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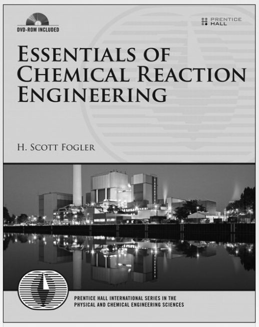

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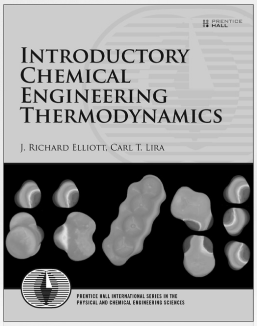

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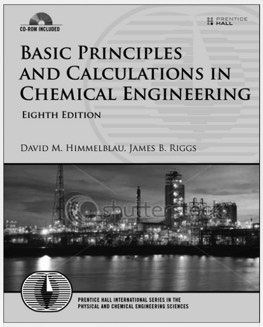

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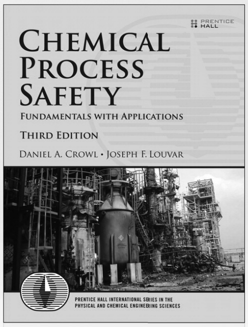

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J. Richard Elliott

Carl T. Lira

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PREFACE

> *"No happy phrase of ours is ever quite original with us; there is nothing of our own in it except some slight change born of our temperament, character, environment, teachings and associations."*
>
> *Mark Twain*

This textbook is designed for chemical engineering students from the sophomore level to the first year of graduate school. The approach blends molecular perspective with principles of thermodynamics to build intuitive reasoning regarding the behavior of species in chemical engineering processes and formulations. The molecular perspective is represented by descriptions encompassing: the relation of kinetic energy to temperature; the origin and consequences of intermolecular potentials; molecular acidity and basicity; methods used to incorporate molecular properties into molecular simulations; and the impact of molecular properties on macroscopic energy and entropy. This text is distinctive in making molecular perspectives accessible at the introductory level and connecting properties with practical implications.

This second edition offers enhanced coverage of biological, pharmaceutical, and electrolyte applications including osmotic pressure, solid solubility, and coupled reactions. Throughout the text, topics are organized to implement hierarchical instruction with increasing levels of detail. Content requiring deeper levels of theory is clearly delineated in separate sections and chapters. Less complex empirical model approaches have been moved forward to provide introductory practice with concepts and to provide motivation for understanding models more fully. The approach also provides more instructor flexibility in selecting topics to cover. Learning objectives have been clearly stated for each chapter along with chapter summaries including "important equations" to enhance student focus. Every chapter includes practice problems with complete solutions available online, as well as numerous homework problems. Online supplements include practice tests spanning many years, coursecasts describing difficult concepts or how to use computational tools, ConcepTests to quickly check comprehension, and objective lists that can be customized for greater detail. We also recommend the related resources available at the www.learncheme.com.

Unique features of the text include the level of pedagogical development of excess function models and electrolytes. For mixture models, the key assumptions and derivation steps are presented, stimulating readers to consider how the molecular phenomena are represented. For electrolytes and biological systems, the text makes connections between pH and speciation and provides tools for rapidly estimating concentrations of dissociated species. We emphasize speciation and problem solving in this introduction, instead of focusing on advanced theories of electrolyte activity. The material is written at an intermediate level to bridge students from the introductions in chemistry to the more complex models of electrolytes provided by process simulators.

We have created a number of homework problems with many variants, intending that different parts can be assigned to different classes or groups, not intending that each student work all parts.

NOTES TO STUDENTS

Thermodynamics is full of terminology and defined properties. Please note that the textbook provides a glossary and a summary of notation just before Unit I. Also consider the index a resource.

We consider the examples to be an integral part of the text, and we use them to illustrate important points. Examples are often cross-referenced and are therefore listed in the table of contents. We enclose important equations in boxes and we use special notation by equation numbers: (*) means that the equation assumes temperature-independent heat capacity; (ig) means the equation is limited to ideal gases. We include margin notes to highlight important concepts or supplemental information.

Computer programs facilitate the solutions to homework problems, but they should not be used to replace an understanding of the material. Computers are tools for calculating, not for thinking. To evaluate your understanding, we recommend that you know how to solve the problem by hand calculations. If you do not understand the formulas in the programs it is a good indication that you need to do more studying before using the program so that the structure of the program makes sense. It is also helpful to rework example problems from the text using the software.

ACKNOWLEDGMENTS

As the above quote from Mark Twain alludes, we are indebted to many others, from informal hallway conversations at meetings, to e-mail messages with suggestions and errata, to classroom testing. In many cases, we are merely the conveyors of others' suggestions. In particular, for the first edition, Dave Hart, Joan Brennecke, Mike Matthews, Bruce Poling, Ross Taylor, and Mark Thies worked with early versions of the text. We have benefited from classroom testing of the second edition by Margot Vigeant, Victor Vasquez, and Joan Brennecke. We have benefited from reviews by Keith Johnston, Ram Gupta, John O'Connell, Mike Greenfield (electrolytes), Andre Anderko (electrolytes), and Paul Mathias (electrolytes). We have adapted some example problems developed by John O'Connell at the NSF BioEMB Workshop, San Jose, CA, 2010. CTL would like to thank Ryoko Yamasaki for her work in typing many parts of the first edition manuscript and problem solutions. CTL also thanks family members Gail, Nicolas, and Adrienne for their patience, as many family sacrifices helped make this book possible. JRE thanks family members Guliz, Serra, and Eileen for their similar forbearance. We acknowledge Dan Friend and NIST, Boulder, for contributions to the steam tables and thermodynamic charts. Lastly, we acknowledge the influences of the many authors of previous thermodynamics texts. We hope we have done justice to this distinguished tradition, while simultaneously bringing deeper insight to a broader audience.

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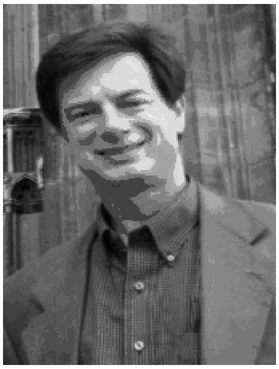

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GLOSSARY

Adiabatic—condition of zero heat interaction at system boundaries.

Association—description of complex formation where all molecules in the complex are of the same type.

Azeotrope—mixture which does not change composition upon vapor-liquid phase change.

Barotropy—the state of a fluid in which surfaces of constant density (or temperature) are coincident with surfaces of constant pressure.

Binodal—condition of binary phase equilibrium.

Dead state—a description of the state of the system when it is in equilibrium with the surroundings, and no work can be obtained by interactions with the surroundings.

Diathermal—heat conducting, and without thermal resistance, but impermeable to mass.

Efficiency—see *isentropic efficiency, thermal efficiency, thermodynamic efficiency.*

EOS—Equation of state.

Fugacity—characterizes the escaping tendency of a component, defined mathematically.

Heteroazeotrope—mixture that is not completely miscible in all proportions in the liquid phase and like an azeotrope cannot be separated by simple distillation. The heteroazeotropic vapor condenses to two liquid phases, each with a different composition than the vapor. Upon partial or total vaporization, the original vapor composition is reproduced.

Infinite dilution—description of a state where a component's composition approaches zero.

Irreversible—a process which generates entropy.

Isenthalpic—condition of constant enthalpy.

Isentropic—condition of constant entropy.

Isentropic efficiency—ratio characterizing actual work relative to ideal work for an isentropic process with the same inlet (or initial) state and the same outlet (or final) pressure. See also *thermodynamic efficiency, thermal efficiency.*

Isobaric—condition of constant pressure.

Isochore—condition of constant volume. See *isosteric*.

Isopiestic—constant or equal pressure.

Isopycnic—condition of equal or constant density.

Isolated—A system that has no interactions of any kind with the surroundings (e.g. mass, heat, and work interactions) is said to be isolated.

Isosteric—condition of constant density. See *isochore*.

Isothermal—condition of constant temperature.

LLE—liquid-liquid equilibria.

Master equation—$U(V,T)$.

Measurable properties—variables from the set $\{P, V, T, C_P, C_V\}$ and derivatives involving only $\{P, V, T\}$.

Metastable—signifies existence of a state which is non-equilibrium, but not unstable, e.g., superheated vapor, subcooled liquid, which may persist until a disturbance creates movement of the system towards equilibrium.

Nozzle—a specially designed device which nearly reversibly converts internal energy to kinetic energy. See *throttling*.

Polytropic exponent—The exponent n in the expression PV^n = constant.

Quality—the mass fraction of a vapor/liquid mixture that is vapor.

rdf—radical distribution function.

Reference state—a state for a pure substance at a specified (T,P) and type of phase (S,L,V). The reference state is invariant to the system (P,T) throughout an entire thermodynamic problem. A problem may have various standard states, but only one reference state. See also *standard state*.

Sensible heat changes—heat effects accompanied by a temperature change.

Specific heat—another term for C_P or C_V with units per mass.

Specific property—an intensive property per unit mass.

SLE—solid-liquid equilibria.

Solvation—description of complex formation where the molecules involved are of a different type.

Spinodal—condition of instability, beyond which metastability is impossible.

Standard conditions—273.15 K and 0.1 MPa (IUPAC), *standard temperature and pressure*.

Standard state—a state for a pure substance at a specified (T,P) and type of phase (S,L,V). The standard state T is always at the T of interest for a given calculation within a problem. As the T of the system changes, the standard state T changes. The standard state P may be a fixed P or may be the P of the system. Gibbs energies and chemical potentials are commonly calculated relative to the standard state. For reacting systems, enthalpies and Gibbs energies of formation are commonly tabulated at a fixed pressure of 1 bar and 298.15 K. A temperature correction must be applied to calculate the standard state value at the temperature of interest. A problem may have various standard states, but only one reference state. See also *reference state.*

State of aggregation—solid, liquid, or gas.

Steady-state—open flow system with no accumulation of mass and where state variables do not change with time inside system boundaries.

STP—standard temperature and pressure, 273.15 K and 1 atm. Also referred to as *standard conditions*.

Subcooled—description of a state where the temperature is below the saturation temperature for the system pressure, e.g., subcooled vapor is metastable or unstable, subcooled liquid is stable relative to the bubble-point temperature; superheated vapor is stable, superheated liquid is metastable or unstable relative to the dew-point temperature; subcooled liquid is metastable or unstable relative to the fusion temperature.

Superheated—description of a state where the temperature is above the saturation temperature for the system pressure. See *subcooled.*

Thermal efficiency—the ratio or work obtained to the heat input to a heat engine. No engine may have a higher thermal efficiency than a Carnot engine.

Thermodynamic efficiency—ratio characterizing actual work relative to reversible work obtainable for exactly the same change in state variables for a process. The heat transfer for the reversible process will differ from the actual heat transfer. See also *isentropic efficiency, thermal efficiency.*

Throttling—a pressure drop without significant change in kinetic energy across a valve, orifice, porous plug, or restriction, which is generally irreversible. See *nozzle*.

Unstable—a state that violates thermodynamic stability, and cannot persist. See also *metastable, spinodal.*

VLE—vapor-liquid equilibrium.

Wet steam—a mixture of water vapor and liquid.

NOTATION

General Symbols

a	Activity, or dimensional equation of state parameter or energetic parameter, or heat capacity or other constant
A	Intensive Helmholtz energy, or dimensionless constant for equation of state, or Antoine, Margules, or other constant
b	Dimensional equation of state parameter or heat capacity or other constant
B	Virial coefficient, or dimensionless constant for other equation of state, or Antoine or other constant
$C, c, \ldots$	Constants, c is a shape factor for the ESD equation of state
C_P	Intensive constant pressure heat capacity
C_V	Intensive constant volume heat capacity
F	Feed
f	Pure fluid fugacity
$\hat{f}_i$	Fugacity of component in mixture
G	Intensive Gibbs energy
g	Gravitational constant (9.8066 m/s^2) or radial distribution function
g_c	Gravitational conversion factor (1 kg-m/N-s^2) (32.174[($1b_m$-ft)/s^2]/$1b_f$)
H	Intensive enthalpy
K_a	Reaction equilibrium constant
k	Boltzmann's constant = R/N_A
k_{ij}	Binary interaction coefficient (Eqn. 1.8, 15.9)
K	Distribution coefficient (vapor-liquid, liquid-liquid, etc.)
M	Generic property or molarity when used as units
M_w	Molecular weight
m	Mass (energy balances), molality (electrolytes)
N	Number of molecules
n	Number of moles
N_A	Avogadro's number = 6.0221 E 23 mol^{-1}
P	Pressure

$\underline{Q}$	Extensive heat transfer across system boundary
Q	Intensive heat transfer across system boundary
q	Quality (mass% vapor)
R	Gas constant (8.31446 cm^3-MPa/mole-K)
S	Intensive entropy
T	Temperature
U	Intensive internal energy
u	Pair potential energy function
V	Intensive volume
v	Velocity
$\underline{W}$	Extensive work done at boundary
W	Intensive work done at boundary
Z	Compressibility factor
z	Height

Greek Symbols

α	Isobaric coefficient of thermal expansion, also Peng-Robinson equation of state parameter, and also an ESD equation of state variable
β	$1/kT$, where k is Boltzmann's constant and T is temperature.
ε	Potential energy parameter
η	Thermal θ, compressor or pump C, turbine or expander E, efficiency, or reduced density, $\eta_P = b/V$
γ	C_P / C_V
γ_i	Activity coefficient
κ_T	Isothermal compressibility
κ_S	Isentropic compressibility
κ	Parameter for Peng-Robinson equation of state
λ	Universal free volume fraction
μ_i	Chemical potential for a component in a mixture
ω	Acentric factor
φ	Pure fluid fugacity coefficient
$\hat{\varphi}_i$	Component fugacity coefficient in a mixture
Φ	Osmotic coefficient or electric potential
Φ_i	Volume fraction of component i
ρ	Intensive density
σ	Molecular diameter
ξ	Reaction coordinate

Operators

Δ	Denotes change: (1) for a closed system, denotes (final state – initial state); (2) for an open steady-state system, denotes (outlet state – inlet state)
ln	Natural logarithm (base e)
log	Common logarithm (base 10)
∂	Partial differential
Π	Cumulative product operator
Σ	Cumulative summation

Special Notation

ig	Equation applies to ideal gas only
*	Equation assumes heat capacity is temperature-independent.
¯ as in $\overline{H}_i$	Partial molar property
_ as in $\underline{U}$	Extensive property
ˆ	Mixture property

$[\equiv]$	Specifies units for variable
$\equiv$	Equivalence or definition
$\approx$	Approximately equal to

Subscripts

b	Property at normal boiling point temperature
EC	Expansion/contraction work
f	Denotes property for formation of molecule from atoms in their naturally occurring pure molecular form
gen	Generated entropy
i	Component in a mixture
m	Property at melting point
mix	Used with Δ to denote property change on mixing
r	Property reduced by critical constant
R	Reference state
S	Shaft work

Superscripts

∞	Infinite dilution
$\square$	Molality standard state
o	Standard state (usually pure)
$*$	Henry's law (rational) standard state
E	Excess property for a mixture
f	Property at final state
fus	Fusion (melting) process
i	Property at initial state
α,β	Denotes phase of interest
ig	Ideal gas property
in	Property at inlet (open system)
is	Ideal solution property
L	Liquid phase
out	Property at outlet (open system)
S	Solid phase
sat	Saturation property
V	Vapor phase
vap	Vaporization process

CHAPTER

1

BASIC CONCEPTS

> *"Aside from the logical and mathematical sciences, there are three great branches of natural science which stand apart by reason of the variety of far reaching deductions drawn from a small number of primary postulates. They are mechanics, electromagnetics, and thermodynamics.*
>
> *These sciences are monuments to the power of the human mind; and their intensive study is amply repaid by the aesthetic and intellectual satisfaction derived from a recognition of order and simplicity which have been discovered among the most complex of natural phenomena... Yet the greatest development of applied thermodynamics is still to come. It has been predicted that the era into which we are passing will be known as the chemical age; but the fullest employment of chemical science in meeting the various needs of society can be made only through the constant use of the methods of thermodynamics."*
>
> *Lewis and Randall (1923)*

Lewis and Randall eloquently summarized the broad significance of thermodynamics as long ago as 1923. They went on to describe a number of the miraculous scientific developments of the time and the relevant roles of thermodynamics. Historically, thermodynamics has guided the development of steam engines, refrigerators, nuclear power plants, and rocket nozzles, to name just a few. The principles remain important today in the refinement of alternative refrigerants, heat pumps, and improved turbines, and also in technological advances including computer chips, superconductors, advanced materials, fermentations, biological cycles, and bioengineered pharmaceuticals. These latter-day "miracles" might appear to have little to do with power generation and refrigeration cycles at first thought. Nevertheless, as Lewis and Randall point out, the implications of the postulates of thermodynamics are far-reaching and will continue to be important in the development of even newer technologies. Much of modern thermodynamics focuses on characterization of the properties of mixtures, as their constituents partition into stable phases or inhomogeneous domains, and react. The capacity of thermodynamics to bring "quantitative precision in place of the old, vague ideas"[1] is as germane today as it was then.

---

[1] Lewis, G.N., Randall, M. 1923. *Thermodynamics and the Free Energy of Chemical Substances,* New York: McGraw-Hill.

Before overwhelming you with the details that comprise thermodynamics, we outline a few "primary postulates" as clearly as possible and put them into the context of what we will refer to as classical equilibrium thermodynamics. In casual terms, our primary premises can be expressed as follows:

1. You can't get something for nothing. (Energy is conserved.)
2. Maintaining order requires work. (Entropy generation leads to lost work.)[2]

Occasionally, it may seem that we are discussing principles that are much more sophisticated. But the fact is that all of our discussions can be reduced to these fundamental principles. The first principle is a casual statement of the **first law of thermodynamics** (conservation of energy) which will be introduced in Chapters 2 and 3. The second principle is a casual statement of the **second law of thermodynamics** (entropy balance) which will be introduced in Chapter 4. When you find yourself in the midst of a difficult problem, it may be helpful to remember the underlying principles. We will see that coupling these two principles with some slightly sophisticated reasoning (mathematics included) leads to many clear and reliable insights about a wide range of subjects from energy crises to high-tech materials, from environmental remediation to biosynthesis. The bad news is that the level of sophistication required is not likely to be instantly assimilated by the average student. The good news is that many students have passed this way before, and the proper trail is about as well marked as one might hope.

There is less-than-universal agreement on what comprises "thermodynamics." If we simply take the word apart, "thermo" sounds like "thermal," which ought to have something to do with heat, temperature, or energy. "Dynamics" ought to have something to do with movement. And if we could just leave the identification of thermodynamics as the study of "energy movements," it would be sufficient for the purposes of this text. Unfortunately, such a definition would not clarify what distinguishes thermodynamics from, say, transport phenomena or kinetics, so we should spend some time clarifying the definition of thermodynamics in this way before moving on to the definitions of temperature, heat, energy, and so on.

The definition of thermodynamics as the study of energy movements has evolved considerably to include classical equilibrium thermodynamics, quantum thermodynamics, statistical thermodynamics, and irreversible thermodynamics as well as nonequilibrium thermodynamics. Classical thermodynamics has the general connotation of referring to the implications of constraints related to multivariable calculus as developed by J.W. Gibbs. We spend a significant effort applying these insights in developing generalized equations for the thermodynamic properties of pure substances. Statistical thermodynamics focuses on the idea that knowing the precise states of 10^{23} atoms is not practical and prescribes ways of computing the average properties of interest based on very limited measurements. We touch on this principle in our introduction to entropy, in our kinetic theory and molecular dynamics, and in the formulation of the internal energy relative to the intermolecular potential energy. We generally refrain from detailed formulation of all the statistical averages, however, maintaining the focus on simple concepts of molecular interactions. Irreversible thermodynamics and nonequilibrium thermodynamics emphasize the ways that local concentrations of atoms and energy evolve over periods of time. At this point, it becomes clear that such a broad characterization of thermodynamics would overlap with transport phenomena and kinetics in a way that would begin to be confusing at the introductory level. Nevertheless, these fields of study represent legitimate subtopics within the general realm of thermodynamics.

---

[2] The term "lost work" refers to the loss of capability to perform useful work, and is discussed in more detail in Sections 2.4 on page 42, 4.2 on page 132, and 4.3 on page 142.

1.1 INTRODUCTION

These considerations should give you some idea of the potential range of applications possible within the general study of thermodynamics. This text will try to find a happy medium. One general unifying principle about the perspective offered by thermodynamics is that there are certain properties that are invariant with respect to time. For example, the process of diffusion may indicate some changes in the system with time, but the diffusion coefficient is a property which only depends on a temperature, density, and composition profile. A thermodynamicist would consider the diffusion process as something straightforward given the diffusion coefficient, and focus on understanding the diffusion coefficient. A transport specialist would just estimate the diffusion coefficient as best as he could and get on with it. A kineticist would want to know how fast the diffusion was relative to other processes involved. In more down-to-earth terms, if we were touring about the countryside, the thermodynamicists would want to know where we were going, the transport specialists would want to know how long it takes to get there, and the kineticists would want to know how fast the fuel was running out.

In thermodynamics we utilize a few basic concepts: energy, entropy, and equilibrium. The ways in which these are related to one another and to temperature, pressure, and density are best understood in terms of the connections provided by molecular mechanisms. These connections, in turn, can be summarized by the thermodynamic model (e.g., ideal gas), our quantitative description of the substance. Showing how energy and entropy couple with molecular characteristics to impact chemical process applications is the primary goal of this text. These insights should stick with you long after you have forgotten how to estimate any particular thermodynamic property, a heat capacity or activity coefficient, for example. We will see how assuming a thermodynamic model and applying the rules of thermodynamics leads to precise and extremely general insights relevant to many applications. A general theme throughout the text (and arguably throughout engineering) is: observe, predict, test, and evaluate. The prediction phase usually involves a model equation. Testing and evaluation expose limitations of the prospective model, which leads to a new cycle of observation, prediction... We terminate this hierarchy at an introductory level, but it never really ends. Extending this hierarchy is the source of innovation that must serve you for the next 50 years.

Chapter Objectives: You Should Be Able to...

1. Explain the definitions and relations between temperature, molecular kinetic energy, molecular potential energy and macroscopic internal energy, including the role of intermolecular potential energy and how it is modeled. Explain why the ideal gas internal energy depends only on temperature.
2. Explain the molecular origin of pressure.
3. Apply the vocabulary of thermodynamics with words such as the following: work, quality, interpolation, sink/reservoir, absolute temperature, open/closed system, intensive/extensive property, subcooled, saturated, superheated.
4. Explain the advantages and limitations of the ideal gas model.
5. Sketch and interpret paths on a P-V diagram.
6. Perform steam table computations like quality determination, double interpolation.

1.2 THE MOLECULAR NATURE OF ENERGY, TEMPERATURE, AND PRESSURE

Energy is a term that applies to many aspects of a system. Its formal definition is in terms of the capability to perform work. We will not quantify the potential for work until the next chapter, but you should have some concept of work from your course in introductory physics. Energy may take the form of kinetic energy or potential energy, and it may refer to energy of a macroscopic or a molecular scale.

Energy is the sum total of all capacity for doing work that is associated with matter: kinetic, potential, submolecular (i.e., molecular rearrangements by reaction), or subatomic (e.g., ionization, fission).

Kinetic energy is the energy associated with motion of a system. Motion can be classified as translational, rotational, or vibrational.

Temperature is related to the "hotness" of a substance, but is fundamentally related to the kinetic energy of the constituitive atoms.

Potential energy is the energy associated with a system due to its position in a force field.

❗ Energy will be tabulated relative to a convenient reference state.

In the study of "energy movements," we will continually ask, "How much energy is here now, and how much is there?" In the process, we need to establish a point for beginning our calculations. According to the definition above, we might intuitively represent zero internal energy by a perfect vacuum. But then, knowing the internal energy of a single proton inside the vacuum would require knowing how much energy it takes to make a proton from nothing. Since this is not entirely practical, this intuitive choice is not a good engineering choice usually. This is essentially the line of reasoning that gives rise to the convention of calculating energy changes relative to a **reference state.** Thus, there is no absolute reference point that is always the most convenient; there are only changes in energy from one state to another. We select reference conditions that are relevant throughout any particular process of interest. Depending on the complexity of the calculation, reference conditions may vary from, say, defining the enthalpy (to be defined later) of liquid water to be zero at 0.01°C (as in the steam tables) to setting it equal to zero for the molecular hydrogen and oxygen at 1 bar and 298.15 K (as in the heat of reaction), depending on the situation. Since this text focuses on changes in kinetic energy, potential energy, and energies of reaction, we need not specify reference states any more fundamental than the elements, and thus we do not consider subatomic particles.

Kinetic Energy and Temperature

Kinetic energy is commonly introduced in detail during introductory physics as $\frac{1}{2} mv^2$, where m is the mass of the object and v is the object velocity. Atomic species that make up solids are frozen in localized positions, but they are continuously vibrating with kinetic energy. Fluids such as liquids and gases are not frozen into fixed positions and move through space with kinetic energy and collide with one another.

❗ Temperature primarily reflects the kinetic energy of the molecules.

The most reliable definition of temperature is that it is a numerical scale for uniquely ordering the "hotness" of a series of objects.[3] However, this "hotness" is coupled to the molecular kinetic energy of the constituent molecules in a fundamental way. The relation between kinetic energy and temperature is surprisingly direct. When we touch a hot object, the kinetic energy of the object is transferred to our hand via the atoms vibrating at the surface. Temperature is proportional to the average molecular kinetic energy. The expression is easiest to use in engineering on a molar basis. For a monatomic substance

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[3] Denbigh, K., 1971. *The Principles of Chemical Equilibrium,* London: Cambridge University Press, p. 9.

$$T = \frac{M_w}{3R}\langle v^2\rangle \text{ (for 3D)} \qquad T_{2D} = \frac{M_w}{2R}\langle v^2\rangle \text{ (for 2D) monatomic fluid.} \qquad 1.1$$

❗Check your units when using this equation.

where <> brackets denote an average, and M_w is the molecular weight. We use a subscript for the temperature of 2D motion to avoid confusion with the more common 3D motion. The differences between 2D and 3D temperature are explained on page 22. For a polyatomic molecule, the temperature is coupled to the average velocity of the individual atoms, but some of the motion of the bonded atoms results in vibrations and rotations rather than a direct translation of the center of mass and thus it is not directly related to the velocity of the center of mass. (See Section 7.10 on page 276.)

Eqn. 1.1 is applicable to any classical monatomic system, including liquids and solids. This means that for a pure system of a monatomic ideal gas in thermal equilibrium with a liquid, the average velocities of the molecules are independent of the phase in which they reside. We can infer this behavior by envisioning gas atoms exchanging energy with the solid container walls and then the solid exchanging energy with the liquid. At equilibrium, all exchanges of energy must reach the same kinetic energy distribution. The liquid molecular environment is different from the gas molecular environment because liquid molecules are confined to move primarily within a much more crowded environment where the potential energies are more significant. When a molecule's kinetic energy is insufficient to escape the potential energy (we discuss the potential energy next) due to molecular attractiveness, the atoms simply collide with a higher frequency in their local environment. What happens if the temperature is raised such that the liquid molecules can escape the potential energies of the neighbors? We call this phenomenon "boiling." Now you can begin to understand what temperature is and how it relates to other important thermodynamic properties.

We are guaranteed that a universal scale of temperature can be developed because of the **zeroth law of thermodynamics:** If two objects are in equilibrium with a third, then they are in equilibrium with one another as we discussed in the previous paragraph. The zeroth law is a law in the sense that it is a fact of experience that must be regarded as an empirical fact of nature. The significance of the zeroth law is that we can calibrate the temperature of any new object by equilibrating it with objects of known temperature. Temperature is therefore an empirical scale that requires calibration according to specific standards. The Celsius and Fahrenheit scales are in everyday use. The conversions are:

$$(T \text{ in °C}) = \frac{5}{9}((T \text{ in °F}) - 32)$$

When we perform thermodynamic calculations, we must usually use **absolute temperature** in Kelvin or Rankine. These scales are related by

$$(T \text{ in K}) = (T \text{ in °C}) + 273.15$$

$$(T \text{ in °R}) = (T \text{ in °F}) + 459.67$$

$$(T \text{ in R}) = 1.8 \cdot (T \text{ in K})$$

❗ Thermodynamic calculations use absolute temperature in °R or K.

The absolute temperature scale has the advantage that the temperature can never be less than absolute zero. This observation is easily understood from the kinetic perspective. The kinetic energy cannot be less than zero; if the atoms are moving, their kinetic energy must be greater than zero.

Potential Energy

Solids and liquids exist due to the intermolecular **potential energy** (molecular “stickiness’) of atoms. If molecules were not “sticky” all matter would be gases or solids. Thus, the principles of molecular potential energy are important for developing a molecular perspective on the nature of liquids, solids, and non-ideal gases. Potential energy is associated with the “work” of moving a system some distance through a force field. On the macroscopic scale, we are well aware of the effect of gravity. As an example, the Earth and the moon are two spherical bodies which are attracted by a force which varies as r^{-2}. The potential energy represents the work of moving the two bodies closer together or farther apart, which is simply the integral of the force over distance. (The force is the negative derivative of potential with respect to distance.) Thus, the potential function varies as r^{-1}. Potential energies are similar at the microscopic level except that the forces vary with position according to different laws. The gravitational attraction between two individual atoms is insignificant because the masses are so small. Rather, the important forces are due to the nature of the atomic orbitals. For a rigorous description, the origin of the intermolecular potential is traced back to the solution of Schrödinger’s quantum mechanics for the motions of electrons around nuclei. However, we do not need to perform quantum mechanics to understand the principles.

Intermolecular Potential Energy

❗ Engineering model potentials permit representation of attractive and repulsive forces in a tractable form.

Atoms are composed of dense nuclei of positive charge with electron densities of negative charge built around the nucleus in shells. The outermost shell is referred to as the valence shell. Electron density often tends to concentrate in lobes in the valence orbitals for common elements like C, N, O, F, S, and Cl. These lobes may be occupied by bonded atoms that are coordinated in specific geometries, such as the tetrahedron in CH_4, or they may be occupied by unbonded electron pairs that fill out the valence as in NH_3 or H_2O, or they may be widely “shared” as in a resonance or aromatic structure. These elements (H, C, N, O, F, S, Cl) and some noble gases like He, Ne, and Ar provide virtually all of the building blocks for the molecules to be considered in this text.

By considering the implications of atomic structure and atomic collisions, it is possible to develop the following subclassifications of intermolecular forces:

1. Electrostatic forces between charged particles (ions) and between permanent dipoles, quadrupoles, and higher multipoles.
2. Induction forces between a permanent dipole (or quadrupole) and an induced dipole.
3. Forces of attraction (dispersion forces) due to the polarizability of electron clouds and repulsion due to prohibited overlap.
4. Specific (chemical) forces leading to association and complex formation, especially evident in the case of hydrogen bonding.

❗ Attractive forces and potential energies are negative. Repulsive forces and potential energies are positive.

Attractive forces are quantified by negative numerical values, and repulsive forces will be characterized by positive numerical values. To a first approximation, these forces can be characterized by a spherically averaged model of the intermolecular potential (aka. “potential” model). **The potential, $u(r)$, is the work (integral of force over distance) of bringing two molecules from infinite distance to a specific distance, r.** When atoms are far apart (as in a low-pressure gas), they do not sense one another and interaction energy approaches zero. When the atoms are within about two diameters, they attract, resulting in a negative energy of interaction. Because they have finite size, as they are brought closer, they resist overlap. Thus, at very close distances, the forces are repulsive and create very large positive potential energies. These intuitive features are illustrated graphically in Fig. 1.1. The discussion below provides a brief background on why these forces exist and how they vary with distance.

Electrostatic Forces

The force between two point charges described by Coulomb's Law is very similar to the law of gravitation and should be familiar from elementary courses in chemistry and physics,

$$F \propto \frac{q_i q_j}{r^2}$$

where q_i and q_j are the charges, and r is the separation of centers. Upon integration, $u = \int F dr$, the potential energy is proportional to inverse distance,

$$u \propto \frac{q_i q_j}{r} \qquad 1.2$$

If all molecules were perfectly spherical and rigid, the only way that these electrostatic interactions could come into play is through the presence of ions. But a molecule like NH_3 is not perfectly spherical. NH_3 has three protons on one side and a lobe of electron density in the unbonded valence shell electron pair. This permanent asymmetric distribution of charge density is modeled mathematically with a dipole (+ and – charge separation) on the NH_3 molecule.[4] This means that ammonia molecules lined up with the electrons facing one another repel while molecules lined up with the electrons facing the protons will attract. Since electrostatic energy drops off as r^{-1}, one might expect that the impact of these forces would be long-range. Fortunately, with the close proximity of the positive charge to the negative charge in a molecule like NH_3, the charges tend to cancel one another as the molecule spins and tumbles about through a fluid. This spinning and tumbling makes it reasonable to consider a spherical average of the intermolecular energy as a function of distance that may be constructed by averaging over all orientations between the molecules at each distance. In a large collection of molecules randomly distributed relative to one another, this averaging approach gives rise to many cancellations, and the net impact is approximately

$$u_{dipole-dipole} \propto \frac{-\varepsilon_{dipole}}{r^6 kT} \qquad 1.3$$

where $k = R/N_A$ is **Boltzmann's constant,** related to the **gas constant**, R, and **Avogadro's number,** N_A. This surprisingly simple result is responsible for a large part of the attractive energy between polar molecules. This energy is attractive because the molecules tend to spend somewhat more time lined up attractively than repulsively, and the r^{-6} power arises from the averaging that occurs as the molecules tumble and the attractive forces decrease with separation. A key feature of dipole-dipole forces is the temperature dependence.

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[4] The dipole is a model of the charge distribution on the molecule, and it is thus an approximate description of the charge distribution.

Induction Forces

When a molecule with a permanent dipole approaches a molecule with no dipole, the positive charge of the dipolar molecule will tend to pull electron density away from the nonpolar molecule and "induce" a dipole moment into the nonpolar molecule. The magnitude of this effect depends on the strength of the dipole and how tightly the orbitals of the nonpolar molecule constrain the electrons spatially in an electric field, characterized by the "polarizability."[5] For example, the pi bonding in benzene makes it fairly polarizable. A similar consideration of the spherical averaging described in relation to electrostatic forces results again in a dependence of r^{-6} as approximately

$$u_{in} \propto \frac{-\varepsilon_{in}}{r^6} \qquad 1.4$$

Disperse Attraction Forces (Dispersion Forces)

❗ The r^{-6} dependence of attractive forces has a theoretical basis.

When two nonpolar molecules approach, they may also induce dipoles into one another owing to fluctuating distributions of electrons. Their dependence on radial distance may be analyzed and gives the form for the attractive forces:

$$u_{disp}^{att} \propto \frac{-\varepsilon_{att}}{r^6} \qquad 1.5$$

Note that dipole-dipole, induction, and dispersion forces all vary as r^{-6}.

Repulsive Forces

The forces become repulsive rapidly as radial distance decreases, and quickly outweighs the attractive force as the atoms are forced into the same space. A common empirical equation is

$$u_{disp}^{rep} \propto \frac{\varepsilon_{rep}}{r^{12}} \qquad 1.6$$

Engineering Potential Models

Based on the forms of these electrostatic, induction, and dispersion forces, it should be easy to appreciate the form of the Lennard-Jones potential in Fig. 1.1. Other approximate models of the potential function are possible, such as the square-well potential or the Sutherland potential also shown in Fig. 1.1. These simplified potential models are accurate enough for many applications.

The key features of all of these potential models are the representation of the size of the molecule by the parameter σ and the attractive strength (i.e. "stickiness") by the parameter ε. We can gain considerable insight about the thermodynamics of fluids by intuitively reasoning about the relatively simple effects of size and stickiness. For example, if we represent molecules by lumping together all the atomic sites, a large molecule like buckminsterfullerene (solid at room temperature) would have a larger value for σ and ε than would methane (gas at room temperature). Water and methane are about the same size, but their difference in boiling temperature indicates a large difference in their stickiness. Considering the molecular perspective, it should become apparent that water

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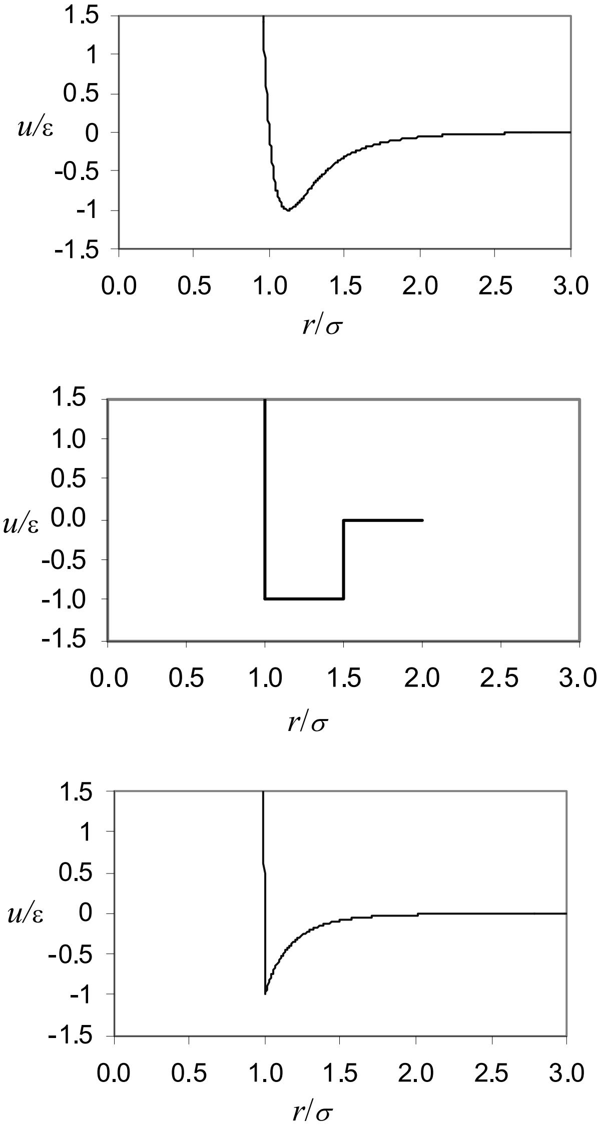
[5] The polarizability is the linear proportionality constant in a model of how easily a dipole is "induced" when the molecule is placed in an electric field.



The Lennard-Jones potential.

$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$

Note that $\varepsilon > 0$ is the depth of the well, and σ is the distance where $u(r) = 0$.

The square-well potential for $\lambda = 1.5$.

$$u(r) = \begin{cases} \infty \text{ if } r \le \sigma \\ -\varepsilon \text{ if } \sigma < r \le \lambda\sigma \\ 0 \text{ if } r > \lambda\sigma \end{cases}$$

The Sutherland potential.

$$u(r) = \begin{cases} \infty \text{ if } r \le \sigma \\ -\varepsilon(\sigma/r)^6 \text{ if } r > \sigma \end{cases}$$

Figure 1.1 *Schematics of three engineering models for pair potentials on a dimensionless basis.*

has a higher boiling temperature because it sticks to itself more strongly than does methane. With these simple insights, you should be able to understand the molecular basis for many macroscopic phenomena. Example 1.1 illustrates several computations for intermolecular potential energy.

Example 1.1 The energy derived from intermolecular potentials

We can develop further appreciation for internal energy by computing the intermolecular potential energy for a well-defined system of molecules. Assume the Lennard-Jones potential model with $\sigma = 0.36$ nm and $\varepsilon = 1.38\text{E-}21$ J:

(a) Compute the potential energy for two molecules located at positions (0,0) and (0, 0.4 nm).

(b) Suppose a third molecule was located at (0.5,0). Compute the potential energy for the system.

(c) To develop a very crude insight on the methods of averaging, we can think of the average potential energy as defining an average distance between the molecules. As the volume expands, the average distance between molecules increases and the magnitude of the average potential energy decreases in accordance with the Lennard-Jones model. For the potential energy from (*b*), compute the average distance, $<r>$, that corresponds to the average potential energy for this system of molecules.

(d) Suppose the volume of the system in (c) expands by a factor of two. How would that affect the average distance, $<r>$, and what would you estimate as the new intermolecular energy?

(e) Assume approximately four molecules can fit around a central molecule in a liquid before it is too crowded and another layer starts to build up. Assuming the Lennard-Jones energy is practically zero beyond the first layer (i.e. ignore all but the first layer), and the average distance between the central molecule and its four neighbors is $<r> = 0.55$ nm, estimate the intermolecular energy around one single molecule and that for one mole of similar molecules.

Solution:

(a) The distance is $r_{12} = [\ (0-0)^2 + (0.4-0)^2\ ]^{½} = 0.4$ nm.
$u(r_{12}) = 4(1.38\text{E-}21)[(0.36/0.40)^{12} - (0.36/0.40)^6] = -1.375\text{E-}21$

(b) The distance $r_{13} = [\ (0.5-0)^2 + (0.5-0)^2\ ]^{½} = 0.5$. So $u(r_{13}) = -0.662\text{E-}21$.
But wait, there's more! $r_{23} = [\ (0.5-0)^2 + (0-0.4)^2\ ]^{½} = 0.6403$. So, $u(r_{23}) = -0.169\text{E-}21$.
The total intermolecular energy is: $-(1.375+0.662+0.169)(1\text{E-}21) = -2.206\text{E-}21$J.

(c) The average intermolecular energy for these three pairs is:
$<u> = -2.206\text{E-}21/3 = -0.735\text{E-}21$J.
Matching this value of $<u>$ by using a solver to adjust $<r>$ in the Lennard-Jones model gives
$<r> = 0.4895$ nm.

(d) Volume is related to the cubic of length. Expanding the volume by a factor of 2 changes the *r*-coordinates by a factor of $2^{1/3}$. So, $<r> = 0.4895(2^{1/3}) = 0.6167$, and $<u> = -0.210\text{E-}21$J.

(e) For $<r> = 0.55$, $<u(r)> = -0.400\text{E-}21$J and $u_1 = 4(-0.400\text{E-}21) = -1.600\text{E-}21$ per atom. For Avogadro's number of such molecules, the summed intermolecular energy becomes
$u_{NA} = N_A<u> = (602.22\text{E}21)(-1.600\text{E-}21) = -963$ J/mole.

❗Configurational energy is the potential energy of a system of molecules in their "configuration."

When we sum the potential energy for a collection of molecules, we often call the sum **configurational energy** to differentiate quantity from the potential energy which is commonly used when discussing atoms or sites.

Note that we would need a more complicated potential model to represent the shape of the molecule. Typically, molecules of different shapes are represented by binding together several potentials like those above with each potential site representing one molecular segment. For example, *n*-butane could be represented by four Lennard-Jones sites that have their relative centers located at distances corresponding to the bond-lengths in *n*-butane. The potential between two butane molecules would then be the sum of the potentials between each of the individual Lennard-Jones sites on the different molecules. In similar fashion, potential models for very complex molecules can be constructed.

Potentials in Mixtures

Our discussion of intermolecular potentials has focused on describing single molecules, but it is actually more interesting to contemplate the potential models for different molecules that are mixed together. Note that the square-well model provides a simple way for use to consider only the potential energy of the closest neighbors. We can use the square-well potential as the basis for this analysis and focus simply on the size (σ_{ij}) and stickiness (ε_{ij}) of each potential model, where the subscript *ij* indicates an interaction of molecule *i* with molecule *j*. Commonly, we assume that λ = 1.5 in discussions of the square-well potential, unless otherwise specified. For example, ε_{11} would be the stickiness of molecule 1 to itself, and ε_{12} would be its stickiness to a molecule of type 2 and $\varepsilon_{21}=\varepsilon_{12}$. We often calculate the interactions of dissimilar molecules by using **combining rules** that relate the interaction to the parameters of the sites. Commonly we use combining rules developed by **Lorentz and Bertholet.** The size parameter for interaction between different molecules is reasonably well represented by

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 \qquad 1.7$$

This rule simply states that the distance between two touching molecules is equal to the radius of the first one plus the radius of the second one. The estimation of the stickiness parameter for interaction between different molecules requires more empirical reasoning. It is conventional to estimate the stickiness by a geometric mean, but to permit flexibility to adjust the approximate rule by adding an adjustable constant that can be refined using experimental measurements, or sometimes using theories like quantum mechanical simulation. For historical reasons, this constant is typically referred to as "k_{ij}" or the **binary interaction parameter,** and defined through the following rule:

$$\varepsilon_{12} = (\varepsilon_{11}\ \varepsilon_{22})^{1/2}(1 - k_{12}) \qquad 1.8$$

The default value is $k_{12} = 0$.

Specific (Chemical) Forces Like Hydrogen Bonding

What happens when the strength of interaction between two molecules is so strong at certain orientations that it does not make sense to spherically average over it? Hydrogen bonding is an example of such an interaction, as you probably know from an introductory chemistry or biology course. For instance, it would not make sense to spherically average when two atoms preferentially interact in a specific orientation. But, if they were covalently bonded, we would call that a chemical reaction and handle it in a different way. An interesting problem arises when the strength of interaction is too strong to be treated entirely by spherically averaging and too weak to be treated as a normal chemical reaction which forms permanent stable chemical species. Clearly, this problem is difficult and it would be tempting to try to ignore it. In fact, most of this course will deal with theories that treat only what can be derived by spherically averaging. But it should be kept in mind that these specific forces are responsible for some rather important properties, especially in the form of hydrogen bonding. Since many systems are aqueous or contain amides or alcohols, ignoring hydrogen bonding entirely would substantially undermine the accuracy of our conceptual foundation. Furthermore, the concept of favorable energetic interactions between acids and bases can lend broad insights into the mysteries of chemical formulations. As an engineering approach, we can make large adjustments to the spherical nature of these forces such that we can often approximate them with a single characteristic constant to obtain a workable engineering model. Example 1.2 illustrates the concept of combining rules that pervades the entirety of mixture thermodynamics.

Example 1.2 Intermolecular potentials for mixtures

Methane (CH_4) has fewer atoms than benzene (C_6H_6), so it is smaller. Roughly, the diameter of methane is 0.36 nm and that of benzene is 0.52 nm. Similarly, methane's boiling temperature is lower so its stickiness must be smaller in magnitude. A crude approximation is $\varepsilon/k = T_c/1.25$, where T_c is the critical temperature listed on the back flap. Not knowing what to assume for k_{12}, we may consider three possibilities: $k_{12} = 0$, $k_{12} < 0$, $k_{12} > 0$. To illustrate, sketch on the same pair of axes the potential models for methane and benzene, assuming that the k_{12} parameter is given by: (a) $k_{12} = 0$ (b) $k_{12} = -0.2$ (c) $k_{12} = +0.2$. In each case, describe in words what is represented by each numerical value (e.g., favorable interactions, or unfavorable interactions...) Assume the square-well potential with $\lambda = 1.5$.

Solution: Following the suggested estimation formula, $\varepsilon/k = 190.6/1.25 = 152.5$ for methane and $562.2/1.25 = 449.8$ for benzene. Applying Eqns. 1.7 and Eqn. 1.8, we obtain Fig. 1.2 where k_{12} = 0.0 refers to case (a); –0.2 refers to the well location for case (b); and +0.2 refers to case (c).

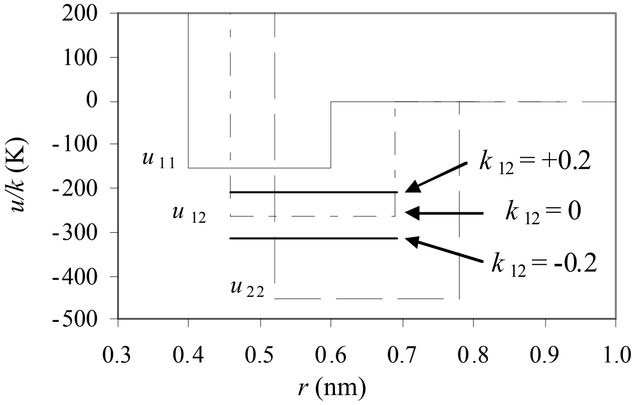


Figure 1.2 *Sketch of intermolecular square-well potential models for a mixture of methane and benzene for $\lambda = 1.5$ as explained in Example 1.1.*

Description of the interactions:

Case (a) corresponds to the molecular interactions being relatively neutral towards one another. This is the default assumption (i.e. $k_{12} = 0$). This would be the best description of methane + benzene (among these three choices) because both are nonpolar.

Case (b) corresponds to extremely favorable interactions, as indicated by the deep attractive well and strongly exothermic interaction. An Lewis acid might interact with a Lewis base in this way.

Case (c) corresponds to unfavorable interactions. The interactions are not zero exactly, so the molecules do attract one another, but the well for the 1-2 interactions is not as deep as expected from the 1-1 and 1-2 interactions. The molecules greatly prefer their own company. A mixture with this type of interaction may lead to liquid-liquid splitting, like oil and water.

Internal Energy

We have taken considerable time to develop the molecular aspects of kinetic and potential energy. These molecular properties are of great importance, but for large-scale macroscopic process system calculations, these microscopic energies are combined and we consider kinetic and configurational energy collectively as the **internal energy** of the system, which is given the symbol U. It may be somewhat confusing that kinetic and potential energy exist on the macroscopic level and the microscopic level. The potential energy (gravitational potential energy) and kinetic energy of the center of mass *of the system* are accounted for separately. The internal energy is a function of the temperature and density (the latter for non-ideal gases) of the system, and it does not usually change if the entire system is placed on, say, an airplane where the kinetic and potential energy of the center of mass differ considerably from a stationary position on the ground. This is the convention followed throughout the remainder of Unit I. In Units II and III, we reexamine the molecular potentials as to how they affect the bulk fluid properties. Thus, throughout the remainder of Unit I, when we refer to kinetic and potential energy of a body of fluid as a system, we are referring to the kinetic energy of the center of mass of the system and the gravitational potential energy of the center of mass of the system.

! The sum of microscopic random kinetic energy and intermolecular potential energies comprises the internal energy.

1.3 THE MOLECULAR NATURE OF ENTROPY

To be fair to both of the central concepts of thermodynamics, we must mention entropy at this point, in parallel with the mention of energy. Unfortunately, there is no simple analogy that can be drawn for entropy like that for potential energy using the gravitational forces between the Earth and moon. The study of entropy is fairly specific to the study of thermodynamics.

What we can say at this point is that entropy has been conceived to account for losses in the prospect of performing useful work. The energy can take on many forms and be completely accounted for without contemplating how much energy has been "wasted" by converting work into something like warm water. To picture how much work this would take, imagine yourself stirring water in a bath tub until the temperature rises by 5°C. Entropy accounts for this kind of wastefulness. It turns out that the generation of such waste can be directly related to the degree of disorder involved in conducting our process. Thus, generation of disorder results in **lost work.** Furthermore, work that is lost by not maintaining order cannot be converted into useful work. To see the difference between energy and entropy, consider the following example. Oxygen and nitrogen are mixed as ideal gases at room temperature and pressure. How much energy is involved in the mixing process? How much (energy) work must be exerted to separate them again? To completely answer the first question we must understand the ideal gas mixture more completely (Chapter 4). We note that ideal gases are point masses with no potential energy to affect the mixing. Thus, the answer to the first question is that no energy is involved. For the answer to the second question regarding work to separate them, however, we must acknowledge that a considerable effort would be involved. The minimum amount required can be calculated as we will show in Chapter 4. To avoid introducing too many concepts at one time, we defer the quantitative development of the topic until Chapter 4.

1.4 BASIC CONCEPTS

The System

A **system** is that portion of the universe which we have chosen to study.

A **closed system** is one in which no mass crosses the system boundaries.

An **open system** is one in which mass crosses the system boundaries. The system may gain or lose mass or simply have some mass pass through it.

An **isolated system** is one devoid of interactions of any kind with the surroundings (including mass exchange, heat, and work interactions).

❗ The placement of system boundaries is a key step in problem solving.

System boundaries are established at the beginning of a problem, and simplification of balance equations depends on whether the system is open or closed. *Therefore, the system boundaries should be clearly identified. If the system boundaries are changed, the simplification of the mass and energy balance equations should be performed again, because different balance terms are likely to be necessary.* These guidelines become more apparent in Chapter 2. In many textbooks, especially those dealing with fluid mechanics, the system is called the **control volume.** The two terms are synonymous.

Equilibrium

A system is in equilibrium when there is no driving force for a change of intensive variables within the system. The system is "relaxed" relative to all forces and potentials.[6]

An isolated system moves spontaneously to an equilibrium state. In the equilibrium state there are no longer any driving forces for spontaneous change of intensive variables.

The Mass Balance

Presumably, students in this course are familiar with mass balances from an introductory course in material and energy balances. The relevant relation is simply:

❗ The mass balance.

$$\begin{bmatrix}\text{rate of mass}\\ \text{accumulation within}\\ \text{system boundaries}\end{bmatrix} = \begin{bmatrix}\text{rate of mass flow}\\ \text{into system}\end{bmatrix} - \begin{bmatrix}\text{rate of mass flow}\\ \text{out of system}\end{bmatrix} \qquad 1.9$$

$$\dot{m} = \sum_{inlets} \dot{m}^{in} - \sum_{outlets} \dot{m}^{out}$$

where $\dot{m} = \frac{dm}{dt}$. $\dot{m}^{in}$ and $\dot{m}^{out}$ are the *absolute values* of mass flow rates entering and leaving, respectively.

We may also write

$$dm = \sum_{inlets} dm^{in} - \sum_{outlets} dm^{out} \qquad 1.10$$

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[6] We qualify this criterion for the purposes of chemical engineering that there is no driving force for "meaningful" change because most of our systems are technically metastable (in a state of local equilibrium). For example, considering air expansion in a piston/cylinder expansion, we neglect the potential corrosion of the piston/cylinder by air oxidation when we state the system has reached mechanical equilibrium.

where mass differentials dm^{in} and dm^{out} are *always positive*. When all the flows of mass are analyzed in detail for several subsystems coupled together, this simple equation may not seem to fully portray the complexity of the application. The general study of thermodynamics is similar in that regard. A number of simple relations like this one are coupled together in a way that requires some training to understand. *In the absence of chemical reactions,* we may also write a mole balance by replacing mass with moles in the balance.

Heat – Sinks and Reservoirs

Heat is energy in transit between the source from which the energy is coming and a destination toward which the energy is going. When developing thermodynamic concepts, we frequently assume that our system transfers heat to/from a **reservoir** or **sink.** A heat reservoir is an infinitely large source or destination of heat transfer. The reservoir is assumed to be so large that the heat transfer does not affect the temperature of the reservoir. A sink is a special name sometimes used for a reservoir which can accept heat without a change in temperature. The assumption of constant temperature makes it easier to concentrate on the thermodynamic behavior of the system while making a reasonable assumption about the part of the universe assigned to be the reservoir.

❗ A reservoir is an infinitely large source or destination for heat transfer.

The mechanics of heat transfer are also easy to picture conceptually from the molecular kinetics perspective. In heat **conduction,** faster-moving molecules collide with slower ones, exchanging kinetic energy and equilibrating the temperatures. In this manner, we can imagine heat being transferred from the hot surface to the center of a pizza in an oven until the center of the pizza is cooked. In heat **convection,** packets of hot mass are circulated and mixed, accelerating the equilibration process. Heat convection is important in getting the heat from the oven flame to the surface of the pizza. Heat **radiation,** the remaining mode of heat transfer, occurs by an entirely different mechanism having to do with waves of electromagnetic energy emitted from a hot body that are absorbed by a cooler body. Radiative heat transfer is typically discussed in detail during courses devoted to heat transfer.

Work

Work is a familiar term from physics. We know that work is a force acting through a distance. There are several ways forces may interact with the system which all fit under this category, including pumps, turbines, agitators, and pistons/cylinders. We will discuss the details of how we calculate work and determine its impact on the system in the next chapter.

Density

Density is a measure of the quantity per unit volume and may be expressed on a molar basis (molar density) or a mass basis (mass density). In some situations, it is expressed as the number of particles per unit volume (number density).

Intensive Properties

Intensive properties are those properties which are independent of the size of the system. For example, in a system at equilibrium without internal rigid/insulating walls, the temperature and pressure are uniform throughout the system and are therefore intensive properties. **Specific properties** are the total property divided by the mass and are intensive. For example, the molar volume ([≡] length^3/mole), mass density ([≡] mass/length^3), and specific internal energy ([≡] energy/mass) are intensive properties. In this text, intensive properties are not underlined.

❗ The distinction between intensive and extensive properties is key in selecting and using variables for problem solving.

Extensive Properties

Extensive properties depend on the size of the system, for example the volume ([≡] length^3) and energy ([≡] energy). Extensive properties are underlined; for example, $\underline{U} = nU$, where n is the number of moles and U is molar internal energy.

States and State Properties – The Phase Rule

Two **state variables** are necessary to specify the state of a *single-phase* pure fluid, that is, two from the set P, V, T, U. Other state variables to be defined later in the text which also fit in this category are molar enthalpy, molar entropy, molar Helmholtz energy, and molar Gibbs energy. *State variables must be intensive properties.* As an example, specifying P and T permits you to find the specific internal energy and specific volume of steam. Note, however, that you need to specify only one variable, the temperature or the pressure, if you want to find the properties of saturated vapor or liquid. This reduction in the needed specifications is referred to as a reduction in the "**degrees of freedom.**" As another example in a ternary, two-phase system, the temperature and the mole fractions of two of the components of the lower phase are state variables (the third component is implicit in summing the mole fractions to unity), but the total number of moles of a certain component is not a state variable because it is extensive. In this example, the pressure and mole fractions of the upper phase may be calculated once the temperature and lower-phase mole fractions have been specified. The number of state variables needed to completely specify the state of a system is given by the Gibbs phase rule for a non-reactive system,[7]:

! The Gibbs phase rule provides the number of state variables (intensive properties) to specify the state of the system.

$$F = C - P + 2 \tag*{1.11}$$

where F is the number of state variables that can be varied while P phases exist in a system where C is the number of components (F is also known as the number of degrees of freedom). More details on the Gibbs phase rule are given in Chapter 16.

Steady-State Open Systems

! Steady-state flow is very common in the process industry.

The term **steady state** is used to refer to open systems in which the inlet and outlet mass flow rates are invariant with time and there is no mass accumulation. In addition, steady state requires that state variables at all locations are invariant with respect to time. Note that state variables may vary with position. Steady state does not require the system to be at equilibrium. For example, in a heat exchanger operating at steady state with a hot and cold stream, each stream has a temperature gradient along its length, and there is always a driving force for heat transfer from the hotter stream to the colder stream. Section 2.13 describes this process in more detail.

The Ideal Gas Law

! The ideal gas law is a *model* that is not always valid, but gives an initial guess.

The **ideal gas** is a "model" fluid where the molecules have no attractive potential energy and no size (and thus, no repulsive potential energy). Properties of the ideal gas are calculated from the ideal gas model:

$$P\underline{V} = nRT \tag*{(ig) 1.12}$$

! An equation of state relates the *P-V-T* properties of a fluid.

Note that scientists who first developed this formula empirically termed it a "law" and the name has persisted, but it should be more appropriately considered a "model." In the terminology we develop, it is also an **equation of state,** relating the *P-V-T* properties of the ideal gas law to one

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[7] For a reactive system, C is replaced with the number of distinct species minus the number of independent reactions.

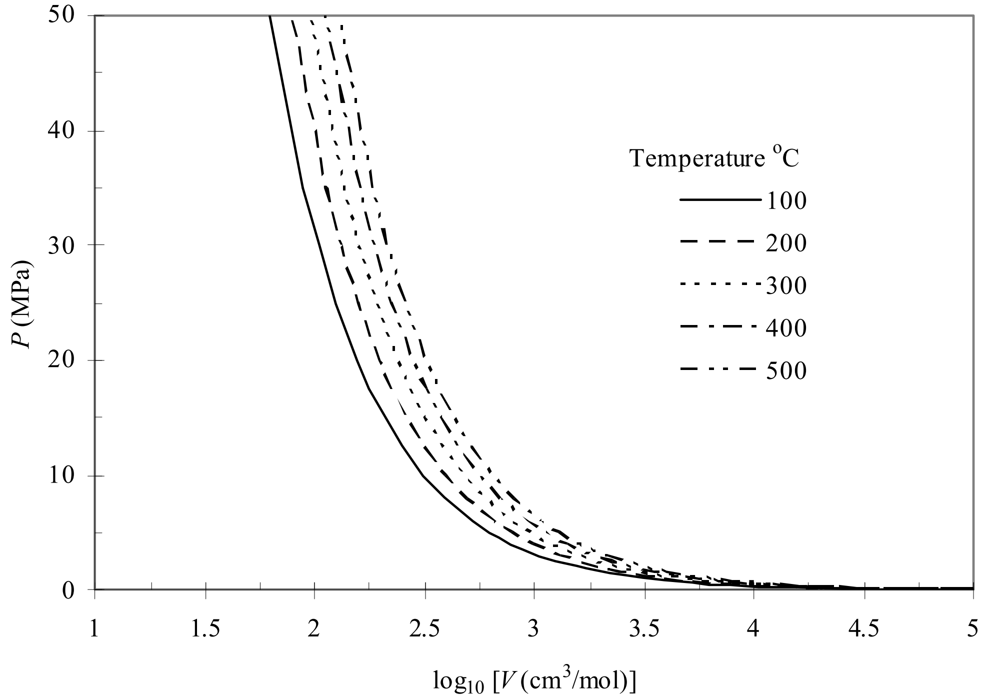


Figure 1.3 *Ideal gas behavior at five temperatures.*

another as shown in Eqn. 1.12 and Fig. 1.3. We know that real molecules have potential energy of attraction and repulsion. Due to the lack of repulsive forces, ideal gas particles can "pass through" one another. Ideal gas molecules are sometimes called "point masses" to communicate this behavior. While the assumptions may seem extreme, we know experimentally that the ideal gas model represents many compounds, such as air, nitrogen, oxygen, and even water vapor at temperatures and pressures near ambient conditions. Use of this model simplifies calculations while the concepts of the energy and entropy balances are developed throughout Unit I. This does not imply that the ideal gas model is applicable to all vapors at all conditions, even for air, oxygen, and nitrogen. Analysis using more complex fluid models is delayed until Unit II. We rely on thermodynamic charts and tables until Unit II to obtain properties for gases that may not be considered ideal gases.

Because kinetic energy is the only form of energy for an ideal gas, the internal energy of a monatomic ideal gas is given by summing the kinetic energy of the atoms and then relating this to temperature (*c.f.* Eqn. 1.1):

$$\boxed{\underline{U}^{ig} = \frac{Nm\langle v^2\rangle}{2} = \frac{nN_A m\langle v^2\rangle}{2} = \frac{nM_w\langle v^2\rangle}{2} = \frac{3}{2}nRT = \frac{3}{2}NkT} \quad \text{(monatomic ideal gas)} \quad \text{(ig)} \quad 1.13$$

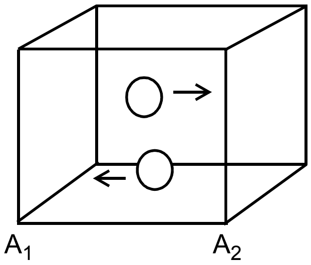
The proportionality constant between temperature and internal energy is known as the ideal gas **heat capacity** at constant volume, denoted C_V. Eqn 1.13 shows that $C_V = 1.5R$ for a monatomic ideal gas. If you refer to the tables of constant pressure heat capacities (C_P) on the back flap of the text and note that $C_P = C_V + R$ for an ideal gas, you may be surprised by how accurate this ultrasimplified theory actually is for species like helium, neon, and argon at 298 K.[8]

While the equality in Eqn. 1.13 is valid for monatomic fluids only, the functionality $U^{ig} = U^{ig}(T)$ is universal for all ideal gases. For more multi-atom molecules, the heat capacity depends on temperature because vibrations hold some energy in a manner that depends on temperature. However, the observation that $U^{ig} = U^{ig}(T)$ is true for any ideal gas, not only for ultrasimplified, monatomic ideal gases. We build on this relation in Chapters 6–8, where we show how to compute changes in energy for any fluid at any temperature and density by systematically correcting the relatively simple ideal gas result. Let us explore more completely the assumptions of the ideal gas law by investigating the molecular origins of pressure.

Pressure

Pressure is the force exerted per unit area. We will be concerned primarily with the pressure exerted by the molecules of fluids upon the walls of their containers. Briefly, when molecules collide with the container walls, they must change momentum. The change in momentum creates a force on the wall. As temperature increases, the particles have more kinetic energy (and momentum) when they collide, so the pressure increases. We can understand this more fully with an ultrasimplified analysis of kinetic theory as it relates to the ideal gas law.

Suppose we have two hard spherical molecules in a container that are bouncing back and forth with 1D velocity in the x-direction only and not contacting one another. We wish to quantify the forces acting on each wall. Since the particles are colliding only with the walls at A_1 and A_2 in our idealized motion, these are the only walls we need to consider. Let us assume that particles bounce off the wall with the same speed which they had before striking the wall, but in the opposite direction (a perfectly elastic collision where the wall is perfectly rigid and absorbs no momentum).



Thus, the kinetic energy of the particles is fixed. If $\vec{v}$ is the initial velocity of the particle (recall that $\vec{v}$ is a vector quantity and notation v represents a scalar) before it strikes a wall, the change in velocity due to striking the wall is $-2\vec{v}$. The change in velocity of the particle indicates the presence of interacting forces between the wall and the particle. If we quantify the force necessary to change the velocity of the particle, we will also quantify the forces of the particle on the wall by Newton's third principle. To quantify the force, we may apply Newton's second principle stated in terms of momentum: *The time rate of change of the momentum of a particle is equal to the resultant force acting on the particle and is in the direction of the resultant force.*

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[8] We will formally define heat capacity and relations for C_P and C_V in Chapter 2.

$$\frac{d\vec{p}}{dt} = \vec{F} \tag{1.14}$$

The application of this formula directly is somewhat problematic since the change in direction is instantaneous, and it might seem that the time scale is important. This can be avoided by determining the time-averaged force,[9] $\vec{F}_{\text{avg}}$ exerted on the wall during time Δt,

$$\int_{t^i}^{t^f} \vec{F} dt = \vec{F}_{\text{avg}} \Delta t = \int_{t^i}^{t^f} \frac{d\vec{p}}{dt} dt = \Delta\vec{p} \tag{1.15}$$

where $\Delta\vec{p}$ is the total change in momentum during time Δt. The momentum change for each collision is $\Delta\vec{p} = -2m\vec{v}$ where m is the mass per particle. Collision frequency can be related easily to the velocity. Each particle will collide with the wall every Δt seconds, where $\Delta t = 2L/v$, where L is the distance between A_1 and A_2. The average force is then

$$\vec{F}_{\text{avg}} = \frac{\Delta\vec{p}}{\Delta t} = -2m\vec{v}\frac{v}{2L} \tag{1.16}$$

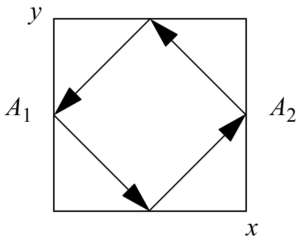
where $\vec{v}$ is the velocity before the collision with the wall. Pressure is the force per unit area, and the area of a wall is L^2, thus

$$P = \frac{m}{L^3}(v_1^2 + v_2^2) \text{ (1D ideal gas motion)} \qquad \text{(ig) } 1.17$$

where the subscripts denote the particles. If you are astute, you will recognize L^3 as the volume of the box and the kinetic energy which we have shown earlier to relate to the temperature.

❗ P is proportional to the number of particles in a volume and to the kinetic energy of the particles.

If the particle motions are generalized to motion in arbitrary directions, collisions with additional walls in the analysis does not complicate the problem dramatically because each component of the velocity may be evaluated independently. To illustrate, consider a particle bouncing around the centers of four walls in a horizontal plane. From the top view, the trajectory would appear as below:



For the same velocity as the first case, the force of each collision would be reduced because the particle strikes merely a glancing blow. The time of collisions between walls is now dependent on the component of velocity perpendicular to the walls. We have chosen a special case to illustrate here, where the box is square and the particle impacts at a 45° angle in the center of each wall. The x-component of the force can be related to the magnitude of the velocity by noting that $v_x = v_y$, such that $v = (v_x^2 + v_y^2)^{½} =$

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[9] See an introductory physics text for further discussion of time-averaged force.

$v_x 2^{1/2}$. The time between collisions with wall A_1 would be $4L/(v2^{1/2})$. The formula for the average force in two dimensions then becomes:

$$F_{avg,A_1} = -2mv_x\frac{v\sqrt{2}}{4L} = -2m\frac{v}{\sqrt{2}}\frac{v\sqrt{2}}{4L} = -2mv\frac{v}{2L} = -\frac{mv^2}{L} \qquad 1.18$$

and the pressure due to two particles that do not collide with one another in two dimensions becomes:

$$P = \frac{m}{2L^3}(v_1^2 + v_2^2) \quad \text{(2D motion)} \qquad \text{(ig) } 1.19$$

(More complicated impact angles and locations will provide the same results but require more tedious derivations.) The extension to three dimensions is more difficult to visualize, but comparing Eqn. 1.17 to Eqn. 1.19, you should not be surprised to learn that the pressure in three dimensions is:

$$P = \frac{m}{3L^3}(v_1^2 + (v_2)^2) = \frac{m}{3\underline{V}}(v_1^2 + v_2^2) \quad \text{(3D motion)} \qquad \text{(ig) } 1.20$$

The problem gets more complicated when collisions between particles occur. We ignored that possibility here because the ideal gases being considered are point masses that do not collide with one another. Including molecular collisions is a straightforward implementation of “billiard ball” physics. This subject is discussed further in Section 7.10 on page 276 and with great interactive graphics in the discontinuous molecular dynamics (DMD) module at Etomica.org.

We see a relation developing between P and kinetic energy. When we insert the relation between temperature and kinetic energy (Eqn. 1.1) into Eqn. 1.20 we find that the ideal gas law results for a spherical (monatomic) molecule in 3D,

❗Check your units when using this equation. 1J = 1kg-m^2/s^2.

$$P\underline{V} = \left(\frac{m}{3\underline{V}}\sum_i^N v_i^2\right)\underline{V} = \frac{N}{3}m\langle v^2\rangle = \frac{nN_A}{3}m\langle v^2\rangle = \frac{nM_w}{3}\langle v^2\rangle = nRT \quad \text{(3D motion)} \qquad \text{(ig) } 1.21$$

where m is the mass per particle and M_w is the molecular weight. A similar derivation with Eqn. 1.19 gives the results for motions restricted to 2D,[10]

$$P\underline{V} = \left(\frac{m}{2\underline{V}}\sum_i v_i^2\right)\underline{V} = \frac{nN_Am}{2}\langle v^2\rangle = \frac{nM_w}{2}\langle v^2\rangle = nRT_{2D} \quad \text{(2D motion)} \qquad \text{(ig) } 1.22$$

1.5 REAL FLUIDS AND TABULATED PROPERTIES

❗ A 3D steam diagram is available as a MATLAB file called PVT.m. The diagram can be rotated to view the 2-D projections.

The thermodynamic behavior of real fluids differs from the behavior of ideal gases in most cases. Real fluids condense, evaporate, freeze, and melt. Characterization of the volume changes and energy changes of these processes is an important skill for the chemical engineer. Many real fluids do behave *as if they are* ideal gases at typical process conditions. P-V behavior of a very common real fluid (i.e., water) and an ideal gas can be compared in Figs. 1.3 and 1.4. Application of the

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[10] This is a pressure [=] force/area where motion is in 2-D and forces are in only two dimensions. In an alternative perspective molecules would only exist in a 2D plane. Then the divisor should be $2L^2$ and we multiply by area L^2, and P_{2D} [=] MPa-m, $P_{2D}L^2 = nRT$.

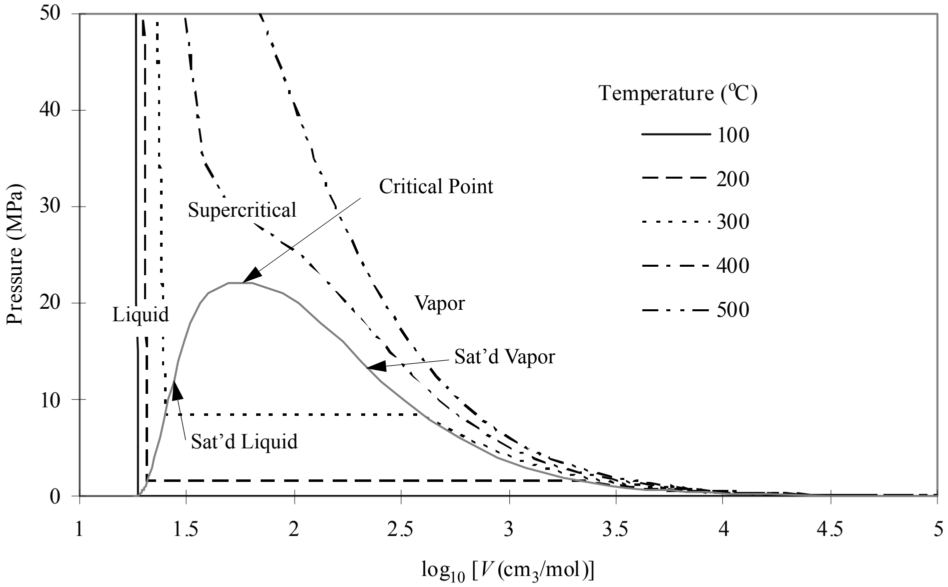

Figure 1.4 *P-V-T behavior of water at the same temperatures used in Fig. 1.3. The plot is prepared from the steam tables in Appendix E.*

ideal gas law simplifies many process calculations for common gases; for example, air at room temperature and pressures below 10 bars. However, you must always remember that the ideal gas law is an approximation (sometimes an excellent approximation) that must be applied carefully to any fluid. The behaviors are presented along **isotherms** (lines of constant temperature) and the deviations from the ideal gas law for water are obvious. Water is one of the most common substances that we work with, and water vapor behaves nearly as an ideal gas at 100°C (P^{sat} = 0.1014 MPa), where experimentally the vapor volume is 1.6718 m^3/kg (30,092 cm^3/mol) and by the ideal gas law we may calculate $V = RT/P$ = 8.314 · 373.15 / 0.1014 = 30,595 cm^3/mol. However, the state is the normal boiling point, and we are well aware that a liquid phase can co-exist at this state. This is because there is another density of water at these conditions that is also stable.[11]

We will frequently find it convenient to work mathematically in terms of molar density or mass density, which is inversely related to molar volume or mass volume, $\rho = 1/V$. Plotting the isotherms in terms of density yields a P-ρ diagram that qualitatively looks like the mirror image of the P-V diagram. Density is convenient to use because it always stays finite as $P \rightarrow 0$, whereas V diverges. Examples of P-ρ diagrams are shown in Fig. 7.1 on page 254.

! Real fluids have saturation conditions, bubble points, and dew points.

The conditions where two phases coexist are called **saturation conditions.** The terms "saturation pressure" and "saturation temperature" are used to refer to the state. The volume (or density) is called the saturated volume (or saturated density). Saturation conditions are shown in Fig. 1.4 as the "hump" on the diagram. The hump is called the **phase envelope.** Two phases coexist when the system conditions result in a state *inside* or *on* the envelope. The horizontal lines *inside* the curves are called **tie lines** that show the two volumes (**saturated liquid** and **saturated vapor**) that can coexist. The curve labeled "Sat'd Liquid" is also called the **bubble line,** since it represents conditions where boiling (bubbles) can occur in the liquid. The curve labeled "Sat'd Vapor" is also called a

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[11] This stability is determined by the Gibbs energy and we will defer proof until Chapter 9.

dew line, since it is the condition where droplets (dew) can occur in the vapor. Therefore, saturation is a term that can refer to either bubble or dew conditions. When the total volume of a system results in a system state *on* the saturated vapor line, only an infinitesimal quantity of liquid exists, and the state is indicated by the term “saturated vapor.” Likewise, when a system state is *on* the saturated liquid line, only an infinitesimal quantity of vapor exists, and the state is indicated by the term “saturated liquid.” When the total volume of the system results in a system *in between* the saturation vapor and saturation liquid volumes, the system will have vapor and liquid phases coexisting, each phase occupying a finite fraction of the overall system. Note that each isotherm has a unique saturation pressure. This pressure is known as the **saturation pressure** or **vapor pressure.** Although the vapor pressure is often used to characterize a pure liquid’s bubble point, recognize that it also represents the dew point for the pure vapor.

Following an isotherm from the right side of the diagram along a path of decreasing volume, the isotherm starts in the vapor region, and the pressure rises as the vapor is isothermally compressed. As the volume reaches the saturation curve at the vapor pressure, a liquid phase begins to form. Notice that further volume decreases do not result in a pressure change until the system reaches the saturated liquid volume, after which further decreases in volume require extremely large pressure changes. Therefore, liquids are often treated as **incompressible** even though the isotherms really do have a finite rather than infinite slope. The accuracy of the incompressible assumption varies with the particular application.

❗Liquids are quite incompressible.

As we work problems involving processes, we need to use properties such as the internal energy of a fluid.[12] Properties such as these are available for many common fluids in terms of a table or chart. For steam, both tables and charts are commonly used, and in this section we introduce the steam tables available in Appendix E. An online supplement is available to visualize the *P-V* and *P-T* representations in MATLAB permitting the user to interactively rotate the surface.

Steam Tables

When dealing with water, some conventions have developed for referring to the states which can be confusing if the terms are not clearly understood. **Steam** refers to a vapor state, and **saturated steam** is vapor at the dew point. For water, in the two-phase region, the term “wet steam” is used to indicate a vapor + liquid system.

Steam properties are divided into four tables. The first table presents saturation conditions indexed by temperature. This table is most convenient to use when the temperature is known. Each row lists the corresponding saturation values for pressure (vapor pressure), internal energy, volume, and two other properties we will use later in the text: enthalpy and entropy. Special columns represent the internal energy, enthalpy, and entropy of vaporization. These properties are tabulated for convenience, although they can be easily calculated by the difference between the saturated vapor value and the saturated liquid value. Notice that the **vaporization** values decrease as the saturation temperature and pressure increase. The vapor and liquid phases are becoming more similar as the saturation curve is followed to higher temperatures and pressures. At the **critical point,** the phases become identical. Notice in Fig. 1.4 that the two phases become identical at the highest temperature and pressure on the saturation curve, so this is the critical point. For a pure fluid, the **critical temperature** is the temperature at which vapor and liquid phases are identical on the saturation curve, and is given the notation T_c. The pressure at which this occurs is called the **critical pressure,** and is given the symbol P_c. A fluid above the critical temperature is often called **supercritical.**

❗The critical temperature and critical pressure are key characteristic properties of a fluid.

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[12] Calculation of these properties requires mastery of several fundamental concepts as well as application of calculus and will be deferred. We calculate energies for ideal gas in Chapter 2 and for real fluids in Chapter 8.

The second steam table organizes saturation properties indexed by pressure, so it is easiest to use when the pressure is known. Like the temperature table, vaporization values are presented. The table duplicates the saturated temperature table, that is, plotting the saturated volumes from the two tables would result in the same curves. The third steam table is the largest portion of the steam tables, consisting of superheated steam values. **Superheated** steam is vapor above its saturation temperature at the given pressure. The adjective "superheated" specifies that the vapor is above the saturation temperature at the system pressure. The adjective is usually used only where necessary for clarity. The difference between the system temperature and the saturation temperature, $(T - T^{sat})$, is termed the **degrees of superheat.** The superheated steam tables are indexed by pressure and temperature. The saturation temperature is provided at the top of each pressure table so that the superheat may be quickly determined without referring to the saturation tables.

Superheat.

The fourth steam table has liquid-phase property values at temperatures below the critical temperature and above each corresponding vapor pressure. Liquid at these states is sometimes called **subcooled liquid** to indicate that the temperature is below the saturation temperature for the specified pressure. Another common way to describe these states is to identify the system as **compressed liquid,** which indicates that the pressure is above the saturation pressure at the specified temperature. The adjectives "subcooled" and "compressed" are usually only used where necessary for clarity. Notice by scanning the table that pressure has a small effect on the volume and internal energy of liquid water. By looking at the saturation conditions together with the general behavior of Fig. 1.4 in our minds, we can determine the **state of aggregation** (vapor, liquid, or mixture) for a particular state.

Subcooled, compressed.

Example 1.3 Introduction to steam tables

For the following states, specify if water exists as vapor, liquid, or a mixture: (a) 110°C and 0.12 MPa; (b) 200°C and 2 MPa; (c) 0.8926 MPa and 175°C.

Solution:

(a) Looking at the saturation temperature table, the saturation pressure at 110°C is 0.143 MPa. Below this pressure, water is vapor (steam).

(b) From the saturation temperature table, the saturation pressure is 1.5549 MPa; therefore, water is liquid.

(c) This is a saturation state listed in the saturation temperature table. The water exists as saturated liquid, saturated vapor, or a mixture.

Linear Interpolation

Since the information in the steam tables is tabular, we must interpolate to find values at states that are not listed. To interpolate, we assume the property we desire (e.g., volume, internal energy) varies linearly with the independent variables specified (e.g., pressure, temperature). The assumption of linearity is almost always an approximation, but is a close estimate if the interval of the calculation is small. Suppose we seek the value of volume, *V,* at pressure, *P,* and temperature, *T,* but the steam tables have only values of volume at P_1 and P_2 which straddle the desired pressure value as shown in Fig. 1.5. The two points represent values available in the tables and the solid line represents the true behavior. The dotted line represents a linear fit to the tabulated points.

Linear interpolation is a necessary skill for problem solving using thermodynamic tables.

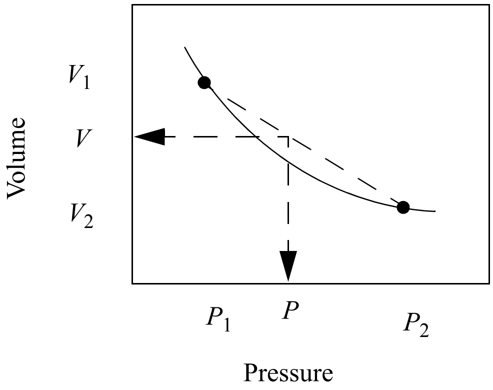


Figure 1.5 *Illustration of linear interpolation.*

If we fit a linear segment to the tabulated points, the equation form is $y = mx + b$, where y is the dependent variable (volume in this case), x is the independent variable (pressure in this case), m is the slope $m = \Delta y/\Delta x = (V_2 - V_1)/(P_2 - P_1)$, and b is the intercept. We can interpolate to find V without directly determining the intercept. Since the point we desire to calculate is also on the line with slope m, it also satisfies the equation $m = \Delta y/\Delta x = (V - V_1)/(P - P_1)$. We can equate the two expressions for m to find the interpolated value of V at P.

There are two quick ways to think about the interpolation. First, since the interpolation is linear, the fractional change in V relative to the volume interval is equal to the fractional change in P relative to the pressure interval. In terms of variables:

$$\frac{V - V_1}{V_2 - V_1} = \frac{P - P_1}{P_2 - P_1}$$

For example, $(V - V_1)$ is 10% of the volume interval $(V_2 - V_1)$, when $(P - P_1)$ is 10% of $(P_2 - P_1)$. We can rearrange this expression to find:

$$V = V_1 + \frac{P - P_1}{P_2 - P_1}(V_2 - V_1) \qquad 1.23$$

If we consider state "1" as the base state, we can think of this expression in words as

V = base V + (fractional change in P) · (volume interval size)

Another way to think of Eqn. 1.23 is by arranging it as:

$$V = V_1 + \frac{V_2 - V_1}{P_2 - P_1}(P - P_1) \qquad 1.24$$

which in words is

V = base V + slope · (change in P from base state)

Note that subscripts for 1 and 2 can be interchanged in any of the formulas if desired, provided that *all* subscripts are interchanged. In general, interpolation can be performed for any generic property M such that (modifying Eqn. 1.23)

$$M = M_1 + \frac{x - x_1}{x_2 - x_1}(M_2 - M_1) \qquad 1.25$$

where M represents the property of interest (e.g., V) and x is the property you know (e.g., P).

Example 1.4 Interpolation

Find the volume and internal energy for water at: (a) 5 MPa and 325°C and (b) 5 MPa and 269°C.

Solution:

(a) Looking at the superheated steam table at 5 MPa, we find the saturation temperature in the column heading as 263.9°C; therefore, the state is superheated. Values are available at 300°C and 350°C. Since we are halfway in the temperature interval, by interpolation the desired U and V will also be halfway in their respective intervals (which may be found by the average values):

$$U = (2699.0 + 2809.5)/2 = 2754.3 \text{ kJ/kg}$$

$$V = (0.0453 + 0.0520)/2 = 0.0487 \text{ m}^3\text{/kg}$$

(b) For this state, we are between the saturation temperature (263.9°C) and 300°C, and we apply the interpolation formula:

$$U = 2597.0 + \frac{269 - 263.9}{300 - 263.9}(2699.0 - 2597.0) = 2611.4 \text{ kJ/kg}$$

$$V = 0.0394 + \frac{269 - 263.9}{300 - 263.9}(0.0453 - 0.0394) = 0.0402 \text{ m}^3\text{/kg}$$

Double Interpolation

Occasionally, we must perform double or multiple interpolation to find values. The following example illustrates these techniques.

Example 1.5 Double interpolation

For water at 160°C and 0.12 MPa, find the internal energy.

Solution: By looking at the saturation tables at 160°C, water is below the saturation pressure, and will exist as superheated vapor, but superheated values at 0.12 MPa are not tabulated in the superheated table. If we tabulate the available values, we find

Example 1.5 Double interpolation (Continued)

	0.1 MPa	0.12 MPa	0.2 MPa
150°C	2582.9		2577.1
160°C			
200°C	2658.2		2654.6

We may either interpolate the first and third columns to find the values at 160°C, followed by an interpolation in the second row at 160°C, or interpolate the first and third rows, followed by the second column. The values found by the two techniques will not be identical because of the nonlinearities of the properties we are interpolating. Generally, the more precise interpolation should be done first, which is over the smaller change in U, which is the pressure interpolation. The pressure increment is 20% of the pressure interval [(0.12 – 0.1)/(0.2 – 0.1)]; therefore, interpolating in the first row,

$$U = 2582.9 + 0.2 \cdot (2577.1 - 2582.9) = 2581.7 \text{ kJ/kg}$$

and in the third row,

$$U = 2658.2 + 0.2 \cdot (2654.6 - 2658.2) = 2657.5 \text{ kJ/kg}$$

and then interpolating between these values, using the value at 150°C as the base value,

$$U = 2581.7 + 0.2 \cdot (2657.5 - 2581.7) = 2596.9 \text{ kJ/kg}$$

The final results are tabulated in the boldface cells in the following table:

	0.1 MPa	0.12 MPa	0.2 MPa
150°C	2582.9	2581.7	2577.1
160°C		2596.9	
200°C	2658.2	2657.5	2654.5

We also may need to interpolate between values in different tables, like the saturated tables and superheated tables. This is also straightforward as shown in the following example.

Example 1.6 Double interpolation using different tables

Find the internal energy for water at 0.12 MPa and 110°C.

Solution: We found in Example 1.3 on page 25 that this is a superheated state. From the superheated table we can interpolate to find the internal energy at 110°C and 0.1 MPa:

$$U = 2506.2 + 0.2 \cdot (2582.9 - 2506.2) = 2521.5 \text{ kJ/kg}$$

Example 1.6 Double interpolation using different tables (Continued)

At 0.2 MPa, 110°C is not found in the superheated table because the saturation temperature is 120.3°C, so the values at this pressure cannot be used. Therefore, we can find the desired internal energy by interpolation using the value above and the saturation value at 110°C and 0.143 MPa from the saturation temperature table:

$$U = 2521.5 + \frac{0.12 - 0.1}{0.143 - 0.1}(2517.7 - 2521.5) = 2519.7 \text{ kJ/kg}$$

Computer-Aided Interpolation

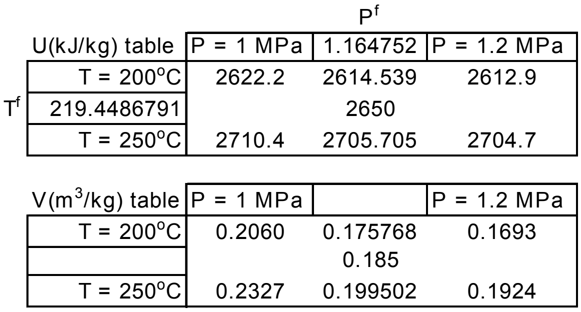
Occasionally, interpolation must be performed when the *T* and *P* are both unknown. Computers or spreadsheets can be helpful as shown in the next example.

Example 1.7 Double interpolation using Excel

Steam undergoes a series of state changes and is at a final state where $U = 2650$ kJ/kg and $V = 0.185$ m^3/kg. Find the *T* and *P*.

Solution: Scanning the steam tables, the final state is in the range 1.0 MPa < *P* < 1.2 MPa, 200°C < *T* < 250°C. The final state requires a double interpolation using *U* and *V*. One easy method is to set up the table in Excel. In each of the tables below, the pressure interpolation is performed first in the top and bottom rows, dependent on the pressure variable in the top of the center column, which can be set at any intermediate pressure to start. The temperature interpolation is then entered in the center cell of each table using the temperature variable. The formulas in both tables reference a common temperature variable cell and a common pressure variable cell. Solver is started and *T* and *P* are adjusted to make $U = 2650$ kJ/kg subject to the constraint $V = 0.185$ m^3/kg. (See Appendix A for Solver instructions.) The converged result is shown at $T = 219.6$°C and $P = 1.17$ MPa.

Example use of Excel for double interpolation.



P^f

	U(kJ/kg) table	P = 1 MPa	1.164752	P = 1.2 MPa
	T = 200°C	2622.2	2614.539	2612.9
T^f	219.4486791		2650	
	T = 250°C	2710.4	2705.705	2704.7

V(m^3/kg) table	P = 1 MPa		P = 1.2 MPa
T = 200°C	0.2060	0.175768	0.1693
		0.185	
T = 250°C	0.2327	0.199502	0.1924

Extrapolation

Occasionally, the values we seek are not conveniently between points in the table and we can apply the "interpolation" formulas to extrapolate as shown in Fig. 1.6. In this case, *T* lies outside the interval. Extrapolation is much less certain than interpolation since we frequently do not know "what curve lies beyond" that we may miss by linear approximation. The formulas used for extrapolation are identical to those used for interpolation.With the steam tables, extrapolation is generally not necessary at normal process conditions and should be avoided if possible.

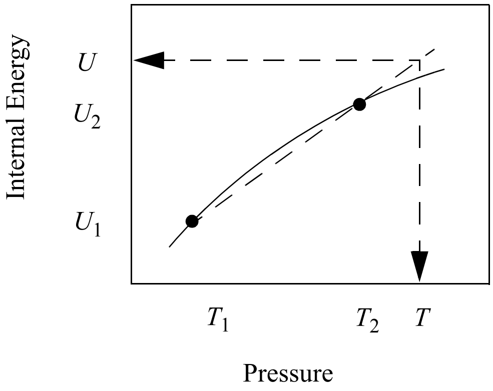

Internal Energy
U
U_2
U_1
T_1
T_2
T
Pressure

Figure 1.6 *Illustration of linear extrapolation.*

Phase Equilibrium and Quality

Along the saturation curve in Fig. 1.4 on page 23, there is just one **degree of freedom** ($F = C - P + 2 = 1 - 2 + 2 = 1$). If we seek saturation, we may choose either a T^{sat} or a P^{sat}, and the other is determined. The vapor pressure increases rapidly with temperature as shown in Fig. 1.7. A plot of ln P^{sat} versus $1/T^{sat}$ is nearly linear and over large intervals, so for accurate interpolations, vapor pressure data should be converted to this form before interpolation. However, the steam tables used

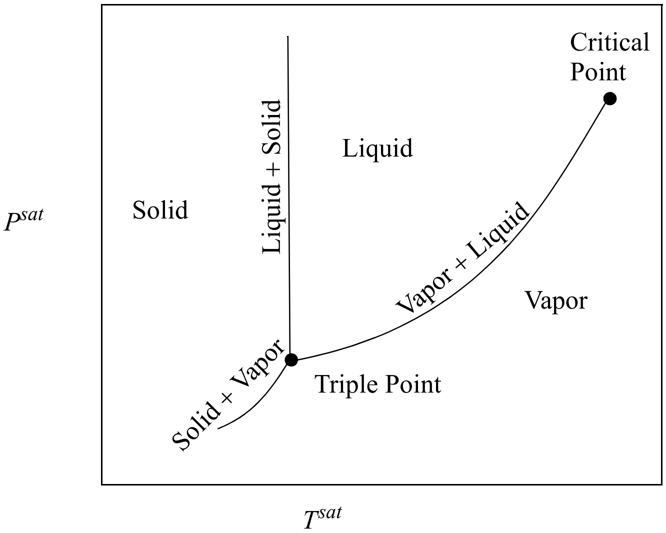

P^{sat}
Critical Point
Liquid + Solid
Liquid
Solid
Vapor + Liquid
Vapor
Solid + Vapor
Triple Point
T^{sat}

Figure 1.7 *P-T representation of real fluid behavior. Note that only vapor and liquid behavior is shown in Fig. 1.4 on page 23.*

with this text have small enough intervals that direct interpolation can be applied to P^{sat} and T^{sat} without appreciable error.

The saturation volume values of the steam tables were used to generate the phase diagram of Fig. 1.4 on page 23. Note that as the critical point is approached, the saturation vapor and liquid values approach one another. The same occurs for internal energy and two properties that will be used in upcoming chapters, enthalpy, *H,* and entropy, *S.* When a mixture of two phases exists, we must characterize the fraction that is vapor, since the vapor and liquid property values differ significantly.

The mass percentage that is vapor is called the **quality** and given the symbol *q*. The properties *V, U, H*, and *S,* may be represented with a generic variable *M.* The **overall value** of the state variable *M* is

❗Quality is the vapor mass percentage of a vapor/liquid mixture.

$$M = (1 - q)\, M^L + qM^V \tag{1.26}$$

which may be rearranged as

$$M = M^L + q(M^V - M^L)$$

but $(M^V - M^L)$ is just ΔM^{vap} and for internal energy, enthalpy, and entropy, it is tabulated in columns of the saturation tables. The value of overall *M* is

$$M = M^L + q\Delta M^{vap} \tag{1.27}$$

Look carefully at Eqn. 1.27 in comparison with Eqn. 1.25; it may be helpful to recognize a quality calculation as an interpolation between saturated liquid and saturated vapor. Two examples help demonstrate the importance of quality calculations.

Example 1.8 Quality calculations

Two kg of water coexists as vapor and liquid at 280°C in a 0.05 m^3 rigid container. What is the pressure, quality, and overall internal energy of the mixture?

Solution: The overall mass volume is $V = 0.05\ \text{m}^3/2\ \text{kg} = 0.025\ \text{m}^3/\text{kg}$. From the saturation temperature table, the pressure is 6.417 MPa. Using the saturation volumes at this condition to find *q,*

$$0.025 = 0.001333 + q\,(0.0302 - 0.0013)\ \text{m}^3/\text{kg}$$

which leads to $q = 0.82$. The overall internal energy is

$$U = 1228.33 + 0.82 \cdot 1358.1 = 2342\ \text{kJ/kg}$$

Example 1.9 Constant volume cooling

Steam is initially contained in a rigid cylinder at $P = 30$ MPa and $V = 10^{2.498}\text{cm}^3$/mole. The cylinder is allowed to cool to 300°C. What is the pressure, quality, and overall internal energy of the final mixture?

Solution: The overall mass volume is $V = 10^{2.498}\text{cm}^3\text{-mole}^{-1} \cdot 10^{-6}(\text{m}^3/\text{cm}^3)/(18.02\text{E-3kg/mole}) = 0.01747\ \text{m}^3/\text{kg}$. From the superheated steam table at 30 MPa, the initial temperature is 900°C. When the cylinder is cooled to 300°C, the path is shown in Fig. 1.8 below. You should notice that there is no pressure in the superheated steam tables that provides a volume of $V = 0.01747\ \text{m}^3/\text{kg}$. Look hard, they are all too large. (Imagine yourself looking for this on a test when you are in a hurry.) Now look in the saturated steam tables at 300°C. Notice that the saturated vapor volume is $0.0217\ \text{m}^3/\text{kg}$. Since that is higher than the desired volume, but it is the lowest vapor volume at this temperature, we must conclude that our condition is somewhere between the saturated liquid and the saturated vapor at a pressure of 8.588 MPa. (When you are in a hurry, it is advisable to check the saturated tables first.) Using the saturation volumes at 300°C condition to find q,

$$0.01747 = 0.001404 + q\ (0.0217 - 0.001404)\ \text{m}^3/\text{kg}$$

which leads to $q = (0.01747 - 0.001404)/(0.0217 - 0.001404) = 0.792$. The overall internal energy is

$$U = 1332.95 + 0.792 \cdot 1230.67 = 2308\ \text{kJ/kg}$$

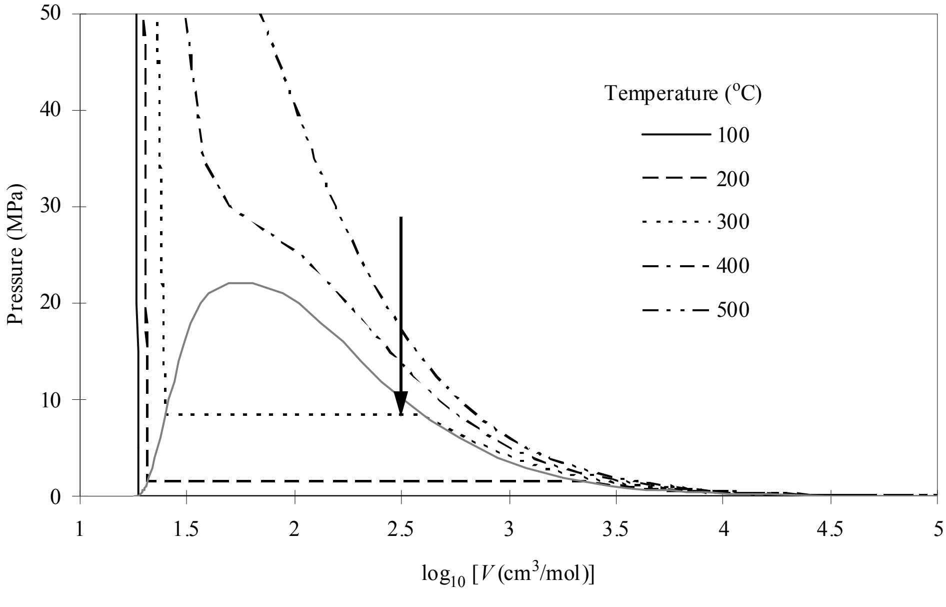


Figure 1.8 *P-V-T behavior of water illustrating a quality calculation.*

1.6 SUMMARY

Years from now you may have some difficulty recalling the details presented in this text. On the other hand, the two basic premises outlined in this introductory section are so fundamental to technically educated people that you really should commit them to long-term memory as soon as possible. Formally, we may state our two basic premises as the first and second "laws" of thermodynamics.[13]

First Law: Overall energy is conserved (you can't get something for nothing).

Second Law: Overall entropy changes are greater than or equal to zero (generation of disorder results in lost work).

The first law is further developed in Chapters 2 and 3. The concepts of entropy and the second law are developed in Chapter 4 and process applications in Chapter 5. The exact relationship between the two basic premises and these two laws may not become apparent until some time later in this text, but you should begin to absorb and contemplate these fundamentals now. There are times when the endeavor to apply these simple laws seems daunting, but the answer appears simple in retrospect, once obtained. By practicing adaptation of the basic principles to many specific problems, you slowly grasp the appropriate connection between the basic premises and finding the details. Try not to be distracted by the vocabulary or the tedious notation that goes into keeping all the coupled systems classified in textbook fashion. Keep in mind that other students have passed through this and found the detailed analysis to be worth the effort.

Important Equations

The content of this chapter is primarily about laying down the fundamental concepts more than deriving equations. Nevertheless, three concepts that we refer to repeatedly can be expressed by equations. Of course, the ideal gas law is important, but an implication of it that may be new is:

$$T = \frac{M_w}{3R}\langle v^2 \rangle \text{ (for monatomic molecules in 3D)} \qquad 1.28$$

This equation conveys that temperature is closely related to molecular kinetic energy. Although derived with the ideal gas assumption, it turns out to be true for real fluids as well. Every time you alter the temperature, you should think about the implications for molecular kinetic energy. Another important equation relates to deviations from the ideal gas law:

$$u(r) = \begin{cases} \infty \text{ if } r \le \sigma \\ -\varepsilon \text{ if } \sigma < r \le \lambda\sigma \\ 0 \text{ if } r > \lambda\sigma \end{cases} \qquad 1.29$$

This is the square well potential model, the simplest characterization of how real molecules attract and repel. As you add energy to the system, real fluids may absorb that energy by moving molecules from inside the square well to outside, converting potential energy into kinetic energy without altering the temperature as an ideal gas would. A simple example is boiling. Ideal gases cannot boil, but real fluids can. This interplay between kinetic energy, temperature, and potential energy pervades many discussions throughout the text.

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[13] There is also a **third law of thermodynamics,** as discussed by Denbigh, K., 1981. *The Principles of Chemical Equilibrium*, London: Cambridge University Press, p. 416. The third law is of less direct interest in this introductory text, however.

Finally, we can write a generic equation that symbolizes the procedure for interpolation:

$$M = M_1 + \frac{x - x_1}{x_2 - x_1}(M_2 - M_1) \qquad 1.30$$

A similar equation is used for quality calculations which can be viewed as an interpolation between saturated liquid and saturated vapor. Throughout Unit I, we refer extensively to the steam tables and interpolation to account for deviations from the ideal gas law.

Test Yourself

1. Draw a sketch of the force model implied by the square-well potential, indicating the position(s) where the force between two atoms is zero and the positions where it is nonzero.
2. Explain in words how the pressure of a fluid against the walls of its container is related to the velocity of the molecules.
3. What is it about molecules that requires us to add heat to convert liquids to gases?
4. If the kinetic energy of pure liquid and vapor molecules at phase equilibrium must be the same, and the internal energy of a system is the sum of the kinetic and potential energies, what does this say about the intensive internal energy of a liquid phase compared with the intensive internal energy of the gas phase?
5. Explain the terms "energy," "potential energy," "kinetic energy," and "internal energy."
6. How is the internal energy of a substance related to the intermolecular pair potentials of the molecules?
7. Are T and P intensive properties? Name two intensive properties and two extensive properties.
8. How many degrees of freedom exist when a pure substance coexists as a liquid and gas?
9. Can an ideal gas condense? Can real fluids that follow the ideal gas law condense?
10. Give examples of bubble, dew, saturation, and superheated conditions. Explain what is meant when wet steam has a quality of 25%.
11. Create and solve a problem that requires double interpolation.

1.7 PRACTICE PROBLEMS

P1.1 Estimate the average speed (mph) of hydrogen molecules at 200 K and 3 bars. (ANS. 3532)

P1.2 Estimate the entropy (J/g-K) of steam at 27.5MPa and 425C. (ANS. 5.1847)

1.8 HOMEWORK PROBLEMS

Note: *Some of the steam table homework problems involve enthalpy, H, which is defined for convenience using properties discussed in this chapter, $H \equiv U + PV$. The enthalpy calculations can be performed by reading the tabulated enthalpy values from the tables in an analogous manner used for internal energy. We expect that students will be introduced to this property in course lectures in parallel with the homework problems that utilize H.*

1.1 In each of the following, sketch your estimates of the intermolecular potentials between the given molecules and their mixture on the same pair of axes.

(a) Chloroform is about 20% larger than acetone and about 10% stickier, but chloroform and acetone stick to one another much more strongly than they stick to themselves.
(b) You have probably heard that “oil and water don’t mix.” What does that mean in molecular terms? Let’s assume that oil can be characterized as benzene and that benzene is four times larger than water, but water is 10% stickier than benzene. If the ε_{12} parameter is practically zero, that would represent that the benzene and water stick to themselves more strongly than to one another. Sketch this.

1.2 For each of the states below, calculate the number of moles of ideal gas held in a three liter container.

(a) $T = 673$ K, $P = 2$ MPa
(b) $T = 500$ K, $P = 0.7$ MPa
(c) $T = 450$ K, $P = 1.5$ MPa

1.3 A 5 m^3 outdoor gas storage tank warms from 10°C to 40°C on a sunny day. If the initial pressure was 0.12 MPa at 10°C, what is the pressure at 40°C, and how many moles of gas are in the tank? Use the ideal gas law.

1.4 An automobile tire has a pressure of 255 kPa (gauge) in the summer when the tire temperature after driving is 50°C. What is the wintertime pressure of the same tire at 0°C if the volume of the tire is considered the same and there are no leaks in the tire?

1.5 A 5 m^3 gas storage tank contains methane. The initial temperature and pressure are $P = 1$ bar, $T = 18$°C. Using the ideal gas law, calculate the P following each of the successive steps.

(a) 1 m^3 (at standard conditions) is withdrawn isothermally.
(b) The sun warms the tank to 40°C.
(c) 1.2 m^3 (at standard conditions) is added to the tank and the final temperature is 35°C.
(d) The tank cools overnight to 18°C.

1.6 Calculate the mass density of the following gases at 298 K and 1 bar.

(a) Nitrogen
(b) Oxygen
(c) Air (use average molecular weight)
(d) CO_2
(e) Argon

1.7 Calculate the mass of air (in kg) that is contained in a classroom that is 12m x 7m x 3m at 293 K and 0.1 MPa.

1.8 Five grams of the specified pure solvent is placed in a variable volume piston. What is the volume of the pure system when 50% and 75% have been evaporated at: (*i*) 30°C, (*ii*) 50°C? Use the Antoine equation (Appendix E) to relate the saturation temperature and saturation pressure. Use the ideal gas law to model the vapor phase. Show that the volume of the system occupied by liquid is negligible compared to the volume occupied by vapor.

(a) Hexane ($\rho^L = 0.66$ g/cm^3)
(b) Benzene ($\rho^L = 0.88$ g/cm^3)
(c) Ethanol ($\rho^L = 0.79$ g/cm^3)
(d) Water without using the steam tables ($\rho^L = 1$ g/cm^3)
(e) Water using the steam tables

1.9 A gasoline spill is approximately 4 liters of liquid. What volume of vapor is created at 1 bar and 293 K when the liquid evaporates? The density of regular gasoline can be estimated by treating it as pure isooctane (2,2,4-trimethylpentane $\rho^L = 0.692$ g/cm^3) at 298 K and 1 bar.

1.10 The gross lifting force of a balloon is given by $(\rho_{air} - \rho_{gas})\underline{V}_{balloon}$. What is the gross lifting force (in kg) of a hot air balloon of volume 1.5E6 L, if the balloon contains gas at 100°C and 1 atm? The hot gas is assumed to have an average molecular weight of 32 due to carbon dioxide from combustion. The surrounding air has an average molecular weight of 29 and is at 25°C and 1 atm.

1.11 LPG is a useful fuel in rural locations without natural gas pipelines. A leak during the filling of a tank can be extremely dangerous because the vapor is denser than air and drifts to low elevations before dispersing, creating an explosion hazard. What volume of vapor is created by a leak of 40L of LPG? Model the liquid before leaking as propane with $\rho^L = 0.24$ g/cm^3. What is the mass density of pure vapor propane after depressurization to 293 K and 1 bar? Compare with the mass density of air at the same conditions.

1.12 The gas phase reaction $A \rightarrow 2R$ is conducted in a 0.1 m^3 spherical tank. The initial temperature and pressure in the tank are 0.05 MPa and 400 K. After species A is 50% reacted, the temperature has fallen to 350 K. What is the pressure in the vessel?

1.13 A gas stream entering an absorber is 20 mol% CO_2 and 80 mol% air. The flowrate is 1 m^3/min at 1 bar and 360 K. When the gas stream exits the absorber, 98% of the incoming CO_2 has been absorbed into a flowing liquid amine stream.

(a) What are the gas stream mass flowrates on the inlet and outlets in g/min?
(b) What is the volumetric flowrate on the gas outlet of the absorber if the stream is at 320 K and 1 bar?

1.14 A permeation membrane separates an inlet air stream, *F,* (79 mol% N_2, 21 mol% O_2), into a permeate stream, *M,* and a reject stream, *J.* The inlet stream conditions are 293 K, 0.5 MPa, and 2 mol/min; the conditions for both outlet streams are 293 K and 0.1 MPa. If the permeate stream is 50 mol% O_2, and the reject stream is 13 mol% O_2, what are the volumetric flowrates (L/min) of the two outlet streams?

1.15 (a) What size vessel holds 2 kg water at 80°C such that 70% is vapor? What are the pressure and internal energy?

(b) A 1.6 m^3 vessel holds 2 kg water at 0.2 MPa. What are the quality, temperature, and internal energy?

1.16 For water at each of the following states, determine the internal energy and enthalpy using the steam tables.

	T(°C)	P(MPa)
(a)	100	0.01
(b)	550	6.25
(c)	475	7.5
(d)	180	0.7

1.17 Determine the temperature, volume, and quality for one kg water under the following conditions:

(a) $U = 3000$ kJ/kg, $P = 0.3$ MPa
(b) $U = 2900$ kJ/kg, $P = 1.7$ MPa
(c) $U = 2500$ kJ/kg, $P = 0.3$ MPa
(d) $U = 350$ kJ/kg, $P = 0.03$ MPa

1.18 Two kg of water exist initially as a vapor and liquid at 90°C in a rigid container of volume 2.42 m^3.

(a) At what pressure is the system?
(b) What is the quality of the system?
(c) The temperature of the container is raised to 100°C. What is the quality of the system, and what is the pressure? What are $\Delta \underline{H}$ and $\Delta \underline{U}$ at this point relative to the initial state?
(d) As the temperature is increased, at what temperature and pressure does the container contain only saturated vapor? What is $\Delta \underline{H}$ and $\Delta \underline{U}$ at this point relative to the initial state?
(e) Make a qualitative sketch of parts (a) through (d) on a P-V diagram, showing the phase envelope.

1.19 Three kg of saturated liquid water are to be evaporated at 60°C.

(a) At what pressure will this occur at equilibrium?
(b) What is the initial volume?
(c) What is the system volume when 2 kg have been evaporated? At this point, what is $\Delta \underline{U}$ relative to the initial state?
(d) What are $\Delta \underline{H}$ and $\Delta \underline{U}$ relative to the initial state for the process when all three kg have been evaporated?
(e) Make a qualitative sketch of parts (b) through (d) on a P-V diagram, showing the phase envelope.

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