatic browning, but neither the isotherm nor the dependence of reaction rate on moisture are linear. Such a situation was analyzed by Mizrahi et al. (1970), using dehydrated cabbage as an example. In this product, at 37°C, the isotherm is expressed by

$$a = \frac{k_1 + m}{k_2 + m} \quad (34)$$

The rate of browning related to moisture content is expressed in

$$\bar{D}' = \frac{d\bar{D}}{dt} = k_3 \left[1 + \sin\left(\frac{-\pi}{2} + \frac{m\pi}{k_4}\right) \right]^{k_5} \quad (35)$$

where \bar{D}' is the rate of browning, \bar{D} is the extent of browning, and k_3, k_4, k_5 are constants.

It was found, furthermore, that the cabbage did not offer important internal resistance to equilibration with infiltrating water and that browning did result in production of additional water through chemical reactions in the product.

The information was then combined with the already familiar permeability equation, and a computer was used to calculate the moisture changes and extent of browning with time. Figure 12.29 shows a simplified iteration scheme. (We shall ignore the water generated by the chemical reaction itself.) In Fig. 12.29 and in our discussion the subscripts 0, t , and $t + \Delta t$ refer, respectively, to zero time and to time at the beginning and end of a time interval Δt . The iteration is as follows:

1. Rate of browning (\bar{D}') at the beginning of the time interval is determined by Eq. (35) and the increase in browning $\Delta\bar{D}$ is added to obtain $\bar{D}_{t+\Delta t}$.
2. The water activity, a , of the food is calculated for the beginning of Δt .
3. The amount of moisture increase due to permeation into the package is calculated using

$$\Delta m = K(a_{\text{out}} - a) \Delta t \tag{36}$$

where a_{out} is the water activity outside the package and

$$k = \frac{bAP^0}{(\Delta X)(s)} \tag{37}$$

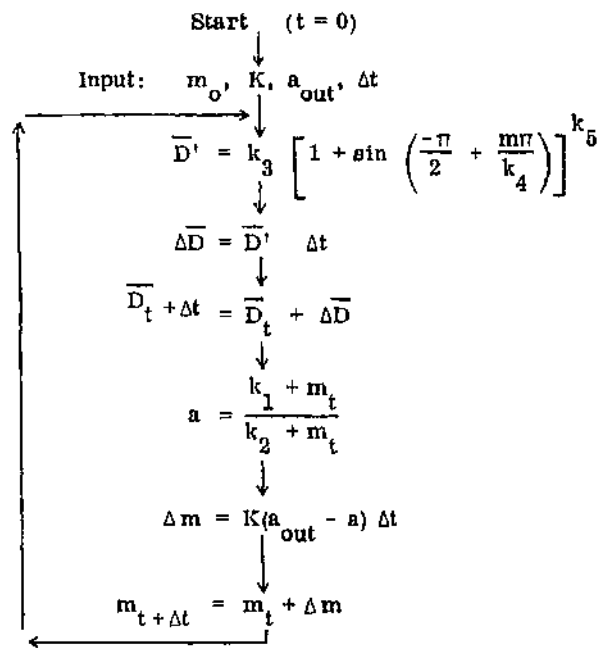


FIGURE 12.29 Iteration procedure.

The process is then repeated to calculate changes occurring in the next time interval.

Predicted values of the increase of moisture content due to permeation, and the predicted extent of browning for samples packaged in two types of materials studied by Mizrahi et al. (1970) are presented in Figs. 12.30 and 12.31. The estimated uncertainties of the calculations are expressed as 2 times the standard deviation and are shown as broken lines. The actual increases in moisture content, obtained by weighing the samples during storage, are scattered around the predicted values with maximum deviation less than 3%. In the case of the extent of browning, the deviations between actual and predicted values are less than 10%.

C. Accelerated Storage Stability Testing

Accelerated tests are necessary for development of valid storage life predictions within a reasonable time span. Acceleration is usually achieved by conducting

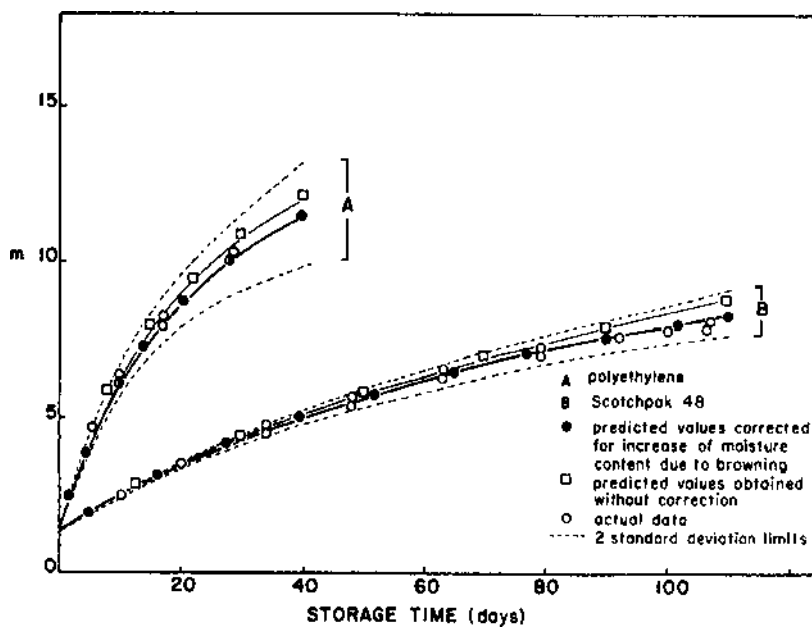


FIGURE 12.30 Predicted and observed increase in moisture content of dehydrated cabbage packaged in two types of packaging materials.

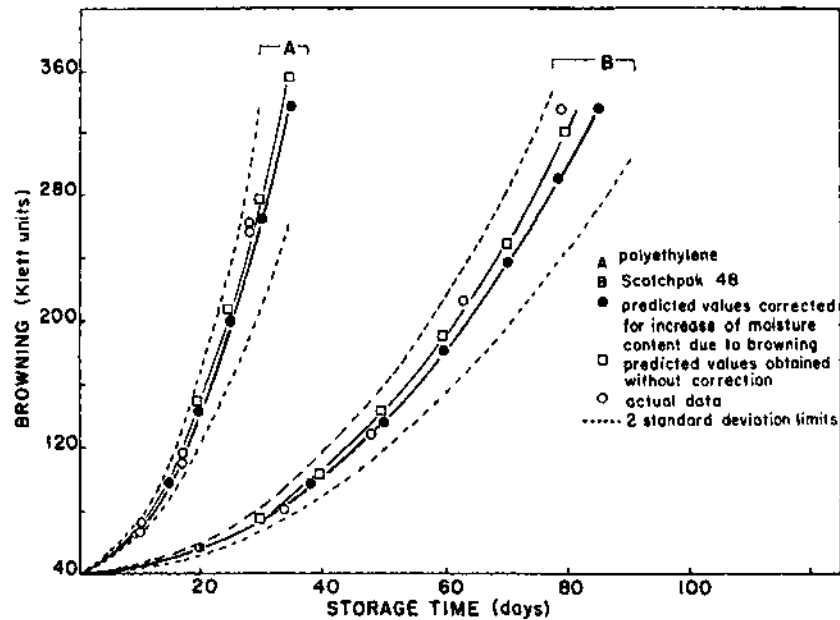


FIGURE 12.31 Predicted and observed browning of dehydrated cabbage packages in two types of packaging materials.

tests at an elevated temperature and using the Arrhenius equation, or similar temperature relations to extrapolate the data to the intended use conditions. In situations in which the stability is controlled primarily by transport of water vapor or of oxygen into the package the acceleration may also be achieved using transport-promoting conditions, provided their effect is known or predictable. These exaggerated transport conditions may include, in addition to elevated temperature increases in relative humidity of and/or increases in oxygen pressure. Accelerated tests may be static (that is conditions remain constant) or dynamic. In dynamic tests temperature is usually increased in a predictable manner (linear or logarithmic or sinusoidal) and the data are analyzed by suitable mathematical models (Labuza and Kamman, 1983; Carstensen and Rhodes, 1986; Davies and Budgett, 1980; Hempenstall, 1983; Irwin et al., 1983).

In most stability issues involving foods the stability is not determined solely by the properties of the package, it is a function of package and food properties, and their interactions. We have seen this situation in the examples shown in the preceding pages. A number of research groups have proposed and used methodologies facilitating accelerated prediction of shelf life. Among the early

researchers in this field were the scientists in Europe. This work was summarized by Heiss (1956). Subsequently the author's group at MIT has devoted a number of studies to this subject, and only a few of these can be mentioned here. An example of shelf life prediction for moisture-sensitive product was presented by Mizrahi et al. (1970), and a review of accelerated testing by Karel et al. (1971); Quast and Karel (1973). Specific problems considered included prediction of moisture transfer in isothermal storage, allowing extrapolation of data to any package-humidity combination (Mizrahi and Karel 1977a), and accelerated tests combining exaggerated moisture gain rates with elevated temperatures (Mizrahi and Karel, 1977b). The subject was treated extensively in a review by Karel (1983), Saguy and Karel (1980), Mizrahi and Karel (1978), and Villota et al. (1980). Various aspects of computer application to shelf life were discussed in the book edited by Saguy (1983).

The subject continues to be the subject of current work in many institutions. An analysis of mass transfer and sorption problems during storage of moisture sensitive foods was recently presented by Taoukis et al. (1987). A recently published book treats many aspects of accelerated testing in detail (Kilcast and Subramanian, 2000).

D. Packaging Requirements of Fresh Fruits and Vegetables

It is desirable to slow respiration rates of fruits and vegetables by lowering oxygen pressure, but the oxygen level must be sufficient to forestall significant anaerobic respiration. In Fig. 12.7 we have noted the relationship between respiration rate and oxygen pressure. The curve represents a function:

$$-\frac{dO_2}{dt} = f(p) \quad (38)$$

where p is partial pressure of oxygen in the package in atmospheres. The minus sign indicates that oxygen is being removed from the package atmosphere by the fruit. Simultaneously, however, oxygen is being supplied through the package wall, and the rate of input is also a function of p .

$$\frac{dO_2}{dt} = \frac{AB}{\Delta X} (0.21 - p) \quad (39)$$

If we set the two functions equal we can calculate the oxygen pressure at which the consumption and supply balance exactly (Fig. 12.32). As long as this pressure is above the critical lower limit of oxygen pressure, and the $RQ \approx 1$, the consumption of oxygen equals evolution of CO_2 and we can calculate the steady-state concentration of CO_2 as well. Figure 12.33 shows that such steady-state concentrations are rapidly attained in a polyethylene bag of apples. By using several materials in parallel it is also possible to independently control both O_2 and CO_2 in a package for considerable periods of time (until the natural aging

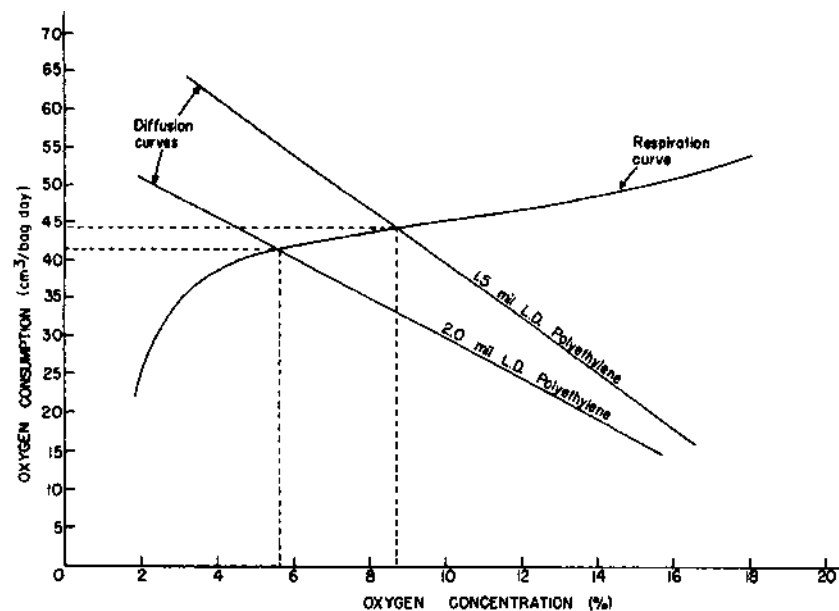


FIGURE 12.32 Graphical estimation of steady-state oxygen concentration in packages containing apples.

process of the fruit changes its response to the environment) (Veeraju and Karel, 1966). Control of gas exchange by semipermeable packages has practical value as well as theoretical interest.

The above relatively simple approach to predicting atmospheres inside packages of fruit was published by the group of Karel in the 1960s (Jurin and Karel, 1963; Karel and Go, 1964; Veeraju and Karel, 1966).

Since the publication of that work the concept of predicting the composition of atmospheres inside packages of respiring plant materials has been the subject of very many publications. Henig and Gilbert (1975) and Hayakawa et al. (1975) developed models for predicting the course of the transient phase of atmosphere adjustment within a package. Kader and his associates carried out very extensive investigations on theoretical and practical aspects of extending the shelf life of plant materials through controlled atmosphere packaging (Kader et al., 1989; Kader, 1986). An important prerequisite for developing predictive equations for atmospheric composition in packages is knowledge of rates of fruit or vegetable respiration as a function of temperature and of oxygen and carbon dioxide

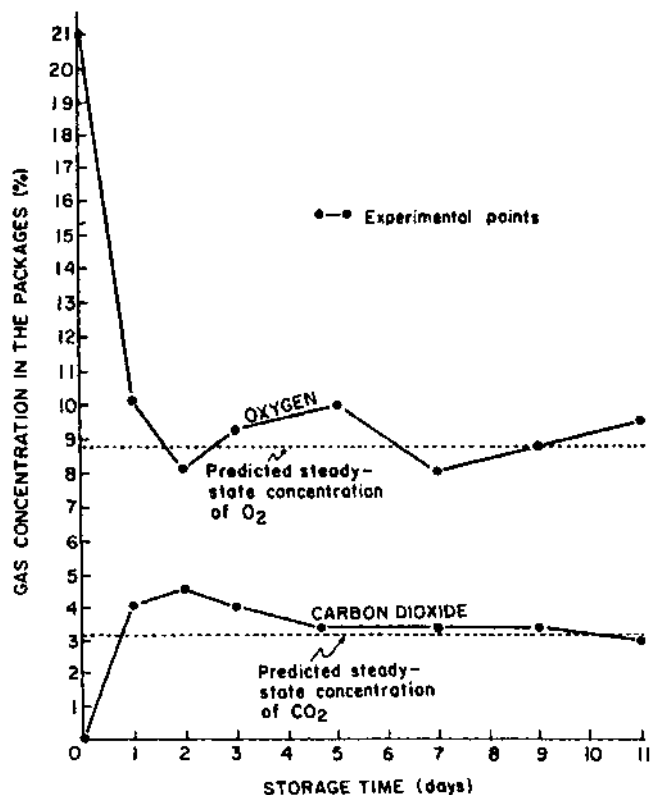


FIGURE 12.33 Predicted and observed gas concentrations in packages containing apples.

concentration. These variables have very substantial impact on the respiration rates (Fidler and North, 1967). It is also well known that the respiratory behavior varies greatly between different fruits and vegetables Robertson (1993) characterized vegetables on the basis of their respiratory rate (in $\text{mg CO}_2 \text{kg}^{-1} \text{h}^{-1}$ at 10°C). Onions, melon, cabbage, and tomato had rates below 20; asparagus lettuce, and spinach between 20 and 100; and broccoli, corn, and peas has extremely high rates, (>100).

Robertson (1993) based a similar classification of fruits using their rates of ethylene production. Among the fruits with low rates were citrus fruits, moderate rate was reported for bananas, and apples had a very high rate. Several papers were devoted to developing mathematical models for dependence of respiration rates on oxygen concentration, [stated in general form in Eq. (38)]. Most of these papers

found that the Michaelis–Menten model, well-known from enzyme kinetics:

$$R_o = \frac{V_m p_o}{K_m + p_o} \quad (40)$$

where

R_o = respiration rate.

V_m = maximum respiration rate.

p_o = partial pressure of oxygen.

K_m = Michaelis Menten constant.

The equation has the advantage of being able to describe the effect of carbon dioxide concentration by considering it as a respiratory inhibitor. Equation (40) can then be modified. The form of the modification depends on whether carbon dioxide is considered a competitive, uncompetitive or noncompetitive inhibitor (Laughlin and O'Beirne, 1999). These authors studied the respiration of dry coleslaw mix and obtained the best fit assuming an uncompetitive inhibition. This gave

$$R_o = \frac{V_m p_o}{K_m + p_o [1 + (p_c / K_i)]} \quad (41)$$

where p_c is partial pressure of carbon dioxide and K_i is inhibition constant. These authors modeled the temperature dependence using the Arrhenius equation with an activation energy for oxygen consumption rate of 75 kJ/mol.

The Michaelis–Menten equation was also used by Jaime et al. (2001). They assumed the rate of oxygen consumption to be independent of carbon dioxide concentration, and described the respiratory behavior of three varieties of cherries in the temperature range of 2 to 20°C. The values of the equation constants were different for the oxygen concentration intervals of 10–20% and for 2–10% and were different for the three temperatures studied (2, 5 and 20°C). The dependence of respiration rates on temperature followed the Arrhenius equation, with average activation energy of 83 kJ/mol. In a subsequent study the same group (Salvador et al., 2002) studied the gas exchange dynamics in packaged Burlat cherries and found that the Michaelis–Menten equation could be used satisfactorily together with data on gas permeability to predict atmosphere composition in packages of cherries, provided the oxygen concentration remained above 2%. They also assumed oxygen absorption to be independent of carbon dioxide concentration.

Makino (1999) published a paper reviewing respiration models for horticultural commodities. He constructed a model based on the Langmuir adsorption isotherm and incorporated in the model the inhibitory effect of carbon dioxide. He used transition state theory model to predict the effect of temperature. He found the model to describe well the respiratory behavior of a wide range of

horticultural commodities, including cabbage, lettuce, broccoli, tomatoes, blueberries and raspberries. The model combined with the standard permeation equations was effective in predicting changes in oxygen and carbon dioxide concentration in packages of shredded lettuce and of shredded cabbage. There were many other recent studies contributing to understanding of the fundamentals governing the control of modified atmosphere packaging (MAP). Only a few can be mentioned here. Skin resistance of the fruit is often a factor in control of gas transfer into fruit. Andrich et al. (1997) reported the temperature effects on this resistance in *Golden Delicious* apples. He found the activation energy for transport of carbon dioxide to be 15 kJ/mol. However the resistance to oxygen transport was independent of temperature in the range of 1 to 21°C.

The use of perforated packages for preventing excessive changes in atmospheric composition of packages for respiring produce have been an established practice in food packaging. The engineering analysis of the effect of perforations on changes in package atmospheres has been undertaken only in recent years. Among recent studies are those of Fishman et al. (1996) and Mannaperuna and Singh (1997).

E. Oxygen-Sensitive Foods

Another packaging problem is the exclusion of oxygen to protect foods containing unsaturated fatty acids. These foods undergo oxidative reactions at rates which depend on oxygen concentration in the package. As mentioned previously, among the oxygen-sensitive nutrients are several vitamins, all of the essential fatty acids, and many amino acid residues.

Past measurements of storage lives of foods deteriorating through oxidation have involved packaging the foods in materials with different permeabilities to oxygen and to water. The foods have been stored at various external conditions and tested periodically either for chemical deterioration, for organoleptic acceptability, or for nutritional value. Recently we have been able to improve this trial-and-error method significantly through the use of mathematical models and computers.

The most complicated storage problem studied so far is that of dehydrated foods, which deteriorate either because of absorption of water or because of oxidation. Shelf life is defined here as the time to reach a critical humidity (which corresponds to a maximum moisture content) or a critical extent of oxidation. If one of these limits is reached before the other, the product is overprotected with respect to the other. Since very impermeable materials are expensive, this overprotection is unnecessarily costly. Therefore, we have developed a computer program to calculate optimal permeabilities so that deterioration caused by water and oxygen reaches the critical point at the end of the desired shelf life (Quast and Karel, 1972).

The significance of optimal permeabilities is best illustrated by the example of a film laminate. If a single film has high oxygen permeability and low water permeability, it must be very thick to prevent oxygen transmission. However, the thickness and oxygen transmission can be greatly reduced if a second film with high water permeability and low oxygen permeability is laminated to the first film. This lamination can significantly reduce cost.

The changes in packaged potato chips during storage can be described by a system of three equations (Quast and Karel, 1972; 1973). When solved with a computer, these equations predict changes with time of (1) oxygen pressure within a package, (2) extent of oxidation expressed as amount of oxygen consumed per unit weight of product, and (3) equilibrium relative humidity. These variables are interrelated because rate of oxidation depends on oxygen pressure and on the equilibrium relative humidity in the package.

Optimization can be calculated for a specified set of conditions: (1) initial environment in the package, (2) weight of product, (3) storage conditions, (4) film area and (5) film thickness.

Mathematical methods for optimization are not simple because of the complex interrelationships among variables. A major advantage of computer simulation, however, is that it allows rapid assessment of the influence of changes in the product or package conditions, without the need of multiple storage studies.

We have mentioned the possibility of inclusion in the package of a desiccant to allow the in-package removal of water from food. This process is called in-package desiccation. An analogous system involves removal of oxygen within the package using "oxygen scavengers." Among the important systems are

1. Use of the enzyme glucose oxidase, along with the substrate glucose. The oxidation of glucose catalyzed by this enzyme removes oxygen from the package. This system is suitable only for situations in which substantial amounts of water are permissible in the container, since some water is required for enzyme activity.
2. For dehydrated foods a more suitable system is the catalyzed oxidation of hydrogen gas to water. The amount of water produced in removing oxygen is not significant. (Removal of oxygen from a 100 cm³ headspace consisting of air at 1 atm pressure produces only 40 mg of water.) The catalysts used for this purpose include palladium and platinum.

The American Can Company has developed a scavenger system incorporated in the packaging material itself, thus avoiding direct contact between the catalyst and the food. In this system the scavenger layer is present in a laminated packaging material separated from the inside of the package by a relatively permeable polyethylene layer. This allows the hydrogen and the oxygen to reach the catalyst system. Toward the outside there are several layers

of essentially impermeable materials, thus assuring that oxygen from the outside does not reach the scavenger. This system has been proposed for packaging dry whole milk, which is very oxygen sensitive.

VI. INTERACTION BETWEEN PRODUCT AND PACKAGE

A. Extraction of Packaging Material Components

Packages are made from many components having varying chemical and physical characteristics. Some of these components can react with the package contents. The toxicological consequences and potential hazards of such interactions have received a great deal of attention. The 1958 Food Additive Amendment specifically included in its definition of food additives substances which become a component of food or affect characteristics of food as a consequence of packaging. Passage of this amendment has stimulated research into food–package interactions. The problem is a complex and difficult one. Determination of the transfer of individual substances from package to food is difficult and regulations have been based on a less difficult procedure involving extraction of constituents of packaging materials into food-simulating solvents, including water, 3% aqueous NaCl, 3% aqueous NaHCO₃, 3% acetic acid, 3% lactic acid, 20% aqueous sucrose, and Lard or vegetable oil. Other countries use different food-stimulating solutions.

The problem of extracting packaging constituents into fatty substances is particularly difficult, because some components of packaging materials are difficult to differentiate from normal components of fatty foods.

Accordingly, fat-simulating solvents, such as heptane, are often used to test the inertness of packaging materials. An even more imposing problem is to correlate the type and amount of extractive with physiological effects in animals.

Concern about potential toxicity of various heavy metals has resulted in research on transfer of contaminants from various metallic containers to food.

Apart from safety considerations, the problem of acceleration of nutritive deterioration by package components has also received some recognition. This problem can be solved by the application of proper packaging methods.

In metal containers, application of inert coatings (enamels and lacquers) guards against reaction between food and package. When foods are unusually corrosive special coatings are required and these must be tested for effectiveness.

Glass has excellent inertness, and when inert liners are used for closures there is essentially no interaction between food and package. Most of the flexible packages also possess adequate inertness.

A related problem concerns penetration of the package by free oil from packaged food products. Free oil is defined as the lipid available for staining the package. Penetration of packaging materials by free oil sets up a focal point for

rancidity development that can affect the nutritional value of the packaged food. The importance of using greaseproof materials to control fat and oil penetration is obvious.

The effects of specific processing methods on the total package–food interaction must be considered. In the case of heat processing and radiation processing, FDA approval has been sought and obtained by the United States Army Natick Laboratory to utilize specific packages for specified foods.

A comprehensive review of food–package interaction was the subject of an ACS symposium (Hotchkiss, 1987).

B. Active Packaging

Recent years have seen a very significant research and development effort directed at development of active packaging for foods, usually defined as use of packaging materials, or package components which have an effect of foods by releasing or absorbing active ingredients, or by creating conditions at the package surfaces which enhance food stability, (Labuza, 1996; Rooney, 1995).

1. Moisture Control

One of the earliest and most widely used examples of such active systems is the use of desiccant inside packages to control the water content at very low level. The use of desiccants is widespread in pharmaceutical as well as food packaging. The desiccants may be used by being packaged in water-permeable sachets or incorporated in the packing films, in which case they are separated from the interior by a water-permeable layer. Major types of desiccants used are activated clays, silica gel and molecular sieves (zeolites).

2. Oxygen Scavenging

As mentioned previously in Sec. V.E, the inclusion in the package of systems scavenging oxygen may enhance greatly the stability of oxidation-sensitive foods. The following systems are among those studied:

1. Platinum catalyst within a film laminate plus hydrogen gas within the package
2. Enzymes oxidizing selected substrates (glucose oxidase, ethanol oxidase)
3. Iron within permeable sachets, often with additives such as ascorbic acid
4. Catechol
5. Reactive redox dyes plus ascorbic acid

Iron sachets have been used most widely, especially in Japanese markets, and Japanese companies produce most of the systems.

3. Carbon Dioxide Scavenging

CaOH has been used in sachets to absorb carbon dioxide evolved from roasted coffee.

4. Antimicrobial Active Packaging Components

Microbial deterioration may be retarded by the use of packaging structures (sachets, or package wall components) which release antimicrobial agents. Ethanol has been used for this purpose in Japan, where ethanol releasing agents in sachets are commercially available. In many situations food surfaces are the most susceptible portions of foods, and coatings made of edible films may be used. This may be achieved by incorporation of antimicrobial agents, in particular of acetic, propionic or sorbic acids. The effectiveness of these acids depends very strongly on pH and some work was directed toward control of both pH and of antimicrobial agents at the surface, through the use of appropriate coatings (Torres et al., 1985a,b; Torres and Karel, 1985; and Torres et al., 1989). More recent work included the use of chitosan as a coating. Chitosan has an antimicrobial effect on many microorganisms by itself, and it was found to inhibit growth of *Listeria monocytogenes* in model systems, and against *Listeria innocua* when used as a coating for cheese, (Coma et al., 2002). *Listeria* was also inhibited on surfaces of refrigerated, ready to eat chicken by zein coatings incorporating the antibiotic nisin, and/or calcium propionate (Janes et al., 2002). A review of antimicrobial packaging was recently provided by Han (2000).

5. Active Packaging to Remove Undesirable Components

Scavenging of oxygen, carbon dioxide and moisture have been mentioned previously. However, the active packaging systems are capable of absorption or reaction with many other components of package contents if they can be brought in contact with the active packaging components. Scavenging of volatile off flavors has been mentioned by Rooney (1995). Del Nobile et al. (2002) reported the use of an aldehyde scavenger film to absorb the oxidation product hexanal in food packages. Use of enzymes immobilized in packaging systems has been proposed for removal of undesirable compounds in liquid foods. Soares and Hotchkiss (1998) use the enzyme naringinase incorporated in cellulose acetate film to reduce the content of naringin, a bitter flavonoid, in grapefruit juice. They noted that the enzyme remained active in the film, and it was possible to hydrolyze 60% of the naringin in the juice in 15 days at 7°C, when the film area to juice volume ratio was 7.2 cm²/ml. Removal of lactose and of cholesterol by using lactase and cholesterol reductase enzymes in active package layers in fluid milk packages has been proposed by Brody and Budny (1995).

6. Controlled Release of Specific Compounds

Advances in the science and technology of controlled release in medical applications have resulted in creation of a potential for similar controlled release in food packages. Reviews of the subject were presented by Karel (1990) and Karel and Langer (1988).

SYMBOLS

| | |
|------------------|--|
| A | area |
| B | permeability |
| B_o | constant |
| B | barrier properties of package |
| C | vitamin content (mg/100 g) |
| D | diffusion coefficient (cm^2/s) |
| \bar{D} | deterioration extent (for instance; browning) of food |
| E_p | activation energy for permeability (kcal/mol) |
| EO | external environment |
| \bar{F} | food properties |
| F_o | initial food properties |
| I | internal environment |
| I_o | light intensity at package surface |
| I_i | light intensity at food surface |
| I_X | light intensity at distance X in food |
| I_{abs} | total light absorbed by food |
| K_m | Michaelis–Menten constant |
| J | flux of gas or vapor (mol/s) |
| P° | vapor pressure of water (torr) |
| PO_2 | oxygen pressure |
| R_o | respiration rate |
| R_p | fraction of light reflected by packaging material |
| R_f | fraction of light reflected by the food |
| R | gas constant |
| RH | relative humidity |
| S | solubility of gas in membrane ($\text{mol}/\text{cm}^3 \text{ atm}$) |
| T | absolute temperature |
| T_g | glass transition temperature |
| Tr_p | fraction of light transmitted by packaging material |
| V_m | maximum R_o |
| a | water activity |
| b | permeability to water vapor ($\text{g mil m}^{-2} \text{ day}^{-1} \text{ torr}^{-1}$) |
| c | concentration of gas in membrane (mol/cm^3) |

| | |
|-------------------|--|
| k_1, \dots, k_n | constants |
| m | moisture content (g H ₂ O/g solids) |
| p | partial pressure |
| s | weight of food solids (g) |
| t | time |

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