



REFRIGERATION

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REFRIGERATION

WHAT IT IS

Refrigeration is the achievement of temperatures below that of the local environment. The main purpose of refrigeration is thermal conditioning (e.g. for food preservation or air conditioning), and the basic apparatus is a refrigerator, a thermal machine producing cold. Other names for special types of refrigerators are freezers, chillers, cryocoolers, as well as the informal word fridge. Small refrigerators usually comprise the cabinet to be cooled (e.g. the fridge), but larger refrigerators are placed in machinery rooms outside the cold storage (applicable to air conditioners too).

It is not so long ago that the only means of keeping food cool were cellars, and putting buckets down a well (a few metres below ground in temperate climates, temperature remains nearly constant at 15 °C all

year around), and the only means of air conditioning were the fan, and splashing some water around (the latter only in dry climates, where porous earthenware pots were used to keep water cool, too).

Producing cold is basically different to and much more difficult than producing heat; people learnt to produce heat 500 000 years ago (in the ice ages), whereas refrigeration started only 150 years ago (in the 19th century).

Refrigeration can be analysed just at a conceptual system level as done here (what purpose it must accomplish, how it can be done in principle, how it can be done in practice), or it can be analysed in more detail to include also the study of the components used in refrigeration equipment: heat exchangers, compressors, valves, absorbers, pumps, piping, supports, controls, selection, design, etc. We here focus on refrigeration cycles more than on the actual components used. Notice already that any power-producing cycle, as those reviewed under [Chapter 17: Power](#), would produce a refrigeration effect if run backwards in the T - s diagram.

Most of the time, heat pumps (used for heating) are considered under the refrigeration heading, since the fundamentals, systems and operations are basically identical: to pump low-temperature thermal energy up to higher-temperature thermal energy; the difference is only the interest of the user: on the cold side for refrigerators, and on the hot side for heat-pumps. Indeed, most air conditioning systems can work as a refrigerator or as a heat pump by properly changing the flow with four-way valves (an overall picture of such a combined system is presented in [Thermal systems](#)).

Refrigeration is sometimes studied under the practice-oriented HVAC-R envelop (HVAC stands for heating, ventilation and air-conditioning (refrigeration) of habitable space, whereas Refrigeration also includes other non-space cooling applications), since all of these disciplines deal with thermal conditioning of some space or component load.

Cold-producing devices are discussed below, but a basic procedure to produce cold in a system at ambient temperature was described already in [Chapter 1](#) in connection with the internal energy equation (1.9-10):

$$mc_v\Delta T = Q + E_{mdf} - \int p dV \quad (1)$$

i.e., in absence of any colder system to download thermal energy to (i.e. with $Q=0$), and knowing that energy dissipated by friction is $E_{mdf} \geq 0$ in any process, we can lower the initial temperature of a system (i.e. achieve $\Delta T < 0$) by forcing a quick expansion in a compressible substance ($dV > 0$). This adiabatic cooling may be used to cool (by normal heat transfer) the load to be refrigerated. Of course, the expansion must end sooner or later, and to restart the cycle we will have to compress the working substance (in most cases by a mechanical vapour compressor), which increases its temperature, and have to get rid of the thermal energy, which demands a heat sink. It is obvious that a highly compressible working fluid, with minimum friction dissipation, is to be preferred.

Instead of the simple expansion of a gas, the expansion of vapours from a liquid is most used in refrigeration. A typical refrigerator consists of a compressor that aspirates vapours from a vaporiser, a condenser where the compressed vapours condense, and an expansion valve that flashes to the vaporiser. In other refrigeration systems, vapours are not mechanically aspirated but absorbed in another liquid or adsorbed in a solid, which are later regenerated.

Besides the typical mechanical compression refrigerator, and its relative, the absorption refrigerator, there are other less used refrigeration processes, such as gas expansion devices, thermoelectric devices, and endothermic mixing (evaporative coolers and freezing mixtures). Freezing mixtures are covered under [Solution properties](#) and under [Cold pads](#). [Cooling towers](#) are studied under [Humid air](#), and are widely used in industry as direct contact evaporative heat exchangers; they are rarely considered under the refrigeration heading, in spite of the fact that they may function as a genuine refrigeration device (lowering the temperature below that of the local environment), because they normally do not operate in that range, and leave the cooled water with a temperature above that of the environment.

Refrigeration presents several genuine problems that must be understood from the beginning, to answer, for instance, the typical question customers ask to air-conditioners sellers: why there are not portable equipment that just plug to the mains and produce cold, without cumbersome installation, just plug and play, as heaters?

Ductless problem

A portable air conditioner (i.e. a room-space refrigerator), cannot work steadily within a room without exchanging fluids with the outdoors (i.e. it cannot work ductless), contrary to a heater. The reason is not obvious but demands deep thermodynamic insight.

Consider a closed room. Its energy balance in steady state must be $dE/dt = \dot{Q} + \dot{W} = 0$, with $\dot{Q} > 0$ in the refrigeration case (heat inputs), and $\dot{Q} < 0$ in the heating case (heat escapes). In the case of heating, you draw electricity from the mains, $\dot{W} > 0$ (work inputs), to balance the heat losses, $\dot{Q} < 0$, to the cold environment. In the steady refrigeration case, however, you would have to get rid of electricity through the socket, $\dot{W} < 0$, to balance the heat gain from the hot outside, $\dot{Q} > 0$.

No, it is not impossible to push electricity on the mains (it is difficult, special equipment and a licence are needed, but it is not impossible); many medium-size consumers do presently sell electricity to the grid, and the trend is in that direction. The problem is that, again, you cannot operate at a steady state a device that injects electrical energy on the plug without exchanging fluids with the outdoors (i.e. it cannot work ductless). Why? Entropy is the final answer.

[Entropy](#) cannot be destroyed (consumed), only generated and transferred from one system to another (in an isolated system, entropy can only increase). In the heating case, there is an entropy flow outwards associated with the heat loss, $\dot{Q}/T_{in} < 0$

$dS/dt = \dot{Q}/T_{in} + \dot{S}_{gen} = 0$.

In the refrigeration case the same equation applies, but now there is an entropy flow inwards, $\dot{Q}/T_{in} > 0$

because entropy generation cannot be negative, i.e., it must be $\dot{S}_{gen} > 0$; the way out to this dilemma is to break the closure condition and allow for some mass transfer and an associated heat transfer and its accompanying entropy flow, outwards. The energy and entropy balances (see [Chapter 5](#)) now stand as $dE/dt = \dot{Q} + \dot{W} + \dot{m}(h_{in} - h_{out}) = 0$ and $dS/dt = \dot{Q}/T_{in} + \dot{S}_{gen} + \dot{m}(s_{in} - s_{out}) = 0$, but now we have in the mass flow a negative term in both equations, which can match the two other positive entries.

It is for the same reason that any living being in a steady state must dissipate heat, i.e. the body must have a temperature above that of the environment (not only the hot blood animals, which are more properly called homeothermic). We can live in environments at more than our 37 °C internal temperature, but only by throwing mass away (sweating), which we cannot keep up for long.

It might be argued that the refrigerator in the kitchen has no ducts to the outdoors; it only has the electrical cord. The answer is that, for the kitchen room as a whole, the refrigerator does not produce cold but heat, i.e. it acts like a stove. And, if one considers the inside space of the refrigerator, there are indeed fluid ducts passing through its walls.

Notice that all this reasoning applies to a steady state; one may conceive non-steady situations in which a simple appliance plugs in and produces cold, if it is able to accumulate the energy and entropy generated within. There is no problem to accumulate a lot of energy in a small place, a fuel could be synthesised, but accumulating a lot of entropy in a small place is much more problematic (one way might be to raise an object to a high temperature, but losses would work against). And, of course, you can produce cold by bringing some cold object inside, as best exemplified by the typical icebox (an insulated cabinet packed with ice for storing food).

Finally notice that some vendors call ‘ductless system’ a system with the ducts within the walls, i.e. with ‘no visible ducts’ or visible outside only.

Humidity problem

Water-vapour condensation is of paramount importance in refrigeration and heat pump systems, because, unlike heating and power applications, cooling generates most of the times a water condensate (liquid in most cases, but solid in some cases) that must be taken care of (piping the liquid drip to a sink, and defrosting the ice if any).

The problem is that cooling (i.e. a decrease in temperature at constant pressure) increases [relative humidity](#), in spite of the fact that moisture is conserved. Moisture measures water contents, and can only be changed by adding or removing water, but relative humidity measures the water content relative to the maximum water content at those p - T conditions (saturation), and temperature decreases when cooling.

Thence, when ambient air is being cooled, humidity increases and can reach saturation (100 % RH at the dew-point) and condensation takes place, either in liquid or solid form, depending on initial conditions; e.g. in the case of ambient air initially at 15 °C and 50 % RH, condensation occurs at $T_{dew}=4.5$ °C in the form of little droplets that usually pour down, whereas in the case of drier or colder air, say at 15 °C and

10 % RH, or at $-7.5\text{ }^{\circ}\text{C}$ and 50 % RH, condensation occurs at $-15\text{ }^{\circ}\text{C}$ in the form of ice crystals that attach to cold surfaces, trapping air among the ice spikes and flakes.

To get rid of condensed water, vaporisers have a drain (although the amount of condensate may seem small, drainage must be done properly to a sewage, or dissolved in outdoor air as in portable air-conditioners, not just let it drop on passing-by people as in some window and over-door installations). And a harder problem is to get rid of water condensed in solid form (see [defrosting](#)). Notice that water condensation takes place inside the refrigerated room, but outside the heat-pumped room (were the problem of ice formation may occur in very cold weather).

Saturated air may be good for the skin and the lungs (at moderate temperatures), but bad for transpiration in hot environments, and worse for porous walls and [food preservation](#). Thence, refrigeration must always be accompanied by dehumidification in the same apparatus (and the cooling load is the sum of cooling the air and condensing the water).

Temperature-range problem

Another big difference between refrigeration and heating is the temperature range available for space conditioning: it is very easy to rise the temperature of a system more than 1000 K (e.g. by burning a fuel in air), achieving great heating power and heat-transfer rates (because of the high ΔT in $\dot{Q} = KA\Delta T$); on the contrary, it is impossible to lower the temperature of our environment by 1000 K, and lowering 100 K is already extremely difficult, with drops of a few tens of kelvin being the state of the art. This implies that undesired heat leakage through a non-perfect adiabatic wall, that for space heating was just an economic burden, for refrigeration is a big issue, as demonstrated by the initial developments of one-metre-thick straw-filled or sawdust-filled insulated walls in the 19th c. and the air-evacuated double-wall of the vacuum-flask invention in 1892 by Dewar (Dewar flask or thermos bottle).

Notice that even if low-thermal-gap systems were developed, e.g. a water-chilled floor at $5\text{ }^{\circ}\text{C}$, similarly to the radiant floor heating at $35\text{ }^{\circ}\text{C}$, to keep a room at $20\text{ }^{\circ}\text{C}$, the humidity problem would have to be separately tackled (moisture gains are naturally vented in winter, but moisture gains in summer are not).

Heat-flow-rate problem

As just said, heat-insulation technology is of paramount importance in refrigeration, and this is for two different reasons: for the small temperature range, and for the small cooling capacity.

On the one hand, real operation of refrigerators demand a temperature jump at the heat exchangers where the working fluid interacts with the surroundings, similar to the normal heat engine case, but there was ample temperature range in the 1000 K typical temperature-span in heat-engines to accommodate for a few-kelvin heat-exchanger jump, what is a much more severe handicap in the few-tens-of-kelvin typical temperature-span in refrigerators.

On the other hand, heating and refrigeration loads are typically of different power size; e.g. at a home kitchen, a fridge has less than 200 W and a cooking range more than 2000 W; the air conditioning at

home may have 2 kW and the heating 20 kW. It is understandable that a spurious heat loss of a given amount will have a major impact on a weak refrigeration system than on a strong heating system.

Noise problem

Typical heating systems are silent, from a simple electrical heater to a central heating system with a quiet gas-heater aside and hot-water radiators on site. However, in a refrigeration and air conditioning system, there are typically three sources of noise: the compressor (in the typical vapour-compression machine), the fans to force the air around in the vaporiser and the condenser, and the two-phase fluid flow (with its characteristic hissing). Even in central air-conditioning systems with machines aside, and cold-air distribution, there is the in-situ air-diffuser noise.

In the typical domestic air-conditioning split system, the compressor and its associated noise is on the outside (on the neighbours side often), but there is a need for a fan in the internal unit to force the air within the refrigerated space, since the natural convection associated to the temperature difference is smaller than in a heating system (typically 10 °C, against 60 °C in a radiator).

WHAT IT IS NOT

Refrigeration is not the flow of heat from cold to hot; thermal energy can only flow as heat from hot to cold regions. In a refrigerator, heat flows from the cold load down to the colder vaporiser (in a common refrigerator), where it increases the refrigerant thermal energy, that is converted adiabatically to a much higher temperature, from where heat flows, down the temperature scale again, to the ambient sink.

Refrigeration is not the same as cooling, in spite of both terms implying a decrease in temperature. Notice the conceptual difference between them:

- Cooling is a heat transfer process, i.e. down the temperature gradient, that can be natural (left alone) or artificially accelerated (e.g. by blowing).
- Refrigeration is getting temperatures below that of the local environment, and is always an artificial process (requiring always an exergy expenditure). There are heat transfer processes in refrigeration but this is not enough; some adiabatic expansion of a fluid or other non-heat-transfer process is required.

Notwithstanding this clear difference in meaning, the words refrigeration and cooling are sometimes used indistinguishably even in the scientific literature (we also take that liberty sometimes, here). Both processes are considered under HVAC.

WHAT IT IS FOR

The purpose of refrigeration is to bring (or maintain) a system to temperatures below that of the environment; but what is the advantage of low temperatures? Human basic resources are: clean air, potable water, and edible food (besides peace, health and appreciation by others and by oneself). Nowadays we want also air conditioning, cold drinks, and refrigerated-store food, so refrigeration is used to better meet all these basic human needs and conveniences.

Perhaps the basic application of refrigeration is food preservation. We must feed regularly, but food shows up in nature in discontinuous chunks: occasional hunting and gathering, or controlled breeding and seasonal cropping. The solution has been food storage, but then the problem is that food is difficult to preserve (implying also it is difficult to transport). Many food-preservation techniques have been developed since ancient times (see Food preservation, below), but the best one seems to be refrigeration, developed since the late 19th c. Although, at global scale, over-population, water and energy shortage and global warming are the most acute problems to humankind, at a local scale lack of food is still a mortal problem to too-many people in the world; although there is enough food globally, it is not available at the right place and the right time.

But refrigeration is not only important to food storage and transport, including slaughtering yards, fermentation cellars of breweries, ice-cream industry, fruit and vegetable stores, etc. Refrigerated spaces are needed for human comfort (air conditioning), animal and vegetal growth optimisation, electronics and precision machinery operations, artificial skating rinks and snow parks, etc. Sometimes, refrigeration is not intended for space cooling but for space dehumidification, instead of desiccants. Refrigeration has even been applied to ease the drilling of shafts in water-logged grounds, freezing it by pumping cold brine through a double wall along the shaft.

In economic terms, the refrigeration industry is comparable to the automobile industry (a third of its sales in 2000); in fact, the largest share of refrigeration sales in 2000 (some 30 % of new systems) were for mobile applications, with other 25 % for fixed air-conditioning, 25 % for domestic refrigerators and freezers (there are some 10^9 units), and 20 % for fixed commercial systems. Refrigeration equipment consumes 15 % of world electricity production. Peaks in electricity demand nowadays occur more frequently during the summer period, not only in southern countries but in most of the EU, because of the increasing use of air-conditioning (mainly dependent on electricity) has surpassed the associated consumption for heating (mainly dependent on gas and oil).

HISTORY

A comparative summary of the historical developments in refrigeration and air conditioning is presented in Table 1.

Table 1. Historical development in refrigeration and air conditioning.

Date	Refrigeration	Air conditioning
15th c. b.C.	First mention of making ice, in ancient Egypt, by night-cooling, for refreshment and fever treatment.	Evaporative cooling used to cool air in dry climate by water splashing.
2nd c. a.D.	Galen proposes four degrees of coldness (and four degrees of heating).	
1700s	First artificial ice production, by aspirating ether vapours, for medical purpose.	
1800s	Natural ice regional and world-wide markets expand. Ferdinand Carré invented in 1846 the ammonia absorption cycle.	J. Gorrie in Florida made a hospital-ward refrigerated by blowing air with a fan over ice, to prevent diseases.
1865	First commercial ice-makers, using Carré's ammonia absorption plants.	

1873	First commercial refrigerator, by von Linde, using an ammonia vapour compressor (he deduced that this method was superior to the absorption one; in 1879 he gave up his professorship to start the Linde company). The first closed-loop vapour compression refrigerator was patented in London by J. Perkins.	Linde also built the first domestic air conditioning (for an Indian Rajah).
1880	First frozen-meat ocean transport, using air compression and expansion. Most breweries in Germany and USA replaced natural-ice cooling by refrigeration machines. However, harvesting natural ice was still dominant (Paris consumed 10 million ton per year, brought from Scandinavia); artificial ice industry was still immature (it used poison fluids, and the machines failed often).	
1900	Development of large artificial ice-making firms, using ammonia compressor driven by a steam engine.	First refrigerated public building in 1901.
1911		Carrier, in an ASME meeting, presented the refrigerator-dehumidifier
1914	Kelvinator introduces the thermostatic valve.	
1918	Frigidaire (assoc. to GM) sells domestic units at \$1000.	
1920s	GE develops the sealed compressor in 1928. Frigidaire units at \$500 (still bulky: 170 kg). One million units sold, mostly using SO ₂ .	Carrier units in theatres and cinemas.
1925	Electrolux developed an absorption refrigerator without moving parts (marketed in USA by Servel).	
1928	T. Midgely found a safe refrigerant, CCl ₂ F ₂ , commercially synthesised in 1929 by DuPont-GM from CCl ₄ and HF, trade-named as Freon.	
1932		Small window units by GE.
1934	Door-shelves were proposed, but were discarded.	
1939	GE develops the two-doors combined frigo-freezer.	Firs car air conditioning unit.
1960	Domestic refrigerators popularise; replacing ice-chests.	Most American shopping centres and hotels conditioned.
1980	Self-defrosting units. Domestic units with ice-cube and chip-ice dispensers.	Domestic air conditioning popularises.

The history of refrigeration is nearly the same as the history of making ice, artificial ice, since the history of natural ice is another story: homo-sapiens era is the quaternary period in the history of Earth, the last 2 million years, and, although there have been little climatic changes during the last 10 000 years (Holocene), during the rest of the quaternary period (Pleistocene) major ice ages occurred, lasting some 100 000 years each (with intermediate warm periods of some 10 000 years), with polar ice caps extending to middle latitudes (although the average Earth surface temperature was just 9 °C below the present 15 °C).

As another cold curiosity, Table 2 shows the most recent climate extremes.

Table 2. Lowest temperature records in the world (by continent) [from NOAA (USA)].

Continent	T [°C]	Place	Altitude [m]	Date
Antarctica	-89	Vostok	3400	21 Jul 1983
Asia	-68	Oimekon, Russia	790	6 Feb 1933

Asia	-68	Verkhoyansk, Russia	105	7 Feb 1892
Greenland	-66	Northice	2300	9 Jan 1954
North America	-63	Snag, Yukon, Canada	636	3 Feb 1947
Europe	-55	Ust'Shchugor, Russia	84	Jan in the 1980s
South America	-33	Sarmiento, Argentina	264	1 Jun 1907
Africa	-24	Ifrane, Morocco	1610	11 Feb 1935
Australia	-23	Charlotte Pass, NSW	1730	29 Jun 1994
Oceania	-10	Haleakala Summit, Maui, HI	2920	2 Jan 1961

HOW IT IS DONE

The aim of refrigeration is get temperatures below that of the local environment, to be able to draw heat from a load by normal heat transfer. Any endothermic process lowers the temperature of the system and is able to produce a refrigeration effect. Notice that natural endothermic processes always demand an entropy increase, since from $\Delta G = \Delta H - T\Delta S$ (with $\Delta G > 0$ for a natural process and $\Delta H < 0$ for an endothermic process), it follows that $\Delta S > 0$; e.g. the expansion of compressed gas and subsequent heat removal, the vaporisation or evaporation of a liquid, etc.

The vast majority of refrigeration and air-conditioning duties are achieved with refrigeration machines (refrigerators) where an internal working fluid (refrigerant) is processed cyclically; the exceptions being the solid-state refrigerators based on Peltier effect, the open-loop compressed-air refrigerators (with moving components or without, as the Hilsch or Ranque or vortex-tube refrigerator), and the freezing mixtures.

Although we only deal here with artificial refrigeration (e.g. making artificial ice), some natural ways of refrigeration exists (e.g. using natural ice), since we live in a non-equilibrium world, and one may brought ice from another time (winter snow, cold night) or another place (high mountains, high latitudes), or simply perform endothermic mixing (the commonest one being water and air in evaporative cooling).

Most refrigerators are based on mechanical vapour compression of a refrigerant fluid. Small and medium-size refrigerators are pre-assembled units ready to connect to the mains and start working, but large machines come in parts and require in-situ piping installations.

Although the T - s diagram still has its academic advantages to understand refrigeration cycles, most practical work refers to the p - h diagram with a logarithmic pressure scale. The main components of a vapour-compression refrigerator, and the diagram of the processes, are presented in Fig. 1. The four basic processes are: step 1-2 is the vapour compression stage, where adiabaticity can be assumed, although entropy increases in real systems (point 2s would correspond to an isentropic compression); step 2-3 is the heat release to the ambient sink, to condense the high-pressure vapour; step 3-4 is the sudden expansion that abruptly drops the temperature of the working fluid due to the provoked vaporisation; and step 4-1 is the actual useful stage where the vaporising fluid draws heat from the load. Of course, the working temperatures of the fluid must be outside the source and sink temperatures, as shown in Fig. 1.

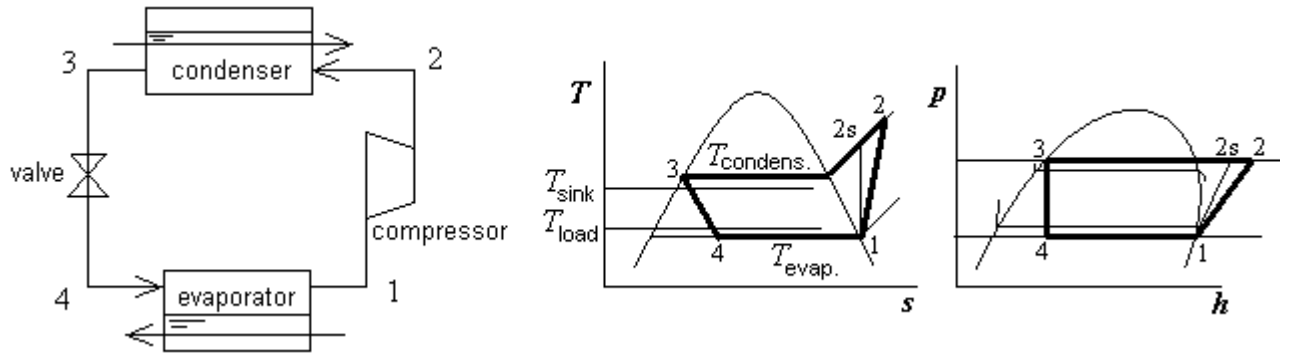


Fig. 1. Main components of a vapour-compression refrigerator, and T - s and p - h diagrams of the processes.

Designing a refrigeration solution in practice usually involve several steps, particularly for large industrial systems: knowing the user requirements, analysing the state of the art, calculating the refrigeration loads in detail, selection of the overall system, layout and dimensioning pipes and ducts, equipment selection (perhaps including a cooling tower for final heat sink), electrical installation, element procurement and installation, finishing and service checking.

Exercise 1. Domestic refrigerator

Refrigeration efficiency definition

Refrigeration requires an external exergy input (see Exergy), and the most rational measure of efficiency is the ratio between the exergy required and the exergy spent. But, as for other technical processes, it is customary to measure efficiency in terms of energy instead of exergy, with the well-known problems of efficiencies greater than unity and so on.

Refrigeration requires an external energy input lower-bounded by Carnot efficiency, as for normal heat engines. Carnot efficiency for taking out an amount of heat Q_2 from a cold source at T_2 , in the presence of a heat sink at T_1 (the environment), by expending a work W (e.g. in a vapour-compression refrigerator), is obtained from the energy and entropy balances of the Carnot engine (see [Exergy](#)): $W=Q_1-Q_2$ and $Q_1/T_1+Q_2/T_2=0$. If efficiency is defined as the cold produced Q_2 (energy extracted) divided by the energy input W , its value is:

$$\eta_R \equiv \frac{Q_2}{W}, \quad \eta_{R,Carnot} \equiv \frac{Q_2}{W} \Big|_{\Delta S=0} = \frac{T_2}{T_1 - T_2} \quad (2)$$

a value usually larger than unity (e.g. the Carnot efficiency to keep a cooled space at 250 K in a 300 K environment is $250/(300-250)=5$) and traditionally known as coefficient of performance (COP). Real refrigeration efficiencies are in the range 1..3 for common work-driven refrigerators (vapour-compression machines), and 0.01..1 for heat-driven refrigeration machines (sorption systems and thermoelectric devices). Notice, by the way, that heat pump efficiency (or COP) is defined in terms of heat added to the hot sink, Q_1 , and not on heat taken out from the cold source, Q_2 , and thus, their Carnot efficiencies are exactly one unit more (i.e. for a heat pump heating a hot space at 300 K from an environment at 250 K, $\eta_{Carnot,HPump}=Q_1/W=T_1/(T_1-T_2)=6$), and real heat-pump efficiencies are in the range 2..4.

For the second in importance type of refrigerator, the absorption machine, the coefficient of performance is now expressed as the cold produced divided by the heat input. This is one reason for the low efficiencies of absorption machines when compared with vapour-compression machines, without paying attention to the fact that heat input worth less than work input, both in economic and in exergetic terms.

As for heat engines, instead of the two constant-temperature heat sources implied in the Carnot cycle, a model with two variable-temperature heat sources may be more realistic, the temperature variation being due to a finite-thermal-capacity source that cools down when heat is extracted and heats up when absorbing heat (e.g. a finite stream of ambient air). In those cases, the cycle that best matches the gliding temperature of the sources, the so-called Lorenz cycle, is the optimal (refrigeration and heat-pump cycles that use a two-phase binary mixture make use of that).

Exercise 2. Chill water refrigerator

Refrigeration capacity

The thermal size of a refrigerator is known as its capacity, i.e. its cooling power, in watts in SI units, but sometimes older units are used in some places, as the frigorie/hour ($4180/3600=1.16$ W) or the ton (3575 W). It might be argued that it is more convenient to have a distinct unit for electrical power (the watt), a distinct unit for heating power (e.g. the calorie), a distinct unit for cooling power (e.g. the frigorie), etc., and then be able to say in a concise and clear manner that a domestic air-conditioner has for instance 1000 W, 1000 frigories and 1000 calories, instead of having to say that it has 1000 W of electrical consumption, and may give 1000 W of heating (used as heat pump) or 1000 W of refrigeration. Well, a more precise naming may help even at a cost of extended vocabulary, but not if different unit-conversion-factors are required.

The range of cooling powers demanded depend on application, from the small mini-bar refrigerator requiring some 100 W of refrigeration (and consuming some 100 W of electricity), to the typical single-room air-conditioner of 2 kW refrigeration (and 1 kW electrical consumption), to a typical bus air conditioning system of some 30 kW refrigeration (usually driven by the bus engine), to a department-store refrigeration system of some 10 MW refrigeration (usually driven by a cogeneration power plant; cogeneration is also termed 'combined heat and power', CHP; combined cooling heating and power, CCHP, is also known as trigeneration).

As a rule of thumb for space conditioning, refrigeration loads are similar to heating loads, since in both cases the objective is to compensate for the heat flow through the envelop, $\dot{Q} = KA\Delta T$, where K depends mainly on wall materials (fix), A is wall area (fix), and ΔT in summer and winter are of the same order of magnitude in temperate climates (well, it can be for instance some 25 °C in winter, 20 °C inside and –5 °C outside, and 20 °C in summer, 25 °C inside and 45 °C outside, but electrical and metabolic loads rest to the heating load in winter and add to the cooling load in summer, compensating somehow).

Vapour compression refrigeration

A common and effective cold-producing technology is based on the vacuum vaporisation of a volatile liquid. Consider pure ether ($\text{C}_4\text{H}_{10}\text{O}$, or $\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$), half-filling a closed container, in thermal equilibrium with an environment at say 20°C ; the interior pressure is 59 kPa corresponding to the two-phase equilibrium $p_v(20^\circ\text{C})$. Aspirating the vapour with a vacuum pump produces cold because some liquid must convert to high-energetic vapour molecules to reach the new two-phase equilibrium conditions. If some system-load were inside the liquid, it would be cooled too.

Because liquid refrigerants like ether have to operate under vacuum, they were replaced late in the 19th c. by gaseous refrigerants (liquefied under pressure): first SO_2 , with a $p_v(20^\circ\text{C})=320$ kPa but extremely toxic, then NH_3 , with a $p_v(20^\circ\text{C})=850$ kPa but extremely irritating, later CO_2 , with a $p_v(20^\circ\text{C})=5600$ kPa, too high for the time, and so on until the chloro-fluoro-carbon compounds were synthesised in 1929 ($p_v(20^\circ\text{C})=565$ kPa for R12) and displaced all others, until their ozone-depletion effect was understood in the 1970s and they were banned in the 1990s. ([Vapour pressure data](#) may be found aside.)

Vapour compression refrigeration is based on a modified reversed Rankine cycle that was the basis for steam engines (see [Power](#)). Saturated or slightly super-saturated vapour, see Fig. 1, is pumped by a compressor to a high pressure, then cooled (ultimately with ambient air) until the compressed gas condenses to a liquid, and the saturated or slightly sub-cooled liquid flashes to the low-pressure vaporiser through a valve. Substitution of the valve by an expander that would generate some work and increase the cooling is never done because the complexities that would be involved overcome the small gain obtained. It is also very important that no wet-vapours enter the compressor, to avoid mechanical damage and thermal degradation.

Vapour compression cycles usually work with single-component refrigerants like $\text{C}_2\text{H}_2\text{F}_4$ (R134a) or n-butane (R600), but mixtures are also used (e.g. R410A, a 50/50 mixture of CH_2F_2 and C_2HF_5); refrigerant mixtures do not change appreciably the efficiency, but provide a better match of operation pressures, and regulate the mass flow-rate by composition change (the volumetric flow-rate is usually constant).

In the theoretical refrigeration cycle, the compressor takes saturated vapour, the expansion valve takes saturated liquid, and there are no pressure drops in the ducts. In practice, however, the vapour is super-heated before entering the compressor to guarantee it is dry, the valve takes sub-cooled liquid (coupled to vapour super-heating), and pressure drop in ducts and heat exchangers do occur.

When the difference between ambient and load temperature is large, first, a single compressor may not be adequate, and a multistage compression may do better (with inter-cooling to the ambient or in multistage mode), and second, a single working fluid may not be convenient for the cycle because it should work under vacuum in the vaporiser, or the condenser might approach the liquid-vapour critical region (e.g. a top ammonia-compression cycle may refrigerate the condenser of a bottoming CO_2 -compression cycle that cools a load at -50°C).

Another use of multistage refrigeration is that several loads may be attended more appropriately (e.g. one stage for normal refrigeration and another for freezing), minimising thermal-jump waste. Notice however that there is no natural heat sink for the intercoolers in the multistage compression process, so that a multistage expansion process is due, what may be done in several ways, as sketched in Fig. 2.

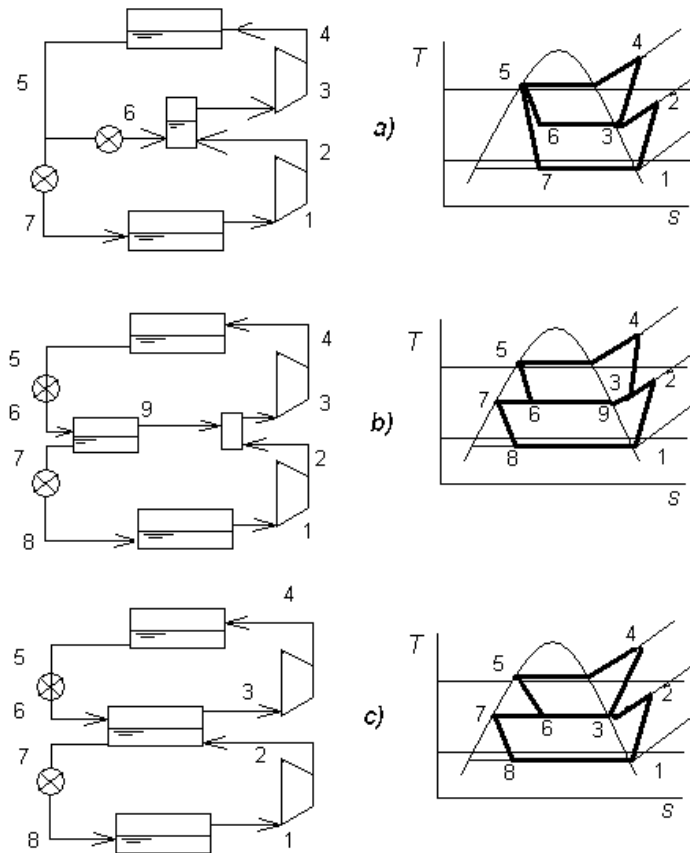


Fig. 2. Variations on the basic vapour-compression cycle (cascading cycles): a) separated throttling to saturate the entry to the second compressor; b) full vapour extraction at the middle; c) full mixing in between.

Finally notice that the basic refrigeration effect is the sudden expansion of a compressible fluid. The necessary recompression to close the cycle may be done directly by means of a mechanical compressor as assumed above, or by absorption in a liquid that is pumped and then desorbed, or by dynamic compression with a steam jet, etc.

Absorption refrigeration

Conceptually, an absorption-refrigeration machine corresponds to a vapour-compression refrigerator in which the compressor is substituted by four elements: a vapour absorber based on another liquid, a pump for the liquid solution, a generator or boiler to release the vapour from solution, and a valve to recycle the absorbent liquid. Its great advantage is that this cycle requires less work to operate (only that of the pump), or none at all if the liquid is naturally pumped by gravity in a thermo-siphon, at the expense of an additional heat source required at the regenerator.

The basic scheme is presented in Fig. 3, where, as in actual practice, the absorber and vaporiser are shown combined in a single vacuum shell, as well as the generator and condenser (often the whole system is within a single shell).

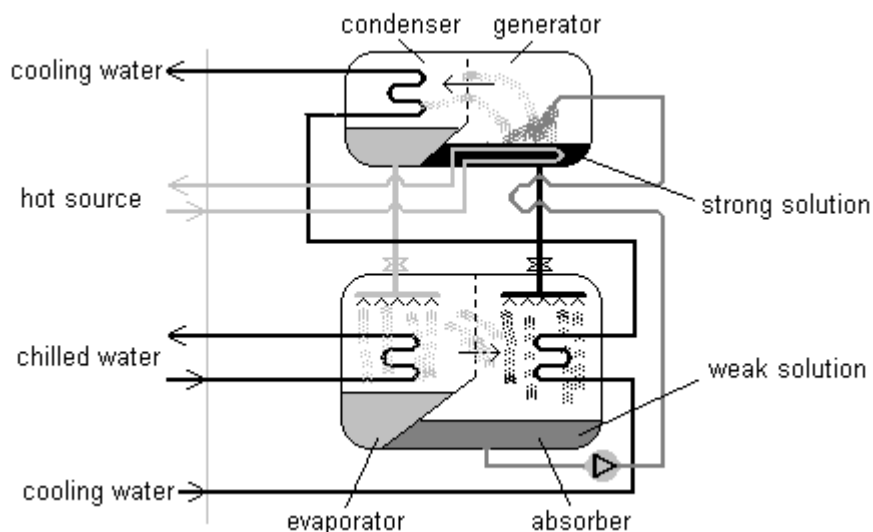


Fig. 3. Layout of an absorption refrigeration machine, showing inputs and outputs.

There are two working fluids in an absorption refrigerator, the refrigerant (as for a vapour-compression refrigerator), and the carrier, that is the auxiliary liquid that absorbs the refrigerant (in the absorber), is pumped up to high pressure, and releases the refrigerant vapours at the generator. Ammonia has been traditionally used as refrigerant in both types of refrigerators, down to the $-40\text{ }^{\circ}\text{C}$ range of commercial refrigeration. In that case, water was used as the carrier of ammonia, although some rectifier equipment has to be added to avoid water-vapour carry-over at the generator.

For non-freezing refrigeration (i.e. down to $0\text{ }^{\circ}\text{C}$, as for air conditioning and water chilling) a simpler choice is to use water as the refrigerant, and an aqueous saline solution of lithium bromide as the absorbent. LiBr- H_2O systems are in use since 1940s, with a practical cooling limit to $5\text{ }^{\circ}\text{C}$). The number of times the solution is heated to produce refrigerant vapours, is referred to as the number of effects, so Fig. 3 corresponds to a single-effect machine (most units are single or double effect).

It was Faraday early in the 19th c. the first to document absorption refrigeration, when he noticed that silver chloride powder eagerly absorbed ammonia, producing a refrigeration effect. The absorption machine was developed by F. Carré in France in 1859, initially using water as a refrigerant and sulfuric acid as absorbent, although he later switched to the ammonia-water system. The advantages of absorption refrigeration are: lower or no electrical consumption (but needs a heat source), possibility of heat recovery or co-generation synergies, low environmental impact working fluids, and low vibrations, but the energy efficiency is smaller (typically half that of a vapour-compression refrigerator).

Electrolux developed in 1925 a household absorption refrigerator (marketed in USA by Servel), which had no need of compressor, based on a 1923 patent by Swedish students C. Munters and B. von Platen. The Electrolux system of fully heat-powered absorption refrigeration is shown in Fig. 4; it has no moving parts and slightly different vaporiser and condenser pressures, allowing for natural-thermal-convection pumping (thermo-siphon). Einstein and Szilard patented in 1928 a similar pump-free absorption refrigerator (using ammonia, water and butane), but the difficulties of dealing with ternary mixtures (and freon panacea at that time) relegated those pump-free refrigerators to a marginal place in the market.

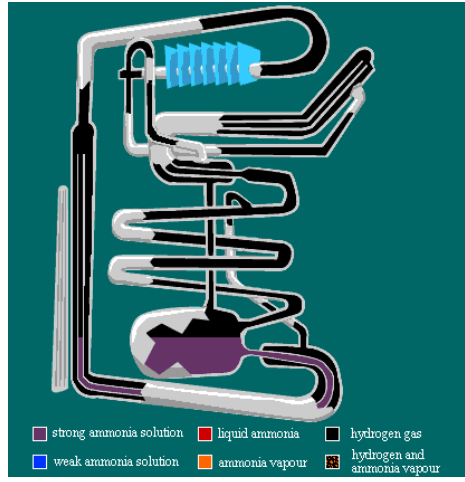


Fig. 4. Absorption refrigerator driven exclusively by heat power.

The absorption refrigeration effect can easily be achieved in a simple intermittent device (named Iceball), which basically consists of two thick spherical steel vessels (to withstand a few MPa) connected at the top through a pipe and holding a two-phase ammonia/water mixture (nearly half and half). An ammonia separator device is needed for effective operation, but we do not consider it in this conceptual mode of operation. First the device is ‘charged’ by heating for some time one sphere (e.g. with a burner) while the other is immersed in room water; in that way, the liquid remaining in the hot vessel gets weak on ammonia, whereas some ammonia-concentrated solution condenses on the room-temperature side (nearly pure ammonia when using the separator). The device is then made to work to produce cold by just cooling the weak liquid in room water, what lowers its pressure and sucks vapours from the other sphere that gets cold due to vaporisation (this sphere can be put inside an ice chest, or some ice-tray built directly on it). With a valve in the connecting pipe, the charged-state can be kept for later use (a pressure jump builds up).

The energy efficiency (coefficient of performance, COP) of heat-driven refrigeration machines which extracts Q_{cold} at T_{cold} by expending Q_{hot} at T_{hot} , in the presence of an environment at T_{amb} , is often defined in terms of energy extracted divided by energy consumed (the Carnot efficiency can be derived by combining a heat engine using Q_{hot} coupled to a mechanical refrigerator pumping Q_{cold} , both working against T_{amb}):

$$\eta_R \equiv \frac{Q_{\text{cold}}}{Q_{\text{hot}}}, \quad \eta_{R,Carnot} \equiv \frac{Q_{\text{cold}}}{Q_{\text{hot}}} \bigg|_{\Delta S_{\text{univ}}=0} = \frac{T_{\text{cold}} (T_{\text{hot}} - T_{\text{amb}})}{T_{\text{hot}} (T_{\text{amb}} - T_{\text{cold}})} \quad (3)$$

what makes difficult the comparison with vapour-compression machines. The use of exergy efficiencies would remediate that situation, not only in refrigeration systems but in heat pumps and heat engines, but this is uncommon.

Energy efficiency of heat-driven refrigeration is much smaller than work-driven refrigeration. However, heat-driven refrigeration systems are common when heat is cheap (e.g. heat recovered from an industrial process), or when electricity is expensive (e.g. in decentralised systems, where absorption refrigeration is more efficient than electricity generation plus vapour-compression refrigeration, although direct

mechanical coupling may help). Even when electricity is locally produced in cogeneration systems, absorption refrigeration is preferred to take advantage of excess heat, and leave the electricity produced to other duties not serviceable by heat (illumination, communications, electrical appliances...).

Notice finally that some systems covered under Evaporative cooling (below), and other sorption and chemically reactive systems (not covered here), are very close to absorption refrigeration machines (the refrigerant is adsorbed by a solid desiccant or by a solid reactant). High endothermic processes like adsorption of ammonia in some halide salts, may be used for freezers (e.g. $\text{BaCl}_2(\text{s}) + 8\text{NH}_3(\text{g}) = \text{BaCl}_2(\text{NH}_3)_8(\text{s})$ has been demonstrated to produce cooling down to $-30\text{ }^\circ\text{C}$; afterwards, the halide is regenerated at some $100\text{ }^\circ\text{C}$ with solar energy or waste heat).

Gas expansion refrigeration

An adiabatic expansion of a closed system always reduces its internal energy (from $\Delta E = Q + W$), with a decrease in temperature, i.e. a refrigeration effect, proportional to the expansion (that is why gases are used instead of condensed matter). An adiabatic expansion in a work-producing flow-system always reduces the enthalpy (from $\Delta h = q + w$), with a decrease in temperature, but an adiabatic expansion in a rigid flow system, maintains the total enthalpy, and may decrease or increase its temperature depending on the relative side of the inversion temperature (e.g. ambient air cools a little when throttled, 2.5 K/MPa , but hydrogen heats instead of cooling; see Joule-Kelvin coefficient in [Chapter 4](#)).

Gas-expansion cycles are only used in special applications, as for cryogenic refrigeration and for special applications where compressed-air is already available, as from gas-turbine engines in cabin-air conditioning on airplanes. Gas-expansion cycles basically correspond to inverted Brayton cycles (see [Power](#)), most of the times with a heat-recuperator or regenerator (R in Fig. 5) to get to lower temperatures without losing too much efficiency.

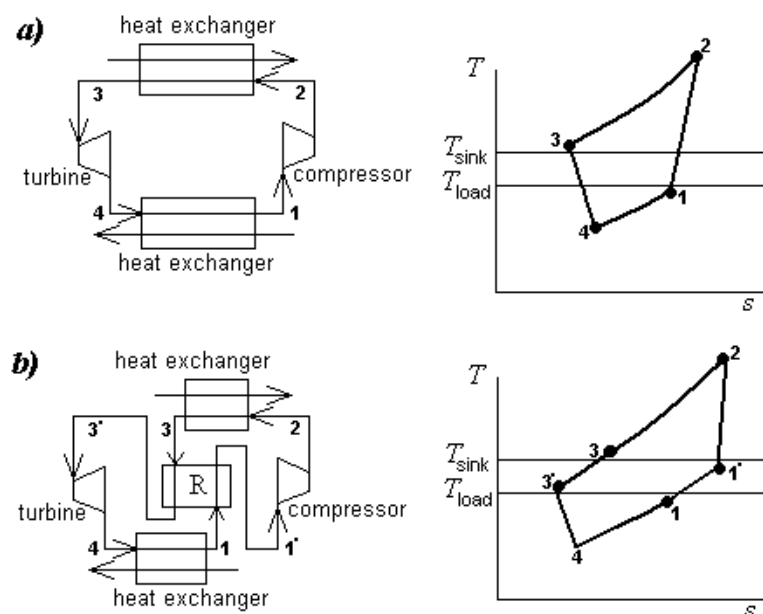


Fig. 5. Gas expansion refrigeration cycles: a) simple, b) recuperative. Non-isentropic adiabatic compression and expansion are shown.

Small Stirling-cycle refrigerators have been developed using helium as working fluid, matching the efficiency of traditional vapour-compression refrigerators ($\eta > 1$), being more compact (1.6 kg for a 40 W refrigeration unit), and reaching lower temperatures (-20 °C instead of 0 °C for that size).

Thermoelectric refrigeration

Solid-state electrically-driven refrigerators (also named thermo-electric coolers, TEC) are based on the Peltier effect. When a DC current flows in a circuit formed by two dissimilar electrical conductors, some heat is absorbed at one junction and some more heat is released at the other junction, reversing the effects when reversing the sense of the current (Joule heating is not reversing; it is always positive).

Although commercial TEC modules only date from 1960s, thermoelectricity studies started in 1821 when T.J. Seebeck discovered that a compass needle deflected, when placed in the vicinity of a closed loop formed from two dissimilar metal conductors, if the junctions were maintained at different temperatures, and that the deflection was proportional to the temperature difference, settings the origin of thermocouple thermometry. When J. Peltier was studying the Seebeck effect in 1834, he realised the heating and cooling effects at the junctions. Thermoelectric effects are due to the free-electron-density variation with temperature and amongst materials, and the associated flows.

Thermoelectric materials should have large Seebeck coefficients, high electrical conductivity (to minimise Joule losses) and low thermal conductivity (to minimise internal heat conduction). The non-dimensional figure of merit for these materials is $\alpha^2 \sigma / (kT)$, where α is the Seebeck coefficient, σ the electrical conductivity, k the thermal conductivity, and T the mean working temperature; the best materials are semiconductors based on bismuth telluride (Bi_2Te_3).

A typical thermoelectric module consists of pairs of p-type and n-type semiconductor thermo-elements (one shown in Fig. 6) forming thermocouples which are connected electrically in series and thermally in parallel. Typical energy conversion efficiencies are 5..15 %, much lower than vapour compression refrigeration values: 100..300 %, but their inherent simplicity and reliability gives them some application niches.

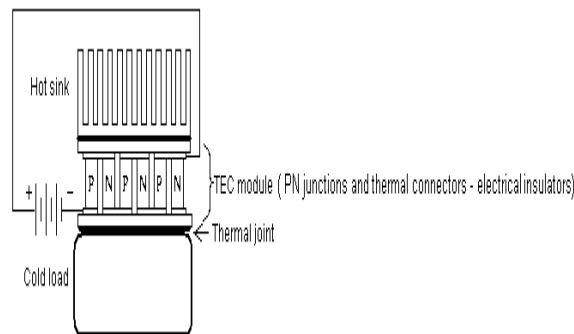


Fig. 6. Sketch of a thermo-electric-cooler (TEC) with three thermo-elements.

When a TEC module is connected to DC power source, the cold side of the module would cool down until the internal heat conduction balances the heat-pump capability (e.g., starting at room temperature of 20 °C, a steady state may be reached with the cold side at -40 °C if well insulated, and the hot side at say 30 °C if fan-cooled or near 20 °C if vigorously cooled; this maximum temperature difference relative to

\dot{Q}_{\max} (notice that they do not correspond to the same process).

Thermoelectric modules need high heat-transfer efficiencies at both the cold and the hot junctions, particularly at the hot one, where fins and fan (or better, liquid cooling) must be provided.

Evaporative cooling

Mixing water and non-saturated air produces a refrigerant effect (i.e. a temperature drop below ambient temperature), an old technique already used by ancient Egyptians to cool drinking water in porous earthen pots, and to cool space by splashing some water on the floor, although the systematic study of evaporative cooling started in the 19th century, when experiments with different liquids (acids and alkalis) were carried out, and the dominant effect of vapour-pressure elucidated.

The basic refrigeration effect is due to the energy demanded by evaporating water (equal to the vaporisation enthalpy), a natural process driven by air dryness. Related to evaporative cooling is vaporisation cooling when vacuum is applied to a liquid or solid (usually aqueous solutions). Lyophilisation is the process of transforming water solutions to solid powder by high vacuum (e.g. instant coffee, powder milk, instant soups, dry juices, vaccines, antibiotics and other medicines).

Evaporative cooling, however, is not usually covered under Refrigeration because it is rather limited in practice to slightly cooling the water or the air that are fed to the system; their main handicap is that evaporation is a slow process, that small inefficiencies in heat exchangers quickly kill the energy efficiency of the process, that water-handling is cumbersome below 0 °C, and that moist air must be desiccated to have a continuous evaporative-cooling process. However, new developments in desiccant regeneration are showing promise particularly for air-conditioning applications (without air desiccants, the growing humidity hindered its effectiveness). A conceptual installation able to produce ice by evaporative cooling is presented in Fig. 7.

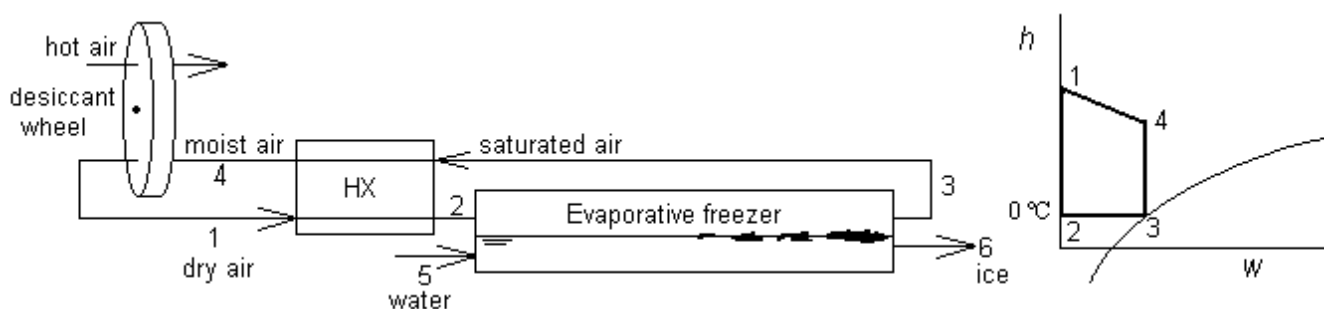


Fig. 7. Sketch of an evaporative freezing installation, producing ice from water with just a hot-air source, and the Mollier diagram for the process.

In fact, adsorption refrigeration machines can be developed in a similar way to absorption refrigeration machines, using a primary working fluid and a solid adsorbent (instead of the liquid absorbent). Although water has been the common working substance and zeolites or silica gel the absorbents, other pairs have

been successfully tried, as ammonia in zeolites or charcoal, methanol in zeolites or silica gel, and ethane in charcoal.

For those that believe evaporative cooling and other endothermic mixing are insignificant refrigeration phenomena, consider the similarity between a combustible mixture and a freezing mixture: it is just a matter of the amount of exergy involved in the physico-chemical combination. An extensive description on desiccants follows, since it is hardly available in compiled form to the thermal engineer.

Desiccants

Desiccants are used to absorb or adsorb water vapour from air, what can be further use to procure evaporative cooling. Desiccants can be either solid or liquid. Liquid desiccant systems have lower pressure drop, require less regeneration energy, and act as disinfectants. Solid desiccant systems are more compact, easy to handle, non-corrosive, non-foaming, and have no carry-over problems; they usually consist on a porous-ceramic wheel, rotating between the air to desiccate on one side, and the hot-air (70..80 °C, might be sun-driven) for regeneration, on the other side (Fig. 7). Solid adsorbents (silica gel, clay, molecular sieves) require a relatively high regeneration temperature, compared with liquid desiccant such as calcium chloride and lithium chloride solutions.

Silica gel is a non-toxic and non-corrosive synthetic desiccant produced by coagulating a colloidal solution of silicic acid H_2SiO_3 obtained from silicon dioxide (SiO_2); i.e. it is an amorphous form of silica constituted by hard irregular granules having the appearance of crystals, which is manufactured from sodium silicate and sulfuric acid. It has 99.5 % SiO_2 + 0.2 % Na_2O + 0.2 % Al_2O_3 +.... Silica gel remains dry after vapour absorption, i.e. it is not deliquescent. It is a naturally occurring mineral that is purified and processed into either granular or beaded form. Silica gel acts like a sponge, the interconnected pores (some 2.4 nm in diameter) holding water by adsorption and capillary condensation (it can adsorb about 40 % of its weight in water vapour at saturation). Silica gel performs best at room temperatures between 25..35 °C and at high humidity between 60 to 90 % RH and will drop the relative humidity in a container to around 40 % RH; at higher temperatures vapour absorption gets less efficient up to 105 °C where it does no longer absorbs. Indicating silica gel, ISG, is just silica gel washed with a concentration of cobalt chloride (a heavy metal salt). The cobalt chloride is a deep blue colour when dry and turns from blue to purple to pink as it becomes saturated with moisture. Typically, the colour changes when the desiccant goes past 8 % moisture levels (by weight) which indicates that it is time to replace the desiccant. Regeneration temperature depends a lot on the type of silica gel: wide pore silica gel has to be heated to 600 °C, but narrow pore silica gel only to 250 °C.

Clay desiccants are naturally occurring, non-corrosive, non-hazardous, moisture adsorbent substances which are created by the controlled drying of a calcium-alumino-silicate clay. Clay is the least expensive of all desiccants, and highly effective within normal temperature (<50 °C) and relative humidity ranges. Clay can adsorb up to 40 % of its weight in water vapour at 100 % humidity. The clay is ground, processed and bagged and regenerates for repeated use at very low temperatures without substantial deterioration or swelling.

A molecular sieve is a synthetic crystalline version of Zeolite minerals containing a network of uniform pores and empty cavities. Molecular sieves are derived from sodium-potassium or calcium-alumina silicates. They are the desiccants of choice for the most demanding and unique applications, holding water up to 250 °C.

Water adsorption by the desiccant is a highly exothermic process since, from $\Delta G = \Delta H - T\Delta S$, with $\Delta G < 0$ for a natural process and $\Delta S < 0$ because vapour condenses on the solid adsorbent, it follows that $\Delta H < 0$. The heat release on adsorption is larger than the vaporisation enthalpy of the fluid (e.g. for water in silica gel $\Delta H = -2.8$ MJ/kg; for water in zeolites it varies with grade from $\Delta H = -3.3$ MJ/kg to $\Delta H = -4.2$ MJ/kg, to be compared with a vaporization enthalpy of 2.4 MJ/kg).

Domestic refrigerators

Nowadays public pools indicate that the domestic refrigerator is the most important home appliance. Domestic refrigeration is always based on a vapour-compression machine, with R12 being the standard refrigerant fluid from 1930 to 1990, banned afterwards because of its ozone-layer depletion effect, and replaced either by R134a, R600 (n-butane), R600a (iso-butane) or R600b (cyclo-pentane). Notice that those hydrocarbons have lower vapour pressures than R12 or R134a, and the vaporiser works under vacuum (some 58 kPa absolute, see Table 3).

Table 3. Comparative properties of main domestic refrigerant working fluids.

Refrigerant	R12	R134a	R600a
Name, formula	Dichloro-difluoro-methane, CCl_2F_2	1,1,1,2-tetrafluoro-ethane, $\text{CF}_3\text{CH}_2\text{F}$	Iso-butane, $(\text{CH}_3)_3\text{CH}$
Molar mass [kg/mol]	0.121	0.102	0.058
Boiling temperature [K]	243.2	246.6	261.5
Critical temperature [K]	388	374	408
Critical pressure [MPa]	4.01	4.07	3.65
Liquid density at -25 °C [kg/m ³]	1470	1370	600
Vapour pressure at -25 °C [kPa]	124	107	58
Vaporisation enthalpy at -25 °C [kJ/kg]	163	216	376

Cooling categories are: ** (2 stars, 1 door simple refrigerators with a special freezer compartment at -12 °C), *** (3 stars, 2 doors refrigerator-freezer combo, with freezer temperature of -18 °C to keep deep-frozen food), **** (4 stars, 2 doors refrigerator-freezer combo, with freezer temperature of -24 °C, to freeze food), top-door freezers. The efficiency categories are A, B, C... The 'tropical category' refers to the permissible ambient temperature: N for normal $T_{\text{amb}} < 32$ °C, ST for semi-tropical $T_{\text{amb}} < 35$ °C, and T for tropical $T_{\text{amb}} < 43$ °C. Common thermal isolation is by flexible polyurethane foam (that used to be expanded with R11 before CFC banning, and is now blown with cyclo-pentane, R600b).

Efficiency labelling is a letter-code (from A to G) based on dividing annual energy consumption by the net volume of the appliance (adjusted to equalise for different temperature zones), and scaled to an average efficiency; it is mandatory to display on sale for most electrical appliances in Europe since 1995 (refrigerators were the first). A-class means that it consumes <55 % of the average, B-class means that it consumes between 55% and 75% of the average, C-class are in the 75..90 % range, D-class 90..100 %, E-

class 100..110 %, and so on. Besides the efficiency letter, the annual consumption of energy (in kWh per year) and the storage volume of the compartments (in litres), must be shown.

Domestic refrigerators have a permanent load of some 0.25 kg of refrigerant, but air-conditioners in cars have > 1 kg, and it used to have to be replenished every year!

Portable and non-electric refrigerators

A portable refrigerator is one that may be brought to a camping site for instance, having a typical conditioned space of some 25 litres, 0.5 m cube dimensions and a mass of under 15 kg. It can be a small traditional electric-driven vapour-compression refrigerator to be battery-operated (e.g. connected to the car battery, consuming some 50 W), or a non-electric heat-driven device, to be powered by a camping-gas cartridge, for instance, consuming some 0.150 kg/day of LPG gas, achieving an interior temperature of 5 °C in a 25 °C ambient. Portable refrigerators driven by solar energy have not yet been developed.

Thermoelectric coolers (TEC) can be used for portable applications in the low-capacity range (say up to 100 W), with the great advantage of having no moving parts, but they are not competitive on energy efficiency, of the order of 0.2 against a value >1 typical of mechanical refrigerators of that cooling power (both, of traditional vapour-compression type, and of Stirling cycle).

Do not confuse a portable refrigerator with an ice-chest (see Ice chest, below)

Magnetic refrigeration

[Magnetic refrigeration](#) is based on the magnetocaloric effect, discovered by E. Warburg in 1881. Similarly to mechanical compression and expansion of gases, there are some materials that raise their temperatures when adiabatically magnetised, and drop their temperature when adiabatically demagnetised. This refrigeration effect has been routinely used since mid 20th c. in the liquefaction of hydrogen and helium, but it is not yet competitive for room refrigeration because of the small cooling effect (it is difficult to drop more than 10 °C even with a strong field of several tesla).

The magnetocaloric effect depends on the pyromagnetic coefficient, $\partial M/\partial T$ (the variation of magnetization with temperature), which is maximum near the Curie point, i.e. the temperature at which a magnetic substance loses its coercive force and transforms from ferromagnetic to paramagnetic, near which the sensitivity of magnetization with temperature is highest in ferromagnetic materials (it is near 0 K for paramagnetic materials). A strong magnetic field applied to a solid material near its Curie point forces the magnetic moments of its atoms to become aligned with the field; the thermal energy that was distributed between the vibration and spin levels is suddenly concentrated in less vibration levels, with a consequent temperature rise (again similarly to adiabatic gas compression: forcing more order, without allowing for entropy to escape, raises the temperature; compare the magnetocaloric cycle, Fig. 8, with the inverse Brayton cycle in gas refrigerators, Fig. 5); other type of cycles may be applied, as for instance the Ericson cycle using heat regenerators (see [Power](#)). The farther away from the Curie point, the weaker the magnetocaloric effect (the useful portion of the magnetocaloric effect usually spans about 25 °C on either side of that point).

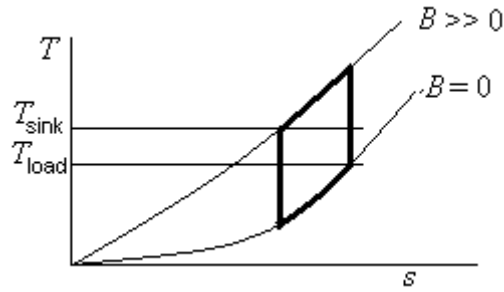


Fig. 8. T - s diagram for magnetic refrigeration using a Brayton-type magnetocaloric cycle.

Materials with advanced magnetic and super conductive properties have been developed to improve magnetic refrigeration efficiency. Materials are magnetized to several tesla using superconductors and electromagnets, and cooled by contact with the high-temperature sink region, then suddenly demagnetized (adiabatically), reaching low temperatures and cooling the load while returning to the initial state.

Most magnetocaloric materials are rare earths; usually gadolinium compounds (Gd and notably $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$), with densities in the range 6000..8000 kg/m³, thermal capacities around 200 J/(kg·K), thermal conductivities around 10 W/m·K), and Curie temperatures around 300 K. A large magnetic entropy change has been found to occur in $\text{MnFeP}_{0.45}\text{As}_{0.55}$ at room temperature, making it an attractive candidate for commercial applications in magnetic refrigeration. Energy efficiency may approach 50 % of Carnot limit, against some 10 % for typical mechanical compression refrigerators, without moving parts and associated noise and maintenance burden.

Another application of the magnetocaloric effect is to drive a magnetic fluid in a cooling fluid loop. A magnetic fluid (a kind of the new substances known as nanofluids) is a normal fluid (usually a hydrocarbon) seeded with magnetic particles (e.g. Mn–Zn ferrites) of nanometric size (of about 10 nm in diameter, coated with a surfactant layer); with typical low concentrations say 5 % in volume) the colloidal fluid has nearly the same flow properties than the base liquid. The driving force is proportional to $H(\partial M/\partial T)\nabla T$, i.e. to the magnetic field, H (usually achieved with a permanent NdFeB magnet), times the pyromagnetic coefficient, times the temperature gradient). Typical velocities achieved are small, say a few mm/s, but the absence of moving parts, the positive response (the speed is directly proportional to the thermal gradient), and the controllability (H is usually achieved with a permanent NdFeB magnet, but), makes this pumping mechanism ideal for thermal control, particularly aboard spacecraft.

Air conditioning

We on Earth have an omnipresent vital atmosphere, full of air to breathe, but we use it also as a heat sink to cool our metabolism. Air temperature, however, may change a lot from summer to winter, from day to night, from place to place, and it has been always necessary to have some thermal conditioning of habitable spaces. Special requirements arise when atmospheric air is not available, as in submarine, outer-space or heavily contaminated environments, and one then deals with whole environmental control and life support systems (ECLSS).

Artificial space heating was practiced by humans since Palaeolithic times, but artificial space refrigeration only started in the 20th c. The common goal of air conditioning was enabling work and leisure anytime, not just when weather allowed. Space refrigeration is so much difficult than space heating, that the term 'air conditioning' used to refer only to refrigeration. As said before, changes in air humidity are very important in air conditioning (refer to [Humid air](#) for further details).

The first refrigerated building was the New York Stock Exchange building in 1901, with a 1 MW of refrigeration (300 ton) steam-driven ammonia absorption machine, designed by Alfred Wolf, who also conditioned a bank and the Museum of Modern Arts before he died in 1909.

Air-conditioning, thence, in the traditional sense, has the purpose of maintaining temperature and humidity within certain limits (the air may also be filtered and purified at the same time). The importance of air conditioning (also named climatisation) is growing exponentially for several reasons:

- Nowadays, people spent more than 90 % of their lives inside closed spaces (in developed countries).
- More and more animals and plants are grown on closed spaces (farms, greenhouses).
- Most goods are stored and handled in closed spaces (from grain-stores to museums).
- New key technologies are avid of conditioned spaces (microelectronics, biotechnology).

Small air-conditioning units may be compact window-units, ready to connect to the electric grid and start working (once the window hole is available), or portable units with large umbilical ducts out of the window, but most air-conditioning units require in-situ installation, with the vaporiser inside the space to cool, the condenser outside, and pipes going through the walls. The best layout for space cooling is placing the cooler near the ceiling or along it, where air is at the hottest, in the same way as floor heating is the best for space heating.

A thumb-rule of some 100 W of refrigeration per square meter of floor space is commonly used as typical load to air conditioning flats and offices.

COMPONENTS

Compressors

The majority of refrigerators use compressors (one or more), which are their key elements. There are two main kinds of compressors:

- Volumetric type (or positive displacement), where a fix amount of fluid is admitted in a chamber (then the chamber volume is reduced to compress the gas, in this case of volumetric compressors, this being the only difference with volumetric pumps), and the fluid trapped is expelled. The typical positive displacement device is the piston-cylinder mechanism, but there are other examples, either reciprocating too (diaphragm compressors) or rotary compressors (with vanes, lobes, scrolls, or screws). Besides displacement volume, the main parameter of volumetric compressors is the compression ratio (volume ratio). Volumetric devices provide a simple means to know the volumetric fluid flow rate (chamber volume times frequency), which is independent on pressure; mass flow rate performance depends on volumetric efficiency, which slightly

decreases with pressure jump (almost linearly). Volumetric compressors are the best for low flow rates and high pressure jumps, and the most used in refrigeration.

- Rotodynamic type, where a rotor device continuously transfers angular momentum to the fluid, which is later recovered into a pressure rise by decelerating the fluid. Rotodynamic compressors may be centrifugal or axial, and are suited to large flow rates and small pressure jumps. The main parameter in dynamic compressors is the pressure ratio.
- Ejector type, where a high-pressure fluid ejected against a converging-diverging nozzle creates a low-pressure region upstream of the nozzle (where vapour from the evaporator is aspirated), and a high-pressure region downstream of the nozzle (but lower than the driving-fluid pressure).

Different types of compressors are used according to refrigeration capacity (size). For <10 kW refrigeration (from car air-conditioners downwards), volumetric compressors are used, either reciprocating (piston-type) or rotary (vane-type), with pressure-ratios in the range 2..6, working nowadays with R134a or R600a. For medium-size and large refrigerators (from 10 kW to 1 MW of refrigeration) screw compressors are used, with pressure ratios in the range 8..20. Centrifugal compressors are only used in very large refrigeration systems (>0.5 MW of refrigeration). Other dynamic compressors, like axial compressors and ejectors, are seldom used. Modern compressors make use of a variable-frequency drive (named 'inverter' and consisting on a AC/DC rectifier, a solid-state oscillator, and a DC/AC converter, the inverter properly, delivering a quasi-sinusoidal output of controllable frequency), able to control shaft speed from some 25 % to 100 % of nominal capacity, instead of using on-off cycling to modulate cooling capacity, with better energy efficiency and less noise.

In a hermetically sealed reciprocating compressor, all components (electrical windings, stator, rotor, crank-shaft, compressor chamber, and exhaust duct) are exposed to both lubricant oil and low-pressure cold gas from the vaporiser, within a single steel shell, as sketched in Fig. 9. The stator coil is cooled by oil at the bottom whereas the rotor coil is cooled by the refrigerant vapours before been compressed. Notice that electrical dissipation adds to the cooling load (and it may represent some 30 % in very small systems), decreasing energy efficiency. Notice also that discharge temperatures in hermetically sealed compressors are limited by oil decomposition temperature (that is why they are not used for deep cooling).

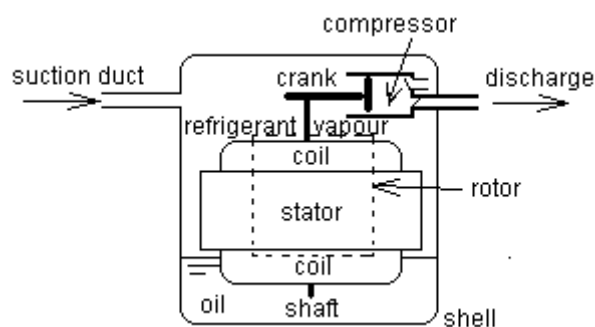


Fig. 9. Sketch of a hermetically sealed reciprocating compressor.

The screw compressor is a positive displacement rotary machine, consisting of a pair of matching screws (helical lobed rotors of several shape, like in Fig. 10) rotating within a tight casing (i.e. with a very small clearance).

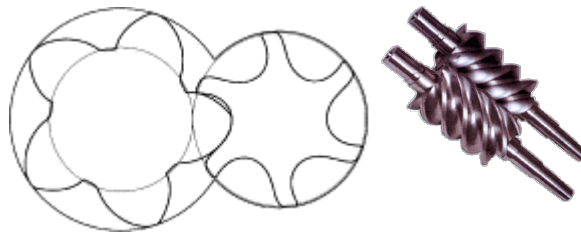


Fig. 10. Typical rotor profiles for a screw compressor.

Vaporisers and condensers

Vaporisers (also named evaporators) and condensers are phase-change heat exchangers. The typical vaporiser is of the recirculation type shown in Fig. 11, to avoid having dry sections (i.e. vapour without liquid) that would have very low heat conductance; condensers may be similar in small systems, but for larger systems the typical shell-and-tubes compact heat exchanger is preferred.

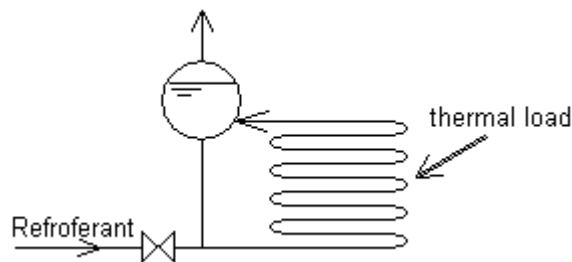


Fig. 11 Sketch of a vaporiser.

The second fluid in vaporisers is air for space conditioning, or a secondary liquid coolant otherwise, perhaps going to a cold plate where the load to be refrigerated is attached.

The simplest condenser is directly cooled by air, even by natural convection for small units as the domestic refrigerator, but for larger units, a secondary liquid coolant is preferred, to be finally cooled in a cooling tower (of the closed type, or of the open type if the same water is used as secondary coolant). Contrary to power-plant condensers, refrigeration condensers work at overpressure and not under vacuum, what simplifies deaeration tasks.

Throttling devices

The throttling device has two purposes; the basic one is producing a flow restriction to maintain the pressure difference between condenser and vaporiser that is the origin of cooling, and the second one is to control the flow-rate to maintain vaporiser temperature against cooling-load variations, ensuring that the refrigerant gets fully vaporised before entering the compressor. This can be achieved by means of a thermostatic expansion valve (TEV) that adjust the pressure drop according to refrigerant superheating (e.g. the valve stays closed until $\Delta T=5\text{ }^{\circ}\text{C}$, and opens proportionally to ΔT until full-open at $\Delta T=15\text{ }^{\circ}\text{C}$), or, in small systems with hermetic circuit, by means of a capillary tube (a fine-bore tube is inexpensive,

and the pressure-loss in it can be accurately predicted, although being constant after manufacture, require control by motor on-off steps).

All parts of refrigeration circuits must be kept clean of dirt, but particularly throttling devices.

Piping

Piping connections between main elements are made with copper tube to avoid contamination, and joints are silver-brazed. External insulation is used on all cold pipes.

Dirt, moisture and air must be getting rid of from the whole circuit before loading the refrigerant and oil. All openings in components and pipes must remain sealed until connected; many service troubles in large refrigeration and air-conditioning systems are caused by lack of adequate precautions during installation. Thorough cleaning is necessary after cutting the copper tube to final fitting, to prevent filings entering the pipe. Special care must be paid when brazing the joints (a nitrogen purge is used to prevent oxidation inside the tubes).

Leak checking is usually done with nitrogen just after the initial installation, and in vacuum and with refrigerant at each loading. Besides checking pressures, the refrigerant supply container is weighted to double check the amount charged.

Fans

Liquid-air heat exchangers, found for instance on all small air-conditioning units, are always built with extended surfaces (fins), and usually fans to enhance heat flow-rate).

Modern domestic refrigerators have two fans: one outside for cooling the compressor and condenser, and a second one inside to move air around within the refrigerator after closing the door, providing more even cooling (enhancing also the defrost process).

Fans are more important in refrigeration and air conditioning than in heating, because of the smaller temperature gap. Care should be taken, however, in air conditioning units to minimise drafts, with exit air velocities in the order of 1 m/s, and not as high as 10 m/s used in industrial refrigeration.

Defrosting

When air contacts the cold vaporiser walls of a refrigerator at $<0\text{ }^{\circ}\text{C}$, ice crystals grow there (air is always humid), and accumulate (contrary to liquid condensation, which pours down), reducing the heat transfer by two contributing effects:

- Ice thermal conductivity is much lower than that of the heat-exchanger walls (copper, aluminium or steel). And it is not bulk-ice that forms, but small irregular crystals with a lot of trapped air within, a porous layer with a density of some $\rho=(130\pm30)\text{ kg/m}^3$ (instead of 920 kg/m^3 for bulk ice), and a thermal conductivity $k=(0.16\pm0.04)\text{ W/(m}\cdot\text{K)}$ (instead of $2.3\text{ W/(m}\cdot\text{K)}$ for bulk ice).
- The ice grown takes space out of the air passage, decreasing air flow-rate when forced convection is imposed by a pressure gradient (or demanding more air-pumping power otherwise).

Consequently, deposited ice must be removed from time to time (defrosting). The water balance of a refrigerator shows that every time the refrigerator door is opened, and with every moist-goods input, there is a net water intake (even in dry climates, warm air usually holds more water-vapour than saturated cold air).

Old refrigerators had the vaporiser inside the cooled space, and the frost had to be manually scrapped. Modern refrigerators are frost-free in the sense that they automatically dispose of the generated frost (thus, they are really defrosting-free, instead of frost-free).

The usual defrost system is an electrical resistance wrapped around the freezer coils. A timer triggers every 6..8 hours, turning off the compressor and powering the resistor for a few-minutes duration (until a local thermistor rises well above 0 °C; local air temperature may rise to 10 °C at the end of defrosting). The ice melts and drips into a collector funnel, ended in a capillary tube that runs through the wall to an outside pan where water evaporates to a non-saturated environment (usually aided by condenser heat). The heater can be distributed along the vaporiser, or concentrated near the bottom side, defrosting mainly by heat conduction in the former case, with heater temperature below 100 °C, or by convection and radiation in the latter, with heater temperatures up to 300 °C. To avoid breaking the cold-chain in the interior, the refrigerator vaporiser is placed outside the cold space, with interior-air being forced (once the door is closed in domestic refrigerators) between the vaporiser and the load (this fan adds a few watts to the cooling load). Defrosting deep freezers may be more complicated due to lower operating temperatures, but sometimes it can be accomplished by sublimating the ice (e.g. heating the vaporiser coils from -25 °C to -5 °C) if the air is dry enough.

Instead of an electrical resistor, defrost can be also achieved by reversing the refrigeration cycle to work as a heat pump (not only in vapour cycles, but in thermoelectric refrigerators too), what is the current practice in large systems. In any case, defrosting always imposes some heating spikes on the refrigerated load around the icy vaporiser coils.

Frosting can be delayed by appropriate coating of the cold surface, either with hydrophobic paints that can sustain a large undercooling by lack of nucleation sites, or with hydrophilic coatings that adsorb the concentrated water-vapour near the surface, retarding solid deposition.

A related phenomenon is the 'automatic defrosting' that can be seen in the glass windows of supermarket freezers. The air inside may be at -25 °C and 90 % RH (a little bit hotter and drier at the rear of the double glass window, and a little bit colder and saturated close to the vaporiser). When you open the door, moist ambient air immediately frosts and fogs the very cold inner glass. When you close the door, the icy layer is exposed to a colder and drier environment, and sublimation starts, pumped by the equilibrium-vapour-pressure gradient sustained by the vaporiser, automatically defrosting and defogging the window, after a while.

REFRIGERANT FLUIDS

The term refrigerant fluids (or just refrigerants), refers to fluids that are made so cold (in a refrigerator) that they can cool a load, not to fluids that generate the cold (as freezing mixtures do).

Desired properties

Desired properties for refrigerants are nearly the same as for any other thermal-energy transport fluid (heating fluids included):

- Large thermal capacity and density (to minimise flow-rate). In some applications, however, the use of gases may be favoured, due to cleanliness, for instance, or to electrical properties.
- Wide temperature margin (to avoid decomposition or freezing).
- High thermal conductivity (to lower residence time).
- Low viscosity (to lower pumping needs).
- Compatibility with piping materials and joints.
- Safe (non-flammable, non-toxic).
- Adequate economic and environmental constraints.

Besides, for primary refrigerants used to generate cold by vaporisation, additional and most important properties are:

- Appropriate vapour pressure values, related to the intended application (preferably above ambient to avoid air intake in vacuum systems). Critical temperature above the ambient, $T_{cr} > T_{amb}$. Water is not used because it has rather high freezing temperature $T_f = 0\text{ }^{\circ}\text{C}$, very low vapour pressure, $p_v(0\text{ }^{\circ}\text{C}) = 0.6\text{ kPa}$ and very low vapour density (large-size compressor). In spite of that, water is being used in some very-large air-conditioning applications, where binary-ice is produced by flashing water to 0.6 kPa, aspirating the vapours with large centrifugal compressors.
- Large vaporisation enthalpy.
- Small isentropic coefficient (to avoid too much heating in the compressor). A steep or even positive slope of the saturated vapour curve in the T - s diagram also helps in this direction.

Types

There are several possible classifications of refrigerant fluids, besides their commercial manufacturer family names (e.g. Isceon®, Forane®), and other occasional names of opportunity (nowadays they are grouped as new refrigerants and old refrigerants, because of the changeover taking place since 1990). Several groupings may be established:

–By purpose. Two kind of refrigerant fluids (or just refrigerants) can be distinguished:

- Primary refrigerants, which are the working fluids of a refrigeration machine, e.g. n-butane, R134a, NH_3 , CO_2 . They get heat from the load and, after some further processes, they give off heat to the sink.
- Secondary refrigerants, which are auxiliary fluids used to transport the low-temperature effect to more convenient places, and they may be chilled water down to $0\text{ }^{\circ}\text{C}$, or antifreeze fluids: glycols, brines, etc.

–By halocarbon numbering system (first adopted by DuPont manufacturers and later by professional association like ASHRAE). The general rule is R-xyzC, with the common initial R standing for ‘refrigerant’, xyz being a 3-digit number related to the particular molecule, and C being a character to extend the identification, according to the conventions in Table 4.

Table 4. Nomenclature of refrigerant fluids (R stands for refrigerant).

Code	Meaning	Example
Rxyz	Halocarbons x=number of carbon atoms -1 y=number of hydrogen atoms +1 z=number of fluor atoms Their molecule is to be completed with chloride atoms up to the carbon valence.	R12: (R012) x=0→ 1 C, y=1→ 0 H, z=2→ 2 F, plus 2 Cl, i.e. dichloro-difluoro-methane, CCl ₂ F ₂ R22: (R022) x=0 → 1 C, y=2→ 1 H, z=2→ 2 F, plus 1 Cl R134a: x=1→ 2 C, y=3→2 H, z=4→ 4 F, and no Cl, i.e. C ₂ H ₂ F ₄ , or 1,1,1,2-tetrafluoroethane, or CH ₂ F-CF ₃ . Plain hydrocarbons were also included: R50=CH ₄ , R170=C ₂ H ₆ , R290=C ₃ H ₈ , R600=n-C ₄ H ₁₀ , R600a=iso-C ₄ H ₁₀ .
R7xx	Inorganic compounds xx = molar mass (rounded) a,b,... for different isomers, as they become accepted.	R717: ammonia (M _{NH3} =17 g/mol) R718: water (M _{H2O} =18 g/mol) R744: carbon dioxide (M _{CO2} =44 g/mol) R764: sulfur dioxide (M _{SO2} =64 g/mol).
R5xx	Azeotropic mixtures xx = chronological order.	R500: 50%R125+50%R134a wt was the first to market R502 : 48.8% R22 + 51.2% R115 was the third to market R507: R125+R143a, 50/50 in %wt.
R4xx	Zeotropic mixtures xx = chronological order A,B,... for different compositions, as they become accepted.	R404A: R125 + R143a + R134a, 44/52/4 in %wt R410A: R32 (CH ₂ F ₂)+ R125 (C ₂ HF ₅), 50/50 in %wt* R407C: R32 + R125 + R134a, 23/25/52 in %wt.
RxyzBt	halons xyz as for CFCs and t = bromine.	R12B1: 1 C, 0 H, 2 F, 1 Br, 1 Cl.
Halon xyzt	halons xyzt for C, F, Cl and Br atoms.	Halon 1211=CF ₂ ClBr, bromochlorodifluoromethane, liquid Halon 1301=CF ₃ Br, bromotrifluoromethane, gas Halon 2402= C ₂ F ₄ Br ₂ , dibromotetrafluoroethane, liquid.

*R410A is a quasi-azeotropic mixture.

-By chemical type (international naming system, IUPAC):

- CFC, i.e. chloro-fluoro-carbon compounds (e.g. R12, R13, R500). They are presently banned because of its ozone depletion potential (ODP); production stopped world-wide in 1-1-1995 and usage in 1-1-2000.
- HCFC=hydro-chloro-fluoro-carbons (e.g. R22, R409). Also banned because of its ODP; production due to stop in 2015 and usage in 2030, worldwide, but in EU, in 2001 for new equipment, in 2010 for old equipment, and in 2015 for any use.
- HFC=hydro-fluoro-carbons (e.g. R134a, R410A, R404A, R407C). Allowed because of its zero ODP, but they contribute to the global warming potential (GWP). Fluorocarbons where all hydrogen atoms are replaced by fluorine atoms are often called perfluorocarbons (PFC).
- HFO=hydro-fluoro-olefin (e.g. R1234yf). Almost equal thermal behaviour that R132a but with much smaller GWP. R1234yf (2,3,3,3-Tetrafluoropropene, C₃H₂F₄) is being used as a replacement for R134a in automobile air conditioners.

- Natural refrigerants (no ODP neither GWP): air, water, ammonia (R717, NH_3), carbon dioxide (R744, CO_2), and hydrocarbons: propane (R290, C_3H_8) and butanes (R600). They are flammable, or toxic, or have very large vapour pressures. Ammonia can be smell at 5 ppm in air; causing mild eye and respiratory irritation at 50 ppm and eye pain at 100 ppm.
- Halons, containing some bromine replacing some chlorine. Developed in the 1960s, were used more as fire-fighting agents, but, because of their ODP, production stopped also in the 1990s (see [Environmental effects and hazards in combustion](#)).

Substitutive refrigerants

Traditional refrigerants, the so-called freons (CFC and HCFC) were first synthesized in 1928 and swept away all other refrigerants previously used, most of them toxic. They were thought to be so safe, that his promoters used to demonstrate it by inhaling the gas and exhaling it to extinguish a lighted candle (it was also typical to pour gas from one bucket to another one and down a stair with a candle at each step, to demonstrate how heavy it was). In the 1960s more than half of the world production of freons was used as propellants of canned liquids (an application first tried for insecticides in the Pacific war). Additional applications of freons in the dry-cleaning and insulation-foams industries followed.

But in the early 1970s a lot of scientific effort was devoted to predict the effect of supersonic airliners and the space shuttle on the stratosphere, and it was found in the late 1970s that freons may have a negatively impact on two worldwide problems: firstly, on the thinning of the protective ozone layer at the stratosphere (protecting from ultra-violet radiation from the sun), a theory published by Rowland and Molina in *Nature*, June 1974, and, of a second importance, on the global warming by the increase of the greenhouse effect of the atmosphere. Anecdotic enough, the head of the freons laboratory at DuPont was precisely at that time trying to match the balance of all produced freons with its actual concentration in the atmosphere, without finding the missing sink: reaction with stratospheric ozone.

Notice that, even with present state-of-the-art technology (beginning of 21st century), there is a typical 10 % loss of refrigerant charge per year in commercial and mobile refrigeration equipment (e.g., some 70 grams per car per year; fortunately domestic refrigerators are sealed), mainly due to leakage through the compressor shaft, and joints, besides handling losses during initial charging, maintenance, and decommission.

To quantify the relative effects of different refrigerants on those two aspects, two variables have been defined:

- ODP=Ozone Depletion Potential relative to the effect of R-12.
- GWP=Global Warming Potential relative to the effect of CO_2 .

ODP and GWP values for several refrigerant fluids are presented in Table 5. Notice in Fig. 12 the conflicting properties that halocarbons exhibit as a function of composition.

Table 5. Ozone Depletion Potential, Global Warming Potential, and mean life in the atmosphere, for several refrigerant fluids.

Refrigerant	Formula	ODP	GWP	Atm. life [yr]
R-11	CCl ₃ F	1	4000	50
R-12	CCl ₂ F ₂	1	8500	100
R-1234yf	CH ₂ CFCF ₃	0	4	
R-134a	CH ₂ FCF ₃	0	1300	13
R-152a	CH ₃ CHF ₂	0	130	2
R-22	CHClF ₂	0.055	1700	13
R-290	C ₃ H ₈	0	11	<1
R-404A	mixture	0	3700	
R-407C	mixture	0	1600	
R-410A	mixture	0	1700	
R-600	C ₄ H ₁₀	0	3	<1
R-717	NH ₃	0	0	0
R-744	CO ₂	0	1	100

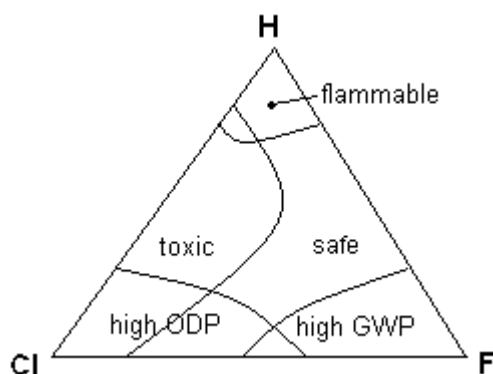


Fig. 12. Characteristics of hydro-chloro-fluoro-carbon compounds in terms of composition.

The ban on traditional refrigerants (and halons) from 1990 onwards (its ozone-depletion effect was finally concluded in 1986 and the ban adopted at the Montreal Protocol in 1987), caused a convulsion in the refrigeration industry (and on fire-extinguishers, can propellants, foaming agents, dry cleaning and other industries).

The impact on refrigeration industry was more severe because the CFC refrigerants were used not only as working fluids (mainly R12), but also to blow the polyurethane-foam insulation (mainly R11), and there were $70 \cdot 10^6$ new-fridges/year in 2000 (growing at 10 %). Nowadays R600a is normally used for both, the refrigerant and the blowing agent. The changeover seems now to have been mastered, and substitutive refrigerants have been found that satisfy every application, as summarised in Table 6.

Table 6. Substitutive refrigerants.

Temp. range	Applications	Old refrigerant	Substitute refrigerant
0..10 °C	Air conditioning	CFC: R11, R12 HCFC: R22	R134a, R123yf R410A, R600 if <1 kW. R717 if >10 kW
–25..0 °C	Refrigeration in general	CFC: R12 HCFC: R22	R134a, R290, R600a, R290/R600a R410A, R600 if <1 kW. R717 if >10 kW
–50.. –25 °C	Low-T food refrigeration	CFC: R502	R507, R407A, R407B
<–50 °C	Ultra-low-T refrigeration	CFC: R13	R23

Notice that zeotropic mixtures (e.g. R410A, R407A, B or C) have different compositions in the liquid and vapour phase, thus, if a leakage occurs, the whole fluid mass must be re-loaded. On the other hand,

zeotropic mixtures vaporise with a temperature drift at constant pressure, making more efficient the process of stream cooling (using mixtures as refrigerants was first proposed by H. Lorentz in 1894).

The basic substitute for the omnipresent R12 has been R134a, commercially available since 1991, although its large GWP (1300) has thrown it out of the mobile refrigeration application (in EU, from 2011 new designed cars, and from 2017 all new builds, must use refrigerants with $GWP < 150$, hence discarding R-134a, R-407C, R-410A, R-404A...).

All halons (1301, 1211, 2402 and their blends) are banned and being substituted by iodotrifluormethane (CF_3I), FM-200 ($R227$, C_3HF_7 , heptafluoropropane), and Inergen (IG-541), a mixture of N_2 , Ar and CO_2 .

Second refrigerants: glycols, brines and binary ice

Second refrigerants are used to store and transport away the cold generated with the primary refrigerant inside the refrigerator. Main second refrigerants are glycols (e.g. propylene-glycol), brines (salt water mixtures), fluid ice, and CO_2 for cold temperatures.

Detailed properties of glycols, brines, and carbon dioxide are presented in the study of [Solution properties](#), and fluid ice is presented below.

Refrigerant-leakage detection

Leakage detection of refrigerant fluids is not easy because they are transparent and most leaks are in the gas state. Detection can be based on odour (natural as for ammonia, or artificial, as marked hydrocarbons), a physical effect (e.g. bubbling), or a chemical effect (e.g. catalytic-reaction heating of a platinum wire, as in explosion-meters).

For all halogenated refrigerants (CFC, HCFC and HFC) the best detection method is by fluorescence excitation with ultra-violet lighting.

ICE MAKING

Ice making has marked the history of refrigeration, which for long time had just one goal: making ice.

Ice can be made on any refrigerator that cools below $0\text{ }^{\circ}\text{C}$ (it is usually handled at about $-5\text{ }^{\circ}\text{C}$ to $-1\text{ }^{\circ}\text{C}$), but we here study special-purpose devices intended just to produce ice, either in batch or in continuous mode. However, the elements are nearly the same as for common refrigerator (e.g. the same compressors are used). Air-cooled condensers are mostly used, because of its simplicity, but water-cooled models are more efficient, and the heat removed in ice making can be discharged outside the building in a cooling tower (one-pass discarded water cooling is too wasteful), thereby not adding to air-conditioning costs.

The segregation associated to the phase change may be used to get ice that is more pure than the original water supply, with an impurity-concentrated water purge, but most of the times there is an active-carbon intake-filter to remove odours and other impurities and all used water is converted to ice. If the supply water has more than 500 ppm total-dissolved-solids, a water-treatment pre-stage should be installed.

Nowadays, every restaurant, hotel, hospital, supermarket, ship and other facilities operate ice-making machines, and even at home, there are more and more refrigerators with chill water and ice dispensers. Small domestic units, using R134a, with some 0.5 kg/h of ice-making capacity have low energy efficiency (some 0.5), whereas industrial units, using R404A, usually have efficiencies above unity.

Heavy duty ice makers may use additional amount of water (up to three times that needed for the ice) to self-clean the machinery, saving maintenance labour but increasing the water bill.

Sun-driven ice-making plants have been developed, but although there is a favourable coupling between sun isolation and ice production needs, there is the unfavourable circumstance that it is cheaper to produce ice by night (when there is no sun) because of the cooler ambient (photovoltaic systems with a battery bank have been demonstrated).

Ice makers may be classified according to the size of ice produced. Large ice bars of 1.5 m long and 0.2 m side, produced in large ice-factories with ammonia absorption plants using metal moulds immersed in a brine pool, were the standard in the first half of the 20th c., but nowadays the typical shapes are the familiar ice cube and the industrial flake ice (slurry ice is gaining markets).

An interesting application of ice making is as a cold storage, to level (or for the optimization of) cooling loads, as when making ice by night to help with air-conditioning the following day, saving in the electricity bill.

Ice has been used even for sculptures (e.g. weddings banquets); large crystal-clear ice blocks up to 1 m wide have been carved with a chisel like marble sculptures.

Ice cubes

Most ice making machines produce so-called ice cubes, used to cool drinks, ranging from rounded cubes to 'square' cylinders of some 2.4 cm size (10..30 g a piece). The amount of liquid water trapped is negligible, but gases and solids may get trapped in ice cubes, particularly at its centre, that becomes whitish.

The explanation of why there may be a bunch of air bubbles in the middle of an ice cube is as follows: we start with tap water at some 10 °C, which can be assumed nearly air-saturated (see Fig. 13), with say 0.003 % by weight of air (see [Solutions](#)). When freezing by external cooling, the first solid forms in the periphery (at about -0.002 °C corresponding to that solution), being nearly pure transparent ice (around 1 ppm air in weight). Further freezing takes place along the *liquidus* line down to the eutectic point for water-air mixtures (0.0036 % by weight air, -0.0024 °C), where the remaining liquid mixture is unable to dissolve any more air and a two-phase freezing process develops with ice trapping a myriad of tiny air-bubbles (the 0.0038 % by weight of air in the liquid degases to 0.0002 % in the solid plus the remaining 0.0036 % by weight of air occupying 3 % of the whole volume), making the ice cube cloudy (i.e. highly dispersive to light).

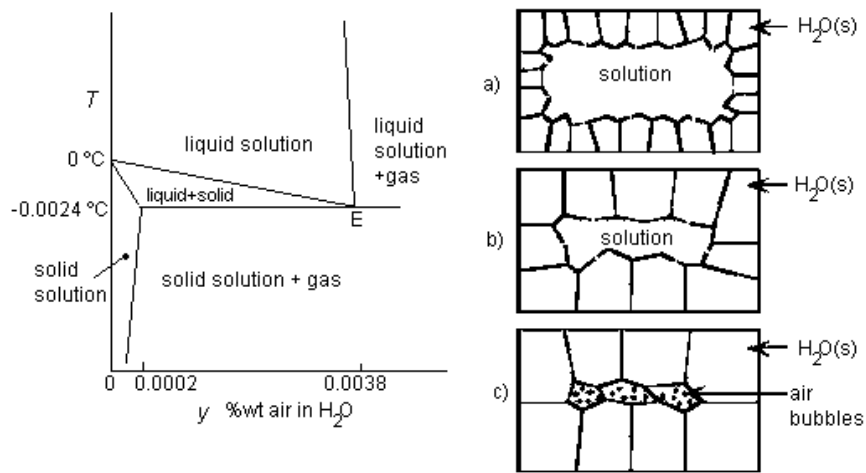


Fig. 13. Phase diagram of air-water mixtures. Air solubility, by weight, is 0.0038 % of air in the liquid, whereas in ice it is 0.0002 %. The eutectic point E is at $-0.0024\text{ }^{\circ}\text{C}$ and 0.0038 % air.

Making clear-crystal ice-cubes requires bubble-free freezing, either by using distilled water, or better by avoiding the eutectic limit of air-dissolved in the liquid (by avoiding the liquid being enriched because it is a close system, i.e. by making ice cubes with running water). The two most common procedures are:

- Using a tilted ice-cube-tray over which water is running.
- Growing ice cups around downward fingers from a refrigerant pipe partially immersed on running water.

Ice cubes must be kept dry to avoid clumping. Many other ice-related details can be found in [Water Thermodynamics](#) (in Spanish).

Flake ice (chip ice)

Flake ice or chip ice is the common industrial type of ice. It is the most convenient form to cool solids, since it tends to conform to the surface of items that rest on it, and is typically used in supermarket display cases and on fishing boats. But flake ice is also used for ice blasting (although dry-ice blasting does not yield liquid waste, it is much more expensive). Flake ice may contain up to 20 % liquid water.

There are several ways to make flake ice, one of the simpler and more effective is the immersed cold drum sketched in Fig. 14. In it, the vaporiser coil of a refrigeration machine cools the immersed drum to freezing temperatures, and a thin layer of ice forms that, upon appropriate values of cooling, rotation rate and diameter, shatters into small pieces when impact with a knife blade, due to accumulated internal stresses; the cylinder may be made with several metal panels separated by flexible rubber to enhance ice-sheet cracking.

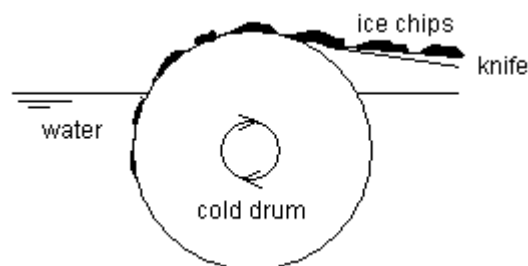


Fig. 14. Making flake ice with a cold drum.

In more compact ice makers, a rotating cold disc with one blade at each side is used in a similar manner. In other setups, no mechanical removing device is used, but a thermal pulse with hot gas from the compressor, or reversing the refrigerant cycle, is used to get the ice detached.

Crushed ice

Crushed ice is scarcely used (just as a quick cooler add for drinks); sometimes the thick ice-slurry obtained is further extruded to yield ice nuggets. It consists of small (about 1 mm in size), irregular pieces made by crushing larger chunks of ice. If water is added to crushed ice, a pumpable slurry is obtained (liquid ice), but it is better to produce it directly from water, to avoid any solids handling.

Fluid ice (or liquid ice, or slurry ice, or binary ice)

Liquid ice is an aqueous ice/liquid slurry mixture, i.e. a two-phase system, with minute ice crystals (<1 mm; usually in the range 0.1..0.4 mm), that can be handled as a fluid (pipes, pumps, valves, heat exchangers, etc.), and used as a high-capacity thermal source for cooling. The slurry must have >20 % by weight of liquid, which can be plain water (for work at $0\text{ }^{\circ}\text{C}$), seawater (for fishing applications at nearly $-2\text{ }^{\circ}\text{C}$), or an antifreeze mixture for cooling at lower temperatures: water/alcohol antifreeze or brines. The slurry must be continuously moving at >0.5 m/s to avoid ice accretion and clogging (tanks are provided with continuous stirrers).

With $y_s < 25$ % (weight percent of ice), the slurry is pumped exactly as if it were just chilled water, with 5 times more cooling power for the same mass flow-rate. In the range of 30..60 %wt ice, the mixture shows a thick slurry behaviour, and in the range 60..80 %wt ice, it is like a soft ice-cream. For $y_s > 10$ % the slurry departs from Newtonian behaviour, and power-law or Bingham fluid models must be used (multiphase flow is seldom used).

Production of slurry ice may be accomplished in several ways, from simply super-cooling the solution in a conventional heat exchanger, to different scrapping systems as for flake-ice, passing by vacuum flashing with compressors or ejectors, or even desiccant systems (Fig. 7). The physical behaviour of the slurry depends somehow on the production method, particularly the apparent viscosity. A typical 2 % by weight ice-in-water slurry has a pressure drop three times that of water at $0\text{ }^{\circ}\text{C}$ for a typical circulating speed of 1 m/s; this figure decreases at higher speeds (e.g. only 1.5 times at 2 m/s) and increases at low speeds (e.g. to ten times at 0.5 m/s). Thin slurries (<25 % of ice by weight) can be pumped with common water pumps, and circulated through common water pipes (even smaller diameters because of the higher cooling power), but conventional valves should not be used.

For a given application, the convective heat transfer coefficient decreases with respect to water some 1 % every 1 % of ice, being always much larger than for solid ice. Thermal conductivity of liquid ice is larger than that of water and smaller than that of ice.

Ice rinks

Ice rinks are large artificial ice surfaces used for sports or entertainment (an Olympic hockey rink has $30\cdot60\text{ m}^2$), and may require from 100 kW to 1 MW refrigeration (30..300 tons). Ice skating dates at least back to 3000 b.C. (a pair of skates made with bones of large animals were found at the bottom of a lake in

Switzerland). In the XIV c. the Dutch started using wooden-platform skates, with flat iron bottom runners, attached to the skater's shoes with leather straps, and using poles to propel themselves.

Ice rinks are always built in situ. First a load bearing floor is laid out (made of concrete over sand if permanent, or made of wood if portable), and a maze of cooling pipes distributed on top. The refrigeration machine, usually a large ammonia-absorption plant, is located nearby, with a secondary refrigerant going to the rink pipes. Several layers of water are sequentially poured upon and frozen, until the desired thickness is achieved. The dashboard is previously installed to avoid water spillage, but even without, water losses may be minimal if water is slowly sprayed, because most of it freezes (Fig. 15).



Fig. 15. Making the ice sheet in an ice rink.

Raw ice would be translucent and greyish, so that several layers of white paint are always applied to have a perfect white background, on top of which, separated by a thin layer of ice to avoid paint mixing (made of deaerated water for better transparency), sport markings or advertising in vivid colours are painted or just adhered, before a final protective deaerated ice layer some 1 cm thick is applied, polished and regenerated daily.

In cold and dry climates the rink may be left outdoors, but other times it is roof-covered and space-heated for public comfort and dehumidification to avoid mists (condenser heat is advantageously used for that purpose). Removing ice is a much faster operation: cooling is stopped, the secondary refrigerant is heated instead of cooled, ice starts to melts below, a mechanical machine breaks the upper ice layer (sometimes helped with hot-water spraying), and the whole mesh is swept off.

Long-lasting seasonal and permanent ice rinks require some ground heating to avoid freezing and fracturing of the foundations (a sand bed of some 0.3 m thick with heating ducts and a water-collector underneath is a typical solution). Portable installations, for less than a month usage, may use wooden floors (it takes anyway nearly one day to set up a portable ice rink). Permanent rinks may use a CaCl_2 brine as secondary refrigerant, most efficient but very corrosive; but for portable systems glycols are more often used.

Cooling ducts under the ice (some 2 cm below the surface), are typically 1 cm in diameter and some 10 cm apart, cooling the ice to $-4\text{ }^{\circ}\text{C}$ because if further cooled it becomes brittle to small chocks, and if hotter it is too soft and gets damaged.

The first indoor ice rink opened in London in 1876, and the first Olympic figure-skating competition was held on an indoor ice rink in 1908 as part of the Summer Games also in London (in 1976, ice dancing became a Winter Olympics sport). Ice rinks may be occasionally used for other purposes if a wooden working floor is put onto the ice.

Artificial snow

Snow refers either to the solid-water precipitation in the form of flakes in the atmosphere, or to the solid-water layer of snowflakes and soft ice on the ground. Artificial snow is nowadays a service in most ski resorts (with hundreds of snow cannons at every one place), since only that can the snow season be guaranteed (what is a must in present tight-planned in advance holiday habits).

Artificial snow can be created by forcing pulverised water to freeze in cold air. A water source must be available, but the consumption may be small if the thawing of the generated snow is recovered. Water (liquid) must be sprayed into cool air in very small droplets to accelerate the freezing and to get flakes and not hail, but getting a water spray is not difficult. The key issue in creating artificial snow is thence cold air and the required residence time to freeze the droplets by heat transfer.

In dry atmospheres, even with air above 0 °C the droplets can freeze because of the evaporative cooling implied (the limit would be the ultimate dry-bulb temperature corresponding to a wet-bulb temperature of 0 °C, that happens to be 10 °C). But most practical snow generators work in the range −10..+2 °C.

Snowmaking may use two different types of systems to create the fine water droplets that will transform into snowflakes in cold air:

- Compressed air duct (from a line or a small compressor) and water supply, with a nozzle where the compressed air pulverises water and eject the spray (a system sometimes called snow-gun). The best for small applications. No electricity required.
- Ambient air blower (a fan run on a heat engine or electricity) and water supply through many tiny nozzles (a system sometimes called snow-cannon). The best for large systems. The snow created by snow-cannons is wetter and denser than that of snow-guns, but it is more durable, and covers terrain features more effectively.

Artificial snow is slightly different from natural snow. Natural snowflakes are soft and light, and have six tiny dendritic arms, whereas artificial snow forms a compact six-sided structure, allowing it to pack more densely and retain less air, making it more firmly to the touch and to skiing, and retaining its durability longer.

Besides mountain ski resorts, snowmaking can be used to other purposes, like indoor ski sites, or mitigation of freezing temperatures in agriculture. As for 2004, there were some 50 large indoor facilities (sometimes called snow domes), around the world: the first one started in 1988 in Belgium, a 500 m ski slope in Tokio opened in 1993 and closed in 2002, a 250·80·50 m³ (10⁹ € investment) snow park in Madrid Xanadú opened in 2003. Indoor temperature is maintained at some −2 °C with powerful refrigeration equipment (the snow is also refrigerated during a few hours by night). They are very much

appreciated for ski training, snow-board and snow-car recreation and gentle snow skiing (all kind of conveniences, no wind problems, all year around...).



Fig. 16. Indoor snow slope.

ICE CHEST

Generally, nowadays an ice chest or ice box is a thermal-insulated all-plastic-container with a top door to put ice chunks and the goods to be cooled inside; e.g., to go picnic). The early ice-chest, however, were wooden boxes lined with tin or zinc (maybe further insulated with cork) with a drain tap to get rid of the water formed; the large ones, resembling the actual home refrigerator, with front door, had a drip pan under the ice box itself, to collect the water melt, and had to be emptied daily (with the inevitable spatter).

In practice, not only ice lumps but any other previously-frozen material (i.e. a secondary refrigerant, solid or encapsulated fluid), can be placed inside and used to cool the load. Several commercial substances have been developed to substitute ice, usually gels and eutectics. Although they are more expensive than the traditional ice lumps or ice cubes, they have the following advantages:

- Long lasting cold, due to dryness (less thermal conductance through the walls).
- More adaptive shapes (they can be flexible polyethylene bags filled with a gel, or shape-keeping bricks).
- Re-usable (the coolant can be refrozen or re-cooled in a normal freezer).
- More hygienic (tap-water ice might have contaminants). Of course, they must be non-toxic even after breakage.

For very long durations (e.g. sailing, remote camping), a second ice chest used as freezer can hold the ice for many days, using a load of dry ice (or carbon dioxide snow) to keep the water ice (at $-78\text{ }^{\circ}\text{C}$).

CRYOGENICS

Cryogenics (from Greek *κρυος*, icy cold), deals with phenomena occurring at very low temperatures. Several arbitrary bounds on the 'low temperatures' may be established: $<120\text{ K}$ was adopted by the XIII Congress of the International Institute of Refrigeration, $<100\text{ K}$ is a more rounded figure (NIST chose 93 K), $-100\text{ }^{\circ}\text{C}$ another one ($<173\text{ K}$), but $<200\text{ K}$ seems a better choice because, in current practice, there is no much interest in the range from the traditional refrigeration applications (i.e. from ambient temperature to some $-50\text{ }^{\circ}\text{C}$ (223 K)), and the nearest colder technique: dry ice, at $-78\text{ }^{\circ}\text{C}$ (195 K). For instance, in naval applications, a cargo at $<-55\text{ }^{\circ}\text{C}$ is classified as cryogenic.

The lower limit for cryogenics, 0 K, can be approached but not attained (Nernst theorem, 1918). The first proposal of a cold limit, i.e. an absolute zero in temperature, was made by G. Amontons in 1702 when improving the gas thermometer initially proposed by Galileo; his estimate of absolute zero, based on air trapped in a mercury-in-glass thermoscope, was $-239\text{ }^{\circ}\text{C}$ instead of the correct value of $-273.15\text{ }^{\circ}\text{C}$.

Cryogenic temperatures may have astonishing effects on materials. After one minute in liquid nitrogen, a flower becomes so hard that when dropped onto the floor it shatters into thousands of pieces, as though it was made from glass. A rubber tube, once cooled in liquid nitrogen, becomes inflexible and so brittle that when hit against a table, it breaks into several fragments. A banana dipped into liquid nitrogen becomes hard enough to hammer a nail onto a piece of wood, although it is made up mostly of water, because it contains fibres that hold the ice crystals together (while ice itself may be very hard and brittle, when arranged with fibres it loses a lot of its brittleness, and some hardness; a similar phenomenon occurs with glass-fibre, which is made up of brittle glass, and a flexible polymer, making it extremely tough).

The study of material properties at cryogenic temperatures is important not only for cryogenic applications, but for computation of absolute entropies, for instance. There is a rapid decrease of thermal capacity at low temperatures; $c_p(T)$ tends to zero as T^3 , in crystals, and the same for thermal conductivity (with an additional linear term in T for metals in both properties, due to electrons contribution).

APPLICATIONS

The main applications of cryogenics (i.e. below 200 K) are briefly presented here (some are explained in detail after the Cryocooling techniques are analysed):

- At about 195 K (CO_2 normal sublimation point), [dry ice](#) production and use.
- At about 150 K, high-temperature [superconductors](#).
- At about 112 K (CH_4 normal boiling point), liquefied natural gas ([LNG](#)), production and transport.
- At about 80 K, [liquid air](#) fractional distillation, liquid nitrogen (much used in cryogenic refrigeration, often abbreviated to [LN2](#), not to be confused with LNG), liquid oxygen (LOX, used in aerospace and submarine propulsion). Satellite passive coolers can get down to 30 K by radiating to the [cosmic background](#), at 2.7 K, if properly insulated from other heat sources (e.g. in [JWST](#)). Used in the cooling of infrared and microwave detectors, to decrease thermal noise of electrons ([Johnson-Nyquist noise](#)). Sensors of most space telescopes (in any band: RW, MW, IR, visible, UV, X-ray, or γ -ray) must be cryocooled to enhance signal-to-noise ratio.
- At about 20 K (hydrogen normal boiling point). Liquid hydrogen ([LH2](#) in the argot) used as fuel in high-performance rockets, with liquid oxygen ([LOX](#)) as oxidiser. Application to deep vacuum space simulators (at 20 K the vapour pressure of nitrogen is some 10^{-8} Pa).
- At about 4 K (helium-4 normal boiling point). Liquid ^4He ([LHE](#)) is used in medical imaging ([MRI](#)). Since the huge price-rise of helium in the 1990s, it is no longer discarded after use but recycled (usually off-line). LHE is kept at 4.2 K (around 100 kPa) inside a dewar flask immersed in a wider dewar flask filled with liquid nitrogen at 77 K.
- Below 4 K is basically for scientific research. Below 10^{-6} K, a new state of matter where quantum phenomena appear at macroscopic level has been found ([Bose-Einstein condensate](#)).

The initial application of cryogenic refrigeration was to liquefy the so-called permanent gases (notably dry air, first liquefy by von Linde in 1896), i.e. to cool the working substance down to its liquefaction temperature.

CRYOCOOLING

Cryogenic refrigeration ([cryocooling](#)) is needed for two tasks: first, to lower the temperature of the system (the sample) from ambient to cryogenic temperatures, and second, to keep the sample at such low temperatures against the inevitable heat transfer input from the environment (and maybe heat dissipation inside).

As for any refrigerator, the cryocooler provides a cold plate that takes the heat from the sample. The cold plate, where the sample is installed, is usually made of copper to provide high thermal conductivity (an electrical insulating film separates the sample from the cold-plate). The cold plate is at the end of a hollow cold finger that provides fluids and electrical connectors to the sample while minimising heat conduction.

Cryogenic refrigeration is not energy efficient; it cannot be: even the ideal Carnot cycle would have an efficiency (COP) of a mere 3 % operating between 300 K and 10 K ($\eta = T_2/(T_1 - T_2) = 10/(300 - 10) = 0.03$). For that reason, thermal insulation of cryogenic loads is a must, what demands a high vacuum within the insulator (be it a multi-layer insulation blanket, MLI, a Dewar flask, or both), because above $p = 1$ kPa the apparent thermal conductivity of a porous material is that of air; i.e., for $p > 1$ kPa, $k_{app} > 0.02$ W/(m·K). Different vacuum levels decrease gas conductivity to negligible values: e.g. with $p < 1$ Pa in low-density solid-foams one gets $k_{app} < 0.002$ W/(m·K), and with $p < 10^{-2}$ Pa in MLI one gets $k_{app} < 0.0002$ W/(m·K).

Obtaining cryogenic temperatures

The free environment on Earth's surface is around 300 K. To extract heat from a lower temperature, an exergy input is needed (usually work), and the sum of the heat removed and the energy spent must be finally rejected to the environment (in the steady-state case).

- Down to about 200 K can be achieved with vapour-compression refrigerators, normally using a two-stage cascade Rankine cycle, to avoid covering large temperature jumps with a single compressor. A simple way to achieve 195 K (normal sublimation point of carbon dioxide), is by simple expansion in a valve of compressed CO₂, as it occurs in CO₂ fire extinguishers.
- Down to 77 K can be achieved with simple regenerative gas cycles: Brayton, Joule-Thomson (JT), Stirling, Vuilleumier, Gifford-McMahon (GM), etc. Sometimes, a combination of a first-stage vapour cycle with a bottom gas cycle is used. Otherwise, LN₂ can be easily purchased and discarded after use (it is relatively cheap, at <1 €/kg).
- Down to 4 K can be achieved with sophisticated regenerative gas cycles, notably Stirling or Gifford-McMahon, usually in a two-stage or three-stage process (e.g. first a copper plate is cooled to around 90 K pumping heat to the outside environment, then another copper plate is cooled to around 20 K pumping heat to the 90 K plate, and finally another copper plate is cooled to around 4 K by pumping heat to the 20 K plate). These cryocoolers can be based on pulse tube refrigerators

([PTR](#)), a modification of the above cryocoolers in which the original mechanical displacers are substituted by acoustic processes. Typical cooling capacity of these cryocoolers range from 0.1 W to 10 W, with cool-down times of a couple of hours, and energy efficiency <1%.

- 1 K is obtained by evaporative cooling of [LHE](#) (aspirating with an external mechanical pump down to about 100 Pa the vapours of some liquid helium entering the 1 K pot from the 4.2 K main LHE bath). One cannot go lower because ^4He solidifies at 0.95 K (in fact, the 1 K pot is around 1.5 K in practice).
- 0.1 K is obtained by evaporative cooling of liquid helium-3 (^3He) using a sorption pump in a hermetic rig, basically consisting on a long vertical tube with three enlargements (top, mid, bottom), with no moving parts. At room temperature, this very-expensive isotope is mostly contained as a high-pressure gas in the relatively-large top chamber, with a long downward duct going along the different stages of cooling (LN2, LHE, and 1 K pot), and ending in a small pot (to be cooled to 0.1 K). The duct has a bulge at mid length, filled with activated charcoal, which absorbs ^3He gas only when at cryogenic temperatures. The working is as follows: when the other coolers in the cryostat are active, some ^3He in thermal contact with the 1 K pot condenses (^3He normal boiling point is 3.2 K) and drips to the ^3He lower pot. But when the charcoal gets cooled down to about 10..20 K, it absorb most of the ^3He gas, lowering the pressure of the helium-3 system below 1 Pa, and its equilibrium liquid-vapour temperature to 0.1 K by evaporative cooling; when all the liquid ^3He gets vaporised from the bottom pot, an electrical resistor heats the charcoal to 40..50 K and the ^3He gets desorbed, re-gaining the high-pressure state in the system that produce ^3He condensation in the 1 K pot (the latent heat release vaporises the ^4He there at a higher rate). In practice, samples in contact with this ^3He pot can be cooled to 0.2..0.3 K.
- 0.01 K is obtained by dilution refrigeration with a $^3\text{He}/^4\text{He}$ mixture. When such a mixture is cooled below 0.87 K, a two-liquid phase separation takes place, with endothermic dilution of ^3He from a ^3He -rich phase to a ^3He -poor phase that lowers the two-phase temperature; the ^3He -poor phase is brought to the 4 K LHE-level, where pure ^3He gas separates from ^4He and is recompressed at ambient temperature, and reliquefied in the 1 K pot (after cooling by LN2 and LHE). This is presently the lowest permanent temperature achievable; below that, only transient cooling can be obtained, down to 10^{-6} K by adiabatic demagnetisation of paramagnetic salts (see Magnetic refrigeration, above). Dilution refrigeration was used in expendable manner on board [Planck spacecraft](#), where one of its sensors worked at [0.1 K](#); cosmic background radiation (at 2.7 K) was advantageously used to provide passive cooling to 75 K; from that, a closed [H₂ sorption cycle](#) cooled down to 20 K, then a closed ^4He Joule-Thomson cycle cooled down to 4 K, and finally the expandable endothermic $^3\text{He}/^4\text{He}$ mixing (what limited its lifespan to 15 months) cooled down the sensor to 0.1 K.

Common challenges for cryogenic refrigeration are the development of efficient small-scale compressors and regenerators (heat exchangers).

DRY ICE

[Dry ice](#), also named carbon dioxide snow, was first made by Thilorier in 1834. It is the solid phase of CO₂, whose phase diagram is shown in Fig 16. Many other properties of pure carbon dioxide, as a function of temperature, can be found in [Solution properties](#), where some applications are also described, as its use on freezing mixtures.

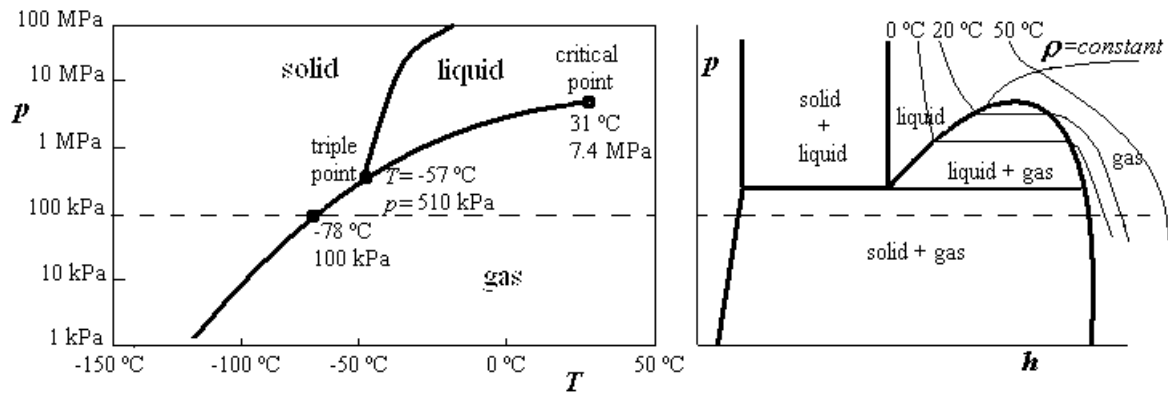


Fig. 16. Phase changes (p - T diagram) and p - h diagram for pure CO₂.

Besides CO₂ being a working fluid in some vapour-compression machines, dry ice is commonly used in many refrigeration applications, as for food freezing (it is fast, clean, and yields a preservative atmosphere), for shrink fitting (cooling large metal pieces for mounting with interference), for adhesive bond breaking, to solidify heavy-oil products for leakage clogging or ease of removal (even for sea spills), and for cleaning objects by dry-ice blasting, where the brisk temperature change due to the swift vaporisation is the cause of cleaning, not the abrasion of the solid chips (that is why it is used to clean delicate printed-circuit boards, besides the fact of leaving no residue). Immersion in compressed-liquid CO₂ at some -60 °C is one of the quickest freezing procedures used in industry (much less expensive than using liquid nitrogen); the vapours produced may be re-liquefied or vented.

Dry-ice flakes or pellets are produced by sudden expansion to ambient pressure of the compressed liquid, obtained from carbon dioxide gas (a sub-product of several industrial processes; see [Gases](#)), once dried and refrigerated by an ammonia or freon machine. Block dry ice is made by ram-compacting the dry-ice snow (density depends on the compactness achieved).

GAS LIQUEFACTION

Gas liquefaction, or condensation, is the conversion of a gas to the liquid phase by cooling or compression (see [Phase change](#); liquefaction also refers to the fluidization of solids, as when the strength and stiffness of a soil is reduced by earthquake shaking). All gases are transported in bulk in liquid phase because of economy (typically hundred times more weight-load for the same cargo volume). Propane, butane, ammonia, and other gases with critical temperature above ambient, can be liquefied by pressure at ambient temperature, although it may be more convenient to handle them refrigerated at some -40 °C, using common refrigerators, to avoid very strong pressurised tanks (the required thickness is proportional to the diameter, for a given pressure).

The first liquefaction of a gas was made in 1780 by G. Monge (the founder of l'École Polytechnique, in 1795), by passing compressed SO_2 through a coil tube immersed in a salt-ice mixture. In 1799 ammonia was liquefied at atmospheric pressure with a more powerful freezing mixture, and many other gases were liquefied in 1823 by M. Faraday, who in 1845 used a most-powerful freezing mixture: dry ice and ether, reaching $-110\text{ }^\circ\text{C}$ and leaving six so-called permanent gases: oxygen, nitrogen, dinitrogen monoxide, carbon monoxide, methane, and hydrogen. Helium, later found in the solar spectrum in 1868, was not discovered on earth until 1882, and isolated in 1895 by W. Ramsay, who isolated all noble gases.

Non-condensable gases like nitrogen or hydrogen must be cooled to cryogenic temperatures for liquefaction. In mid-19th century, beyond the reach of freezing mixtures, liquefaction was achieved by refrigeration in three basic steps: an auxiliary fluid was compressed as much as possible (usually up to 5 MPa), cooled as much as possible with a freezing mixture (to some 100 K with ether and dry ice), and expanded as much as possible in a valve (Joule-Thomson throttling) into an vaporiser being aspirated by a vacuum pump; the gas to liquefy was introduced in a high-pressure vessel inside the vaporiser at that machine, and it liquefied. Von Wroblewski was the first, in 1883, using ethylene as working refrigerant, to get liquid air and liquid oxygen statically, i.e. at the bottom of a vessel, with a meniscus, and not just as a mist upon sudden expansion.

A major breakthrough occurred in 1895 when C. von Linde introduced regenerative Joule-Thomson throttling, i.e. the gas that is cooled in the expansion process is later used to cool the incoming compressed gas before expansion. In that way, Linde started commercial cryogenics in that year, in Germany; he could obtain a few litres per hour of liquid air (after a few days of transient time to cool the equipment to steady state); before that, only minute amounts of cryogenic liquids could be obtained, and at great expense. The following year there were liquid-air plants in Britain, and the following one in USA. It was in those years that all noble gases were discovered, and liquefied. In 1902, G. Claude improved Linde's process by adding an expansion device in parallel to the liquefier, starting up the Air Liquide company in France, that together with the Linde company in Germany, have been the major world players in industrial cryogenics in the 20th century.

In 1898, James Dewar used Linde's process to become the first to liquefy hydrogen, using liquid air as coolant before entering the regenerator, and the insulating vessel he had developed earlier. The end of the pioneering period in cryogenics can be set on 10 July 1908 when Kammerling-Onnes in Leiden liquefied helium (he discovered electrical superconductivity in 1911).

Notice that Joule-Thomson cooling (i.e. the temperature drop on an isenthalpic expansion of a gas through a valve or porous plug) requires the entrance temperature to be below the inversion temperature; most gases, including air, cool a little when throttled from ambient temperature, but hydrogen, neon, and helium would heat a little; H_2 must be first cooled below its inversion temperature of $T_{\text{inv}}=205\text{ K}$ for cooling when throttled ($T_{\text{inv}}=51\text{ K}$ for helium).

Boiling temperatures (at 100 kPa) of cryogenic fluids below 100 K are: 90 K for O₂, 87 K for Ar, 77 K for N₂, 26 K for Ne, 20 K for H₂ and 4.2 K for He (⁴He; 3.2 K for ³He). Representative wholesale prices in 2000 were: LN2 0.2 €/L, LH2 0.3 €/L, LHE 4 €/L, LNE 100 €/L, and LHE-3 up to 2000 €/L.

Exercise 3. Nitrogen liquefier

Liquefied natural gas (LNG)

Natural gas is transported as a compressed gas in gasoducts (gas pipelines) for thousands of kilometres, but it is difficult to lay down pipes at the sea-floor, and, even if an alternative land route might be available, distance and uncertainty may dictate that batch transport by sea is economically better (more than ¼ of the world consumption of natural gas followed that path, in 2002). For that purpose, a gasoduct from the source (35 % of the world LNG comes from Indonesia) to a sea side is built, a liquefaction plant is built there, LNG tankers load the liquid at 111 K and 105 kPa in very-large tanks, and navigate to the destination sea-shore (which may be from <1000 km away, i.e. one day journey, to >5000 km away, i.e. >1 week journey), unload there (it takes nearly a day, and the same for loading), where large LNG storage tanks and a re-gasification plant has to be built, and gasoducts are built from there to the consumers area. On mass and economic terms, the transport of liquefied natural gas by ship is the largest commercial cryogenic application.

From its source, natural gas, compressed to some 6 MPa, is first dried (removing water and liquid hydrocarbons), then sweetened (removing CO₂ and sulfur compounds), lightened (butane and propane removed by cooling to –30 °C with a propane refrigeration machine) and then fed to the cryogenic liquefier, after which nitrogen is separated (at the 110 K of LNG, nitrogen is still a gas), and the LNG stored aside. The cryogenic liquefier is usually a vapour-compression-refrigerator (with its condenser cooled by a propane refrigerator at some –35 °C) using a working fluid mixture of nitrogen, methane, ethane and propane, that cools the natural gas (at some 6 MPa) down to some –135 °C, before a throttling process to atmospheric pressure (really 105..110 kPa) yields the final –161 °C storage conditions.

LNG is transported by sea in LNG tankers, having nowadays >150 000 m³ capacity (>70·10⁶ kg of natural gas), in four or five very-large tanks that basically may be of two types: the classical supported sphere (of aluminium alloy about 50 mm thick, with some 0.4 m thick polyurethane insulation outside, or the modern double-membrane hull-integrated membrane type (usually both membranes of invar, 0.7 mm thick, with two 0.25 m thick polyurethane insulation envelopes, held in wooden cases, with each of these thermal barriers behind an invar mass barrier). On the ballast trip, some 1..2 % of the LNG cargo must be kept in the tanks to keep them cryogenic. Some 1000 m³ of LNG are required to initially cool the tanks to cryogenic temperatures, before first loading. LNG tankers, one of the most-expensive types of ships, were the last resort of steam propulsion plants for commercial ships, because of the need to get rid of boiling-off natural gas (about 0.1 % of the load per day) by burning it on the boilers, but nowadays dual-fuel diesel engines have been developed that burn fuel-oil and natural gas (the first in LNG in 2004). The first LNG tanker (1959) was the Methane Pioneer, a modified Liberty ship, had 5000 m³ capacity.

Re-liquefaction of boil-off LNG within the ship is not a simple task because a powerful cryogenic cooler is required. The boil-off gas, more rich in light components, with up to 20 % N₂, at some (–100..–150) °C and 100..105 kPa, is compressed to 300..500 kPa (reaching some –50 °C), and cooled in a heat exchanger to some –165 °C, at which point all components except the N₂ content are liquefied and fed back into the tanks (non-condensable gas can be vented, or injected and re-dissolved in the LNG tanks). The cooler is a cascade system (using different hydrocarbons as working fluids), or an inverse Brayton cycle using nitrogen as a refrigerant, with three intercooled compression stages (e.g. from 1 MPa to 6 MPa, with steps at 2 MPa and 3,5 MPa), after which the gas cools to some –100 °C in a regenerative sub-cooler, before expanding in a turbine to 1 MPa (reaching –165 °C) and recycled through the sub-cooler.

Re-gasification of LNG at the terminal port is not a simple task (e.g. just leave the ambient do the work) because of the large flow-rates involved and the fact that the gas must be delivered under pressure. The approach is, as always, first compress and then heat (not vice versa). The liquid phase should be compressed separately for proper pump operation; the best approach to deal with the boil-off gas is to compress it from the 0.1 MPa ambient pressure not to the final delivery pressure of nearly 10 MPa, but to the minimum pressure that, according to flow-rates needed, will dissolve the compressed gas into the rest of the liquid-flow-rate (usually 1 MPa), and then to pump the whole flow-rate for re-gasification to the large sea-water heat exchangers (which might have to be supplemented with some natural-gas burner at peak demands!).

SUPERCONDUCTIVITY

Superconductivity is the property of some materials to abruptly drop their electrical resistivity at cryogenic temperatures. Already in the 19th century, it was known that the electrical resistivity of metals decreases with falling temperatures (e.g. for copper near room temperature $\rho=17\cdot10^{-9} \Omega\cdot\text{m}$ (0.017 $\Omega\cdot\text{mm}^2/\text{m}$) and $\text{dln}\rho/\text{d}T=0.004 \text{ K}^{-1}$, and for the platinum resistance thermometer Pt-100 $\rho=106\cdot10^{-9} \Omega\cdot\text{m}$ and $\text{dln}\rho/\text{d}T=0.0039 \text{ K}^{-1}$ at 0 °C, where $R=100 \Omega$). But a most striking discovery was made by Kamerling Onnes in 1911 when he found that the electrical resistivity of mercury was practically nil at liquid-helium temperatures (4 K).

Transport of electricity in the grids already causes some 10 % energy-loss world-wide, by Joule heating, and many electrical applications are limited by the same resistivity effect, so that a quest for electrical superconductors has developed (up to now, the highest-temperature superconductors only work below 150 K). Applications of superconductivity are usually coupled to the very-high-magnetic fields that only superconductors can create (say >1 T), which are used for levitation (MAGLEV, magnetic-levitation trains), plasma control and nuclear fusion (high-energy physics and tokamaks), and medical diagnosis like MRI. Magnetic resonance imaging ([MRI](#)), also known as nuclear magnetic resonance ([NMR](#)) is based on three main ideas:

- a) nuclear (life tissues are plenty of hydrogen nuclei, protons, that have a spin, behaving as a small magnet);
- b) magnetic (a very strong and stable static magnetic induction (about 1 T), only achievable nowadays with superconducting magnets; is applied to keep aligned most of the protons; three gradient magnets, a thousand times weaker, are also applied with an oscillatory sequence);

- c) resonance (a radio-frequency pulse is focussed on a small spot of the tissue, with the precise frequency to excite the non-aligned protons, what depends on the type of tissue); pulse absorption depends on the variation of the local magnetic field, what is related to the type and state of the tissue (healthy or ill), and a 2D or 3D image may be computed and interpreted by specialists.

Superconductivity disappears when increasing temperature and/or magnetic field strength. The highest superconducting temperature for pure materials is just 10 K, but with rare-earth compounds superconducting temperatures up to 150 K have been found. Superconductivity in metals disappears if a magnetic field of a few 1 A/m is imposed, but for alloys and high-temperature superconductors much greater fields are needed to suppress it. A typical model for the combined effect is $T_s(H) = T_{s0}(1 - H/H_0)^{1/2}$, where T_{s0} is the maximum temperature for superconductivity without magnetic field, and H_0 is the maximum magnetic field for superconductivity in the limit $T=0$ K.

A superconductor will not allow a magnetic field to penetrate its interior (Meisner effect, 1933). It seems as if electrons in a superconductor condense into a quantum ground state and travel together collectively and coherently.

Another effect related to superconductivity was found by B.D. Josephson in 1962 while studying the electrical properties of a junction between two superconductors. When two superconductors are separated by an electrical insulator (of the order of nanometres!), known as Josephson junction, the following quantum effects arise:

- At low currents a Josephson junction behaves like an ordinary superconductor: it carries lossless a current without any voltage drop across.
- When a critical value of the current is surpassed, a DC-voltage of a few mV shows-up across the junction, and an oscillating AC-current appears (superposed to a larger DC-current), with a frequency $f = 2eV/h$ (independent of the insulator), e being the electron charge, V the applied DC-voltage and h Plank's constant. A photon of that frequency is either emitted or absorbed, what helps the diagnosis. In summary, when a few millivolts are applied to a Josephson junction, microwave radiation is emitted at a frequency proportional to the voltage. In January 1990 a value of $K_J = 483597.9$ GHz/V was adopted for the Josephson constant $K_J \equiv h/(2e)$, and arrays of several thousand Josephson junctions are now used as voltage standards.

Josephson junctions are used in certain specialized instruments such as highly-sensitive microwave detectors, magnetometers, superconducting quantum interference devices (QUID) and the fastest switching devices.

Finally notice that there is not a similar thermal superconductivity (i.e. an abrupt increase in thermal conductivity).

SUPERFLUIDITY. HELIUM ANOMALY

Superfluidity is the property of liquid helium to abruptly drop its viscosity at cryogenic temperatures. No other substance has been found with that property. Helium is the only substance that remains liquid close to 0 K (if the pressure is below 2.5 MPa; indeed, all other substances solidify at temperatures higher than 10 K).

Helium has two stable isotopes: the most abundant is ^4He (or He-4), the other is ^3He (or He-3), the latter with less than 1.4 ppm natural abundance. At 100 kPa, their mixture spontaneously separates at temperatures below 0.8 K. ^4He is a boson gas that liquefies at 4.2 K and becomes superfluid at 2.17 K, whereas ^3He is a fermion gas that liquefies at 3.2 K and becomes superfluid at 0.0025 K. This behaviour can only be explained in terms of quantum mechanics. Their phase diagrams are shown in Fig. 17.

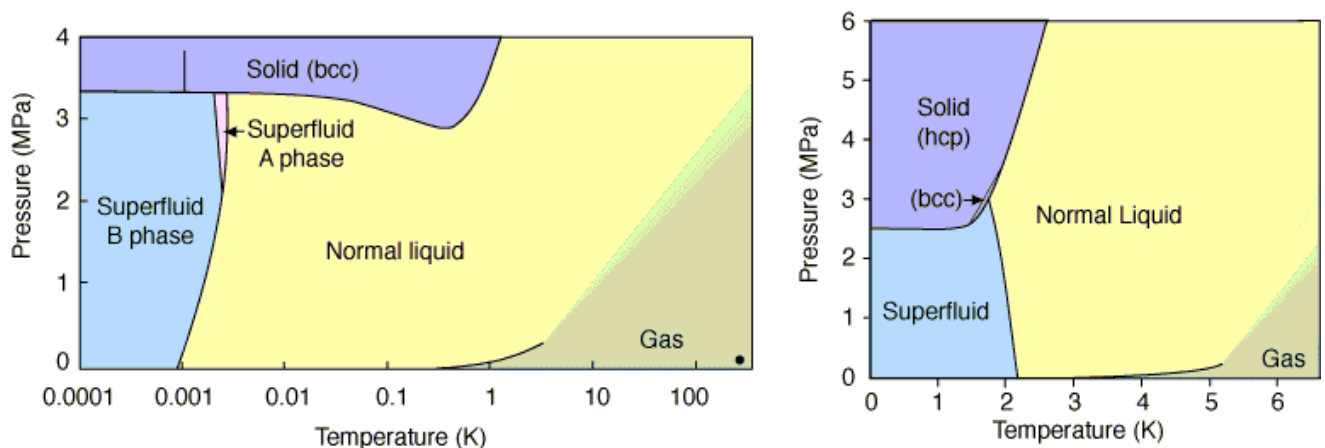


Fig. 17. Phase diagram for the two stable isotopes of helium: He-3 (left) and He-4 (right).

COLD EFFECTS ON LIVING MATTER

Thermal effects are those caused by a temperature change, or a redistribution of internal energy in a system. Thermal effects on materials (mainly on structural materials), may be widely varied; e.g., dimensional change by thermal expansion, elasto-plastic changes due to thermal stresses, brittle/ductile transition temperature, and so on (see below), but thermal effects on living matter focuses on the biological effects, i.e. on metabolic processes. We consider here the effect of low temperatures on large organisms (hypothermia and frostbite) and on microorganisms and tissues (food refrigeration and cryopreservation). The effect of high temperatures is considered apart (thermal suffocation and chock, protein denaturising, sterilisation, burns, and incineration).

Living tissues and life processes are, to a first approximation, water solutions of macromolecules, undergoing temperature-dependent chemical reactions.

HYPOTHERMIA

Hypothermia is the lowering of body temperature in homoeothermic living beings, due to a prolonged exposure to cold (not necessarily freezing), what may hurt and kill. All systems, alive or inert, have a certain temperature margin for proper operation; it may be several hundred degrees for a metal in a structure, several tens of degrees for an electrical battery, or several degrees for a living being. In humans,

body temperature is $37\pm0,5$ °C in healthy persons, which may change by some degrees in stressing conditions, but it usually goes irreversibly to dead if above 42 °C or below 32 °C, by heartbeat loss.

Hypothermia may be caused by chilling winds, but it is relatively easy to protect the body against heat losses to air, because of its low thermal conductance, e.g. by finding a shelter place, by putting some clothes on, by lying on the floor, by lying close to other animals, etc. Immersed on water, however, it is much difficult to protect a body from heat loss and, although remarkable survival records exist, a normal person cannot compensate the energy loss in a whole day immersed in waters as hot as 26 °C. In cold waters, say at 10 °C, shivering starts almost immediately, and after several minutes blue coloration by lack of surface blood irrigation appears (cyanosis); lack of muscular control and somnolence follows after some half an hour, with dead before the first hour. Half of all casualties due to wreckage and people falling to the sea are attributed to hypothermia, and not to drowning. The best practice for hypothermia treatment is to stop heat losses, by dry insulation, without heating or giving warm drinks, or rubbing the extremities; just insulation.

Hypothermia may be caused also by intravenous injection of cold plasma, by the effect of certain drugs (anaesthesia), or by a malfunction of the thermal regulator in the brain. But hypothermia may be used advantageously; hypothermia is a recognized way of trying to treat stroke because it reduces stroke metabolism.

Hyperthermia is the increase of body temperature in homoeothermic living beings, due to some disease, or a prolonged exposure to a hot environment. Human beings may tolerate inverse temperature gradients by evaporative cooling, but they usually faint after prolonged exposure to >43 °C, with only a few hours of tolerance at 50 °C, and vascular collapse soon after, particularly in humid environments.

FROSTBITE

Frostbite is the freezing of the skin and other tissues under the skin due to exposure to freezing temperatures, usually by direct contact with a thermal-conductive system at < 0 °C (e.g. by touching an iron object at -5 °C with a wet hand). Frostbite causes an injury by freezing body fluids, particularly capillary blood vessels, which get irreversible damaged and can no longer sustain metabolism.

Mild frostbite affects only the outer skin layer, producing first reddishness (erythema) then yellowness and finally a whitening of the skin, with some loss of touch (numb feeling). Usually, these symptoms disappear as warming occurs, but the skin may appear red for several hours. Severe frostbite looks like burning: similar pain, similar blisters and swelling. In severe frostbite, the frozen part (usually an exposed part: toes, fingers, ears, nose, cheeks, feet, hands...) has to be amputated.

To fight frostbite, first protect from the freezing and then start natural re-warming: flexing the fingers and toes, stamping the feet, clapping hands, blowing on them or placing them in the armpits; do not rub the affected area. If it hurts a lot, it was a mild frostbite that is recovering; if not, go for medical help even if with frozen feet. Frostbite is a cause of morbidity, not mortality, unless combined with hypothermia.

FOOD PRESERVATION BY REFRIGERATION

The first historical mention of refrigeration refers to food preservation, and even nowadays more than 90 % of world refrigeration power is applied to food preservation.

Food preservation

Food preservation techniques are any of a number of methods by which food is kept from spoilage after harvest or slaughter. It is done by sluggish or suspended cell life (the organism is already killed in fish and meat dealings), and by avoiding external attack (by microorganisms, oxygen, radiations...). Since life needs water, appropriate temperatures, diluted solution concentrations, non-ionising radiation, and so, food preservation may be achieved by changing some of these parameters, which may be grouped as:

- Physical methods: drying, heating (pasteurization, boiling, ultra-high temperature), cooling (cold, freeze, or cryopreservation), packaging (under vacuum, canning (tinning), or with a controlled atmosphere), electromagnetic sterilization (UV, X-ray, γ -ray), pulsed electric fields, etc. A novel food-preservation technique is ultra-high pressure, up to 1 GPa, what causes the denaturising of proteins, the inactivation of enzymes, and the inactivation of micro-organisms, while aroma compounds and vitamins are preserved. Advances in packaging materials (e.g. metalized plastic coatings, tetrabrick) have played an important role in modern food preservation.
- Chemical methods: high concentration of salts (dry salting, brine soaking), or species (spicing), or sugars (jams); by life-suppressing baths (e.g. oils, vinegar); by surface reactions (e.g. smoking), by adding preservatives, etc.
- Biological methods: fermentation. Some micro-organisms (moulds and yeast) react with food (wine, beer, milk and its derivatives) and produce an environment (acidic or alcoholic) that is toxic for themselves and other pathogen micro-organisms.

Human raw food may be grouped as:

- Vegetal food (vegetables and fruits): once cropped, it continues living (breathing) so it cannot be enclosed. When rotting (putrefaction) it gives off ethylene gas (bad smell). Typical metabolic rate is 0.1 W/kg (but it varies from 0.003 W/kg for oranges at 0 °C to 0.4 W/kg for pears at 30 °C).
- Animal food (fish or meat): once killed, it starts to decompose (outgas, bad smell). Typical metabolic rate (only alive) is 1 W/kg.

The effect of temperature is most important: disease-causing microorganisms (such as bacteria) grow very slowly at low temperatures, multiply rapidly in mid-range temperatures, and are killed at high temperatures (the temperature-danger zone is between 6 °C and 60 °C). Spoiled food is an infection source that cannot be recovered and must be isolated and disposed of as soon as possible (neither stored nor transported with food).

The causes for food spoilage may be:

- Internal
 - Natural biological evolution due to its own enzymes (catalytic proteins), that may consume food's own sugars and water once harvested (e.g. peas and corn lose 40 % of their sugars

in 6 hours at ambient temperature), or the fermentation of sugars and rancidity of fats. Bad smell.

- External (start at the surface)
 - Biological attack: e.g. decomposition due to the growth of foreign microorganisms that secrete enzymes which act as above. Bad smell.
 - Chemical attack: e.g. oxidation in air. Bad colour.
 - Physical attack: e.g. dehydration in dry air, overheating by sun-beam, asphyxiating in enclosures. Bad texture.

Food must be preserved not only for edibility (safe=non-poison, flavour=taste, odour=smell), but for appearance and appeal (colour for sight, texture for sight and touch).

Food-preservation by refrigeration

Low temperatures reduces metabolism but does not kill living cells (large organisms die of hypothermia). Freezing, besides the low-temperature effect, has other mechanical effects (rigidity, abrupt expansion, and so on). It is also termed cool-store if not frozen ($T \geq -2\text{ }^{\circ}\text{C}$), and cold-store if frozen ($T < -2\text{ }^{\circ}\text{C}$). The two types of refrigerated stores (fridge and freezer) may be on a single cabinet with a single door, in the same cabinet but with independent doors, or in different cabinets. In large facilities (supermarkets, ships, and large kitchens in general) two rooms are available for refrigerated storage: the cool room, entered through a hatch, and the refrigeration room, entered by a door from the cool room, the whole lot with fully insulated walls, floors, and ceilings.

Refrigeration reduces enzymatic activity but do not kill it, thus, refrigeration at $6\text{ }^{\circ}\text{C}$ preserves for a few days but $-18\text{ }^{\circ}\text{C}$ is required for preservation during a few months. However, the best preservation temperature is not always the lowest, since other factors come to play; thus, tropical fruits should be kept near $15\text{ }^{\circ}\text{C}$, some vegetables, fruits and dairy in the range $0\text{ }^{\circ}\text{C}$ to $6\text{ }^{\circ}\text{C}$, fish, meat and some vegetables frozen at $-20\text{ }^{\circ}\text{C}$, and ice-cream at $-25\text{ }^{\circ}\text{C}$. Besides low temperature, food preservation requires appropriate humidity: very high for vegetables ($>90\%$), and no so high for meat (around 80%).

Freezing may be achieved by water cooling, air cooling, vacuum cooling or liquid-ice cooling: water-cooling is used for fruits and vegetables; air-cooling is the most used (for meat, citrus fruits, grapes, melons, green beans, cherries, etc.); vacuum cooling (at $<1\text{ kPa}$) is used for flowers, mushrooms, lettuce and strawberries. Before freezing, a quick blanching (scalding), by immersion in boiling water or vapour for one or two minutes, is always applied to kill surface microorganisms and stop surface enzyme processes.

Quick-freeze usually means reaching from $25\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$ in less than 30 minutes. Slow-freeze may take from 3 hours to 3 days (home freezers may take from 3 h to 24 h). Freezing does not sterilize food; the extreme cold simply retards growth of microorganisms and slows down changes affecting quality or causing spoilage in food. Freezing requires rapid cooling (at least from $0\text{ }^{\circ}\text{C}$ to $-5\text{ }^{\circ}\text{C}$) before refrigerated storage, to avoid large ice-crystals and protein denaturation, and, for meat and fish, a slow thermalisation (thawing), to avoid the releases of a lot of water if cooked without thawing (vegetables can be cooked

directly from the frozen state). One of the early advocates of frozen food was the skin merchant C. Birdeys, that in 1912, reported that Labrador natives kept fish in ice without spoilage.

Lyophilisation (or freeze-drying) is a combined refrigeration-drying technique where food, in liquid or moist-powder forms, is first quick-frozen (to prevent the growth of large ice-crystals) in a stream of cold dry air, then exposed to high vacuum for dehydration by sublimation, and finally packed at delivered at ambient temperature; the food is re-hydrated before use. Lyophilisation is used to preserve coffee, juice, soup, medicines... and to decreases transportation and storage costs.

Some thermal properties of typical foods are collected in Table 7. A useful model in terms of the moisture content w in mass-percent basis, is:

- Fresh food ($T > -2$ °C):
density, $\rho = 1100 - 100w$ in kg/m³
thermal capacity, $c = 1300 + 2900w$ in J/(kg·K)
thermal conductivity, $k = 0.15 + 0.50w$ in W/(m·K).
- Frozen food ($T < -2$ °C):
density, $\rho = (1100 - 100w)/(1 + 0.1w)$ in kg/m³
thermal capacity, $c = 3800 - 2400w$ in J/(kg·K)
thermal conductivity, $k = 0.40 + 1.5w$ in W/(m·K).

Table 7. Food thermal properties (fresh at 20 °C, or frozen at -20 °C).

	Moisture [% mass]	ρ [kg/m ³]		c J/(kg·K)]		k [W/(m·K)]		T_f [°C]	h_{sl} [kJ/kg]
		Fresh	Frozen	Fresh	Frozen	Fresh	Frozen		
Water	100	1000	917	4180	2000	0.56	2.2	0	333
Bacon	20			2300	1400				70
Beef	50..70	1020..1160	1000..1100	3500	1870	0.35		-2	260
Butter	10			2900	1600				40
Cheese	35			2900	1600				100
Chicken	60			3700	1900				220
Cod	78			3600	1800			-2.2	280
Eggs	73			3500	1800				270
Fish	76			3700	1900				280
Ice-cream	67			3600	2000				240
Milk	87	1030		4100	2000			-0.52	300
Pork	40..46			2300	1370				170
Potato	74		1180	3400	1800		2.5	-1	275
Tuna	64			3430				-2.2	235

Talking about refrigerated food, ice-cream, the frozen food per se, should be pinpointed. An ice-cream is a flavoured frozen mixture of milk and cream, not just frozen sweetened water as in frozen drinks (hard), frosties (slurries), sorbets (smooth) or cold juices (e.g. horchata). Ice-cream must be stored at < -24 °C for long times (at -18 °C ice crystals slowly grow with time), and served at -10 °C for consistency (at -3 °C they drip). Nero Emperor is credited with mixing snow with honey to prepare a kind of ice-cream, but real ice-cream dates at least from the court of Catherine de Medici in 16th c. In 1670 there was a Café in

Paris offering ice-creams to the public. Ice-cream was made in a 'hand-crank' freezer with a rock-salt / crashed-ice mixture. Freezing mixtures were first described in Muslim Spain in the 13th century, and first explained by Raoult in 1878.

Transport of refrigerated food is gaining importance, particularly by sea because it takes the longest, with frozen meat and refrigerated banana and citrics holding the largest share, followed by fish. Refrigerated containers are used for meat transport, but bulk refrigeration is still prevalent, with a tendency to pallet-load and containers. Controlled atmospheres (CO_2 , H_2O , O_2 y C_2H_4) are being implemented in most cases.

Problematic of food-preservation by refrigeration

Food refrigeration is an expensive endeavour: it requires continuous expense from production, for transport, for storage, down to final consumption (see Cold chain, below), and introduces a risk: interruption of cooling power and/or shortage of cooling agent (ice, freezing mixtures) may spoil the entire load.

Refrigeration rises relative humidity, what may increase mould growth at the surface of food. Packed enclosure prevents it, but it asphyxiates vegetables. Vegetables can recover moisture after some drying, but meat and fish cannot, so humidity changes spoil them. It is a trade-off for vegetables; they should be kept in enclosures to keep a high humidity that prevents wilting (in a box, or paper-wrapped), but they must also keep respiring and thus some ventilation is needed; holes in the wrapping is the common answer. Notice that ambient humidity is not relevant for frozen food, and that frozen vegetables do not respire and can be kept wrapped.

Each kind of refrigerated food has its best storage temperature (e.g. between $-28\text{ }^{\circ}\text{C}$ to $-18\text{ }^{\circ}\text{C}$ for ice-cream and frozen food, $-5\text{ }^{\circ}\text{C}$ to $-1\text{ }^{\circ}\text{C}$ for seafood and fish, $-3\text{ }^{\circ}\text{C}$ to $+3\text{ }^{\circ}\text{C}$ for some dairy products, $-1\text{ }^{\circ}\text{C}$ to $+5\text{ }^{\circ}\text{C}$ for meat and poultry, and between $0\text{ }^{\circ}\text{C}$ to $10\text{ }^{\circ}\text{C}$ for vegetables and fruits). The usual solution is to have just two kind of refrigeration equipment: low-temperature systems (with vaporisation temperatures in the range $-35\text{ }^{\circ}\text{C}$ to $-25\text{ }^{\circ}\text{C}$, usually working with R-507 or R404A), and mid-temperature system (with vaporisation temperatures in the range $-15\text{ }^{\circ}\text{C}$ to $-10\text{ }^{\circ}\text{C}$, working with R-134a). The vaporiser can be inside the refrigerated space, or outside (in that case connected to the inside space by a secondary fluid: propylene-glycol or fluid ice).

There may be compatibility problems too. In mixed spaces some foods give off odours (e.g. potatoes) and others take in odours (dairy products, eggs). Some stores require ventilation for fresh air renewal, or air treatment for controlled atmosphere.

Freezing may damage food (e.g. tomatoes and banana-skin get black). Fruits are not frozen because we want to consume them uncooked and firm. Freezing causes a volume expansion that affects food texture and may break cell membranes (that is why some frozen meats release a lot a bloody juice when thawing), it may denaturalise proteins, and may break emulsions (as when milk is frozen and fat globules segregate). Frozen food must be appropriately thawed; the best is in the refrigeration compartment

(between 0 °C and 6 °C), but it takes many hours; the quickest is to thaw food in the microwave oven, but then the food must be immediately cooked, since some parts went too warm; thawing in cold water requires leak-proof packaging and water waste; thawing in the kitchen counter or in hot water is dangerous because it promotes bacteria growth.

Some frequently-asked questions are worth commenting:

- Why fish in the market is kept on ice, and not meat? (Asked by my son Eduardo on 15-04-2002). Because, when alive, fish is at 10..15 °C and meat is at 35..40 °C, what implies that, in an ambient at 20 °C, fish-food-reactions progress at a quicker pace than naturally at sea, whereas meat-food-reactions progress at lower speed. The lower the rate of reaction once dead, the longer the food takes to spoil, so that fish at 20 °C would spoil within hours, whereas meat at 20 °C spoils in days.
- Why putting hot food inside the fridge is no good? Not just because it causes energy expenditure, but mainly because it may spoil other food inside (there is only 0.3 kg of cold air inside, so the effect of placing 1 kg of warm water at 40 °C is very great indeed).

The cold chain

The cold chain is the set of processes and associated infrastructure involved in assuring a certain low-temperature history of a product from its source to its final destination and consumption; e.g., for fresh milk, it is related to the temperature-time record from cow milking to drinking (refrigeration at the farm, refrigerated transportation, thermal processing at the plant, and refrigerated storage. The cold chain is important for food preservation but also for other vital goods, as vaccines, blood, etc.

The distribution chain of food-products is generally composed of many different steps of storage and transportation until consumption. Product temperature may vary in each step, especially when loading and unloading is performed outside controlled temperature conditions, and after final sale to the consumer. Best practice is usually quick freezing (not only to avoid bacteria growth but to prevent ice-crystal growth), constancy in refrigeration, and smooth thawing.

A challenging step in the cold chain is food exposure to the public at retail stores in display cabinets, both for chilled and frozen stores. Frozen-food display cabinets may be closed with transparent doors (horizontal or vertical, the latter making best use of floor-space and customer accessibility), or open cabinets to better catch customer attention. To minimise heat losses in open cabinets, top access is commonly used (cold air being trapped on the top, by negative buoyancy), or sophisticated vertical open-displays with two or three forced-air curtains at different temperatures, to reduce heat gains nearly an order of magnitude (otherwise, heat gain from ambient-air entrainment would be some 70 % of the cabinet heat load).

The cold chain is not only important for food. All vaccines used in immunization programmes are thermo-sensitive: most vaccines lose their curing power if not refrigerated, and some may be damaged by freezing. It is therefore crucial to ensure proper storage and distribution at appropriate temperatures (most vaccines between 0 °C and 8 °C, but those for yellow fever at –25 °C to –40 °C). Blood for

transfusions must be kept near 4 °C. Nowadays, for sensitive goods, every sample is shipped with a temperature-sensitive label (safe/spoiled).

Refrigerators and cold containers (ice chest) are labelled with their ‘un-powered life’ or ‘hold-over time’, i.e. the time it takes for the refrigerated interior to reach 10 °C in an environment at 40 °C, unopened.

The concept of cold traceability has been proposed and existing tools include thermometers, temperature recorders, temperature indicators and time temperature integrators (TTI). These tools make it possible to have a better knowledge of the cold chain.

CRYOSURGERY AND CRYOPRESERVATION

Most tissues develop necrosis when subjected to in-vivo freezing for some time (the frostbite bitterly experienced by some alpinists), due to the unavailability of liquids to distribute nutrients and excreta, and to the breaking of cellular membranes on expansion and contraction on freezing and thawing. The necrosis can be used to destroy malign cells, and it has been used particularly on skin cancer tumours (for internal tumours, a cryo-probe can be used, guided by ultrasounds). The main advantage of cryosurgery is that it is less invasive than normal surgery, with shorter recovery periods.

But extreme cold is not only a deadly danger. Biological activity does not cease at the freezing point of water, the basic life-support fluid. Many single-celled organisms and some small tissue fragments can be frozen in vitro, with chemical additives, to cryogenic temperatures and revived (recovering activity) after a long time, if the cooling and thawing rates are appropriate, a technique called cryopreservation, now routinely used to store eggs, semen, embryos and other types of cells and tissues from animals and humans, mainly for assisted reproduction, but also for genetic research. The process starts by putting the biological sample in a cryo-protective solution (glycols, glycerol and sugars are used; see [Solutions](#)) that retards the freezing and avoid cell disruption by early ice formation; then the stuff (usually a straw holding the sample in solution) is slowly refrigerated to say –50 °C, at about 0.01 K/s, to help dehydrate the biological sample, before putting it on liquid nitrogen at 77 K. When time comes for use, the straw-sample is put out of the liquid nitrogen, thawed, washed of cryo-protective solution and put in a culture fluid in an incubator for checking (not all cells survive the freezing and thawing process) before implantation. The first human pregnancy from a frozen, stored and thawed embryo took place in 1983.

COLD EFFECTS ON MATERIALS

A general discussion on thermal effects (both low-temperature and high-temperature), can be found aside in [Thermal effects on materials](#), covering Thermal properties, Thermal analysis, Thermal effects on mechanical properties, Thermal effects of machining, Thermal treatments, and so on. Focussing on the effect of cold, the ductile-to-brittle transition at low temperatures was one of the key issues. Some cold effects on non-structural materials have been already discussed above (e.g. superconductivity and superfluidity, or the rapid decrease of thermal capacity with low temperatures), as well as cold effects on living matter.

HEAT PUMPS

A heat pump is a thermal machine that pumps heat from a lower temperature to a higher temperature, the goal being the heating effect provided; if the goal is the cooling, the device is a refrigerator; in special cases, the goal is at the same time the cooling and heating effect, and then the device is also named heat pump. Notice that, similarly to a water pump, heat can only flow downwards the temperature scale (as water can only flow downwards the total-pressure scale), and the heat pump must 'discharge' at a higher temperature than the system to heat, and 'suck' the lower-temperature heat by a lower sink. This lower-temperature heat source can be natural (ambient air, river or sea water, or geothermal), or recovered from another process (residual heat).

Heat pumps are conceptually similar to refrigerators in concept, challenges and how they are solved, systems, components, and working fluids. Heat pumping requires an expenditure of exergy (as for refrigeration), and types of heat pumps are classified accordingly in:

- Work-driven heat pumps, the most common system being the vapour-compression machine (as for refrigerators). Gas-expansion machines, and thermoelectric devices belong to this type, but their use is very rare.
- Heat-driven heat pumps, including traditional absorption machines, and not-so-frequently-used adsorption machines and heat transformers. Another thermally-driven heat-pump type uses ejectors to compress the working vapours.

In spite of the great energy saving associated to the use of heat-pumps for heating applications (e.g. a typical domestic heat pump may deliver as high-temperature heat ;four-times! the electrical energy it consumes), they can only compete with traditional fuel-fired heating systems (and even with direct electrical heating) for very large systems, or in all cases when heating and cooling are required (either at the same time or seasonally), because of much higher initial costs.

According to the type of installation, heat pumps and air conditioners can be classified as:

- Compact system, where the refrigerant fluid loop is all enclosed in one apparatus, can be:
 - Window systems (but also trough-wall systems), where a compact systems is part of the room envelop.
 - Indoors systems (usually portable), with a connecting air duct (usually flexible) that must cross the room envelop.
 - Outdoors systems, also named indirect systems, where an outdoors compact system cools/heats a secondary fluid (air or water usually) which finally cools/heats the room to be conditioned. If a liquid is used as secondary fluid, fan coil units are usually the final cooling/heating element (the fan is needed to enhance heat transfer due to lower temperature jumps than in conventional heating systems). This is the most versatile and easy to maintain system, but demands the most complex installation.
- Split (and multi-split) systems, where the refrigerant condenser and vaporiser are standing one inside and the other outside the conditioned room, with refrigerant pipes crossing the walls. In multi-split systems, one outdoor unit can serve several indoor units.

TYPE OF PROBLEMS

Notice how few equations are included in this chapter (and they are just reminders). That is because the refrigeration systems described are just a combination of more simple processes studied in previous chapters (as gas compressions, heat exchangers, fluid expansions, fluid mixing, humid air processes, and so on), or are not further analysed in detail (as absorption processes, ejectors, thermoelectric devices, and so on). Most practical refrigeration problems are based on the inverse Rankine cycle, which is analysed with the p - h diagram of the refrigerant under work (an ideal-fluid model may suffice sometimes), or with a computer-based program for thermodynamic cycles (including accurate property data).

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