4
Freezing

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4.1
Introduction

To describe refrigeration process as a mere temperature decrease in the product is simplistic. Many studies in literature show the influence of this preservation process on important quality attributes of food, such as texture, colour, flavour and nutrient content [1–4]. It is clear that refrigeration affects biological materials in various ways, depending on their chemical composition, microstructure and physical properties. Additionally, processing parameters such as the cooling method used, the cooling rate and the final temperature play an important role in defining the keeping quality of food.

In this chapter, the term refrigeration covers both *chilling* and *freezing*, which can be distinguished on the basis of the final temperature to which a material is cooled and the type of heat removed. In chilling, only sensible heat is extracted, whereas freezing involves the crystallisation of water which requires the removal of latent heat and, therefore, the expenditure of more energy and time to complete the process.

This chapter is broadly divided into three sections: the first relates to the refrigeration equipment used to generate low temperatures and the mechanisms by which the heat removed from the food is transferred to a 'heat sink', the second section deals with the kinetics of this process and the third section addresses the effect of refrigeration on food quality.

4.2
Refrigeration Methods and Equipment

In earlier days, low temperatures were achieved by using ice obtained from high mountains, the polar regions of the earth, or that saved during winter. In the Roman empire, the use of natural ice was widespread; and food, water and beverages placed in isolated cabinets were cooled by the latent heat required to melt the ice (ca. 333 kJ kg^{-1}). Nowadays, industrial cooling systems can be divided into four

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main categories: (a) plate contact systems, (b) gas contact systems, (c) immersion and liquid contact systems and (d) cryogenic freezing systems.

The first three systems involve indirect cooling, i.e. the food and the refrigerant are not brought into direct contact. An inherent advantage of indirect heat removal is that the final temperature of the product can be easily controlled and, therefore, these methods can be used for both chilling and freezing. However, cryogenic methods are only used to freeze foods.

4.2.1
Plate Contact Systems

In this kind of equipment the food is placed in contact with a cold surface; and the temperature difference transfers heat from the food. It is common to find plate freezers in which the sample is positioned between two cold metallic plates. Pressure is applied to the plates in order to ensure good contact between the cold surfaces and the object to be cooled. It is clear that the presence of regular shapes in the food produce better results in this type of equipment. Moreover, since high levels of overall heat transfer coefficients can be achieved, plate refrigerators are commonly used in production lines for solid or packaged food.

Other types of contact surfaces involve conveyor belts and rotating drums. In the former, the food (usually packaged) is placed on a temperature-controlled metallic belt conveyor and is expected to reach the desired low temperature at the end of the conveyor run. The refrigeration time is therefore controlled by the speed of the belt. The drum refrigerator, in contrast, is used to cool or freeze high viscosity liquids by introducing them at the top of the rotating refrigerated drum and scrapping the product off as the drum rotates through about 270 degrees.

Both drum and belt refrigerators use secondary refrigerants such as brine in order to cool down their metallic surfaces, while the plate type uses direct evaporation of a refrigerant to lower its temperature.

Gas Contact Refrigerators In this type of equipment, a cold gas (usually air) flows through the food absorbing heat from it. Depending on the air velocity and temperature, such a system can be used either for freezing or for cold storage. Even though air blast refrigeration systems are widely used for food processing [5], it does not mean that this kind of equipment is suitable for all types of materials.

A commonly used configuration is the refrigeration tunnel, where food is transported through a cold chamber on a conveyor. Cold air, forced inside the tunnel, establishes contact with the food and causes the heat transfer. Higher air velocities can achieve higher heat transfer rates, but there are limits [6]. Above a certain range of velocities, heat transfer through the food controls the overall rate; and this should be considered in order to avoid unnecessary wastage of energy. In the case of particulate or granular materials, high speed air can be used to fluidise the material, which can result in a faster temperature drop [3].

The above procedures are sometimes combined with vacuum cooling, in which the food is introduced in a chamber where the pressure is reduced. Due to the drop in pressure, a fraction of the water present in the product vaporises (usually surface water) carrying with it latent heat which reduces the temperature rapidly. The food is then transferred to an air cooled chamber to further reduce its temperature, or sent directly for storage. Although vacuum cooling is rapid, it is more expensive than other refrigeration methods. However, this technique is more appropriate for highly priced products where quality considerations dominate.

4.2.3
Immersion and Liquid Contact Refrigeration

In this method, the product is brought into direct contact with a fast flowing chilled liquid. It therefore tends to attain the temperature of the liquid rapidly. Chilled water, brines (salt and sugar solutions) and other type of liquids such as alcohol or ethylene glycol are commonly used. The food (sometimes unpacked) can be brought into contact with the flowing liquid in two different ways: by immersion or by spraying. In spray contacting, the liquid is normally sprayed over the food, which makes heat transfer more efficient. Further, less liquid is used, cutting costs and lowering environmental impact.

4.2.4
Cryogenic freezing

This type of refrigeration differs from other procedures because it does not depend on external low temperature production systems. Low temperatures are produced due to the phase change of the cryogenic liquids themselves which are brought into contact with the food in freezing cabinets. The process is very rapid, but at the same time very expensive. In some cases, cryogenic freezing is combined with air contact freezing as a two-stage process, in order to increase freezing rates whilst reducing process costs. In this process, also known as the cryomechanical process, a cold hard crust is produced on the material by cryogenic freezing, before sending it to a cold chamber to finish off the solidification process.

The most common cryogenic liquid used is nitrogen, which boils at –195.8 °C. It is odourless, colourless and chemically stable; however, high costs restrict its use to high value products.

4.3
Low Temperature Production

Low temperatures are commonly achieved by mechanical refrigeration systems and by the use of cryogenic fluids [7]. However, other ways have been studied and used. Some of these are described in Table 4.1 [8].

Table 4.1 Some nontraditional methods of producing low temperatures; from [8].

Name	Description	Applications
Peltier cooling effect	In 1834, Peltier observed the inverse thermocouple effect: if electricity is forced into a thermocouple circuit, one of the metals cools down	Home freezers, water coolers and air conditioning systems in the USSR and USA since 1949
Vortex cooling effect	In 1931, G. Ranqe discovered the vortex effect in which the injection of air into a cylinder at a tangent produces a spinning expansion of the air accompanied by the simultaneous production of cold and warm air streams.	Cooling chocolate
Acoustic cooling	A hollow cylindrical tube filled with helium and xenon is used in combination with a 300 Hz speaker and a Helmholtz resounder. Sound waves compress the gas mixture and it is heated up. During decompression the gas cools down and absorbs heat from the structure. Inside the system, the noise is high (180 db). A well insulated system is not more noisy than any mechanical system.	Expensive home freezers have been produced with this environmental ly friendly system.
Cooling with gadoline	Gadoline is an element that increases its temperature while exposed to magnetic fields; and when exposure ceases, it reduces its temperature to a value lower than the initial.	A prototype refrigerator has been built.
Cooling with hydrogen	Dr. Feldman from Thermal Electric Devices has used hydrogen to refrigerate. The 'HyFrig' device uses metal hydrides that are capable of absorbing large amounts of hydrogen (gas) and produce a significant decrease in temperature when the hydrogen is eliminated.	Vehicle air conditioning

4.3.1
Mechanical Refrigeration Cycle

This method takes advantage of the latent heat needed for a refrigerant to change phase. The refrigerant – which is a fluid evaporating at very low temperatures – is circulated in an evaporation-condensation cycle and the energy it absorbs during evaporation is used to transfer heat from the refrigeration chamber (which contains the food) to a heat sink.

Basic components of typical refrigeration system are depicted in Fig. 4.1 (a compressor, two heat exchangers, an expansion engine and a refrigerant).

The most efficient refrigeration cycle is known as Carnot cycle, which consists of the following two steps:

- frictionless and adiabatic compression and expansion (constant entropy);
- heat rejection and absorption with a refrigerant at constant temperature.

It should be pointed out that frictionless compressions and expansions are highly ideal; therefore, the Carnot cycle is only useful to describe a perfect process. It is commonly used to evaluate the extent to which a real system deviates from ideal behaviour.

From Fig. 4.1, it can be seen that the cycle follows a specific path. The four stages of the cycle can be described as follows:

- Compression (points 1–2). Initially, the refrigerant is in a gaseous state (point 1). Work is done on it by the compressor, when its pressure and temperature are elevated, resulting in a superheated gas with increased enthalpy (point 2).

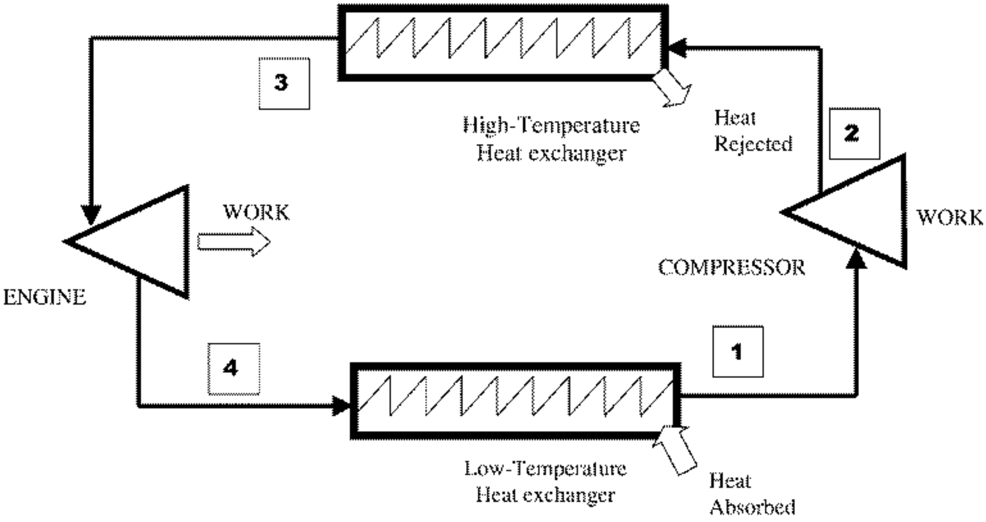

Fig. 4.1 Basic components of a mechanical refrigeration cycle.

- Condensation (points 2–3). The superheated gas enters a heat exchanger, commonly referred to as a high temperature exchanger or condenser. Using either air cooled or water cooled atmospheres, the refrigerant gives up heat to the surroundings and condenses to form a saturated liquid. By the time all the refrigerant has liquified, its temperature may fall below the condensation point and a subcooled liquid may be obtained.
- Expansion (points 3–4). The liquefied refrigerant enters the expansion engine, which separates the high and low pressure regions of the system. As the refrigerant passes through the engine, it experiences a pressure drop together with a drop in temperature. A mixture of liquid and gas leaves this process.
- Evaporation (points 4–1). Due to the energy received in the heat exchanger, also known as the low temperature exchanger or evaporator, the refrigerant evaporates. The saturated vapour may gain more energy and become superheated before entering the compressor and continuing the cycle.

The Pressure and Enthalpy Diagram The basic refrigeration cycle shown in Fig. 4.1 allows one to have a glimpse of the changes undergone by the refrigerant (energy absorption and rejection). However, other charts and diagrams are more useful while quantifying these changes. Using pressure-enthalpy charts, it is possible to estimate the changes in refrigerant properties as it goes through the process. Such charts are extremely useful in designing a refrigeration system. The most common charts depict variations in enthalpy (*x* axis) with pressure (*y* axis), and are known as p-h diagrams. However, there are other useful charts such as T-s diagrams that show variation of entropy (*x* axis) with temperature (*y* axis). Figures 4.2 and 4.3 show the Carnot refrigeration cycle on a p-h diagram and T-s diagram, respectively. The domes depicted in these figures

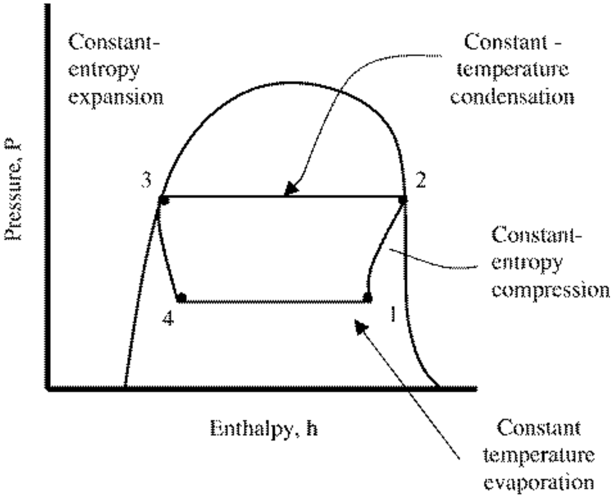

Fig. 4.2 Pressure-enthalpy diagram of the Carnot cycle.

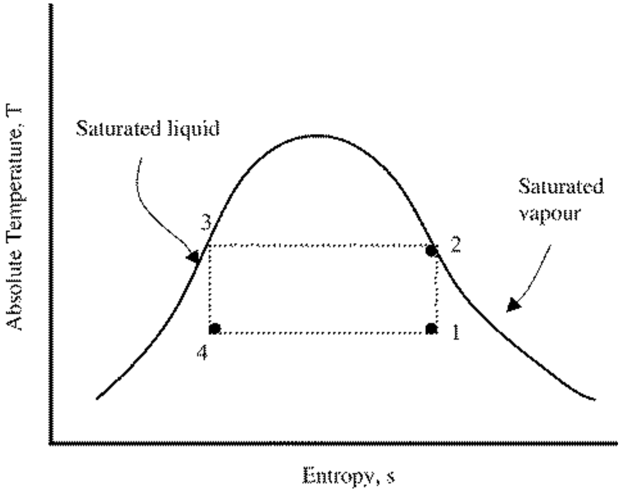

Fig. 4.3 Temperature-entropy diagram of the Carnot cycle.

represent the saturation points. To the left of the dome is the subcooled liquid region; and to the right lies the superheated vapour region. The region beneath the dome represents two phase (gas-liquid) mixtures.

From Figs. 4.2 and 4.3 it is clear that condensation (points 2–3) and evaporation (points 4-1) occur under constant temperature and pressure conditions, while expansion (points 3–4) and compression (points 1–2) occur under constant entropy conditions, as discussed earlier.

4.3.1 2 **The Real Refrigeration Cycle (Standard Vapour Compression Cycle)**

If attempts are made to operate equipment under the conditions proposed by the Carnot Cycle, severe mechanical problems are encountered, such as continuous valve breakdown, lack of good lubrication in the compression cycle, etc. Therefore a real refrigeration cycle should be adapted, considering the mechanical possibilities [7]. The main differences between the ideal Carnot cycle and that achieved in reality will be described in the following paragraphs.

Compression: Wet vs Dry The compression process observed in the ideal cycle (Fig. 4.2, points 1–2) is commonly described as wet compression because it starts with a mixture of gas and vapour (point 1), and occurs completely in the two-phase region (beneath the dome). The presence of a liquid phase can diminish lubrication effectiveness of some compressors. Moreover, droplets can also damage valves. Therefore, a real compression process should be carried out in the dry region shown in Fig. 4.4 (process 1′–2′).

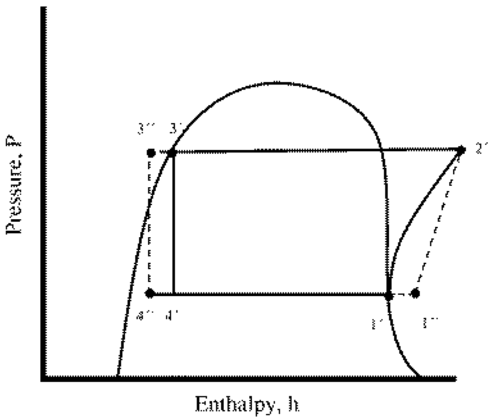

Fig. 4.4 Standard refrigeration cycle and modified standard cycle.

Expansion: Engine vs Valve Expansion process 3–4 described in the ideal cycle (see Fig. 4.2) assumes that the engine extracts energy from the refrigerant and uses it to reduce the compressor work. Practical problems include finding a suitable engine, controlling it and transferring its power to the compressor; therefore, it is uncommon to find expansion engines in refrigeration systems nowadays. Instead, the pressure drop is accomplished by a throttle valve (also called the expansion valve). Due to this change, the energy loss during expansion is negligible, thus $h'_3 = h'_4$. The changes made from cycle 1–2–3–4 to cycle 1′–2′–3′–4′ (see Fig. 4.4) results in a cycle known as the standard vapour compression cycle. Even this standard cycle has been modified further, in order to adapt it to more efficient conditions, e.g. cycle 1″–2′–3″–4″, where the vapour leaves the evaporator superheated and the liquid leaves the condenser subcooled.

4.3.2
Equipment for a Mechanical Refrigeration System

As mentioned earlier in this chapter, the basic components of a refrigeration system are the heat exchangers (evaporator and condenser), the compressor, the expansion valve and the refrigerant.

4.3.2.1 Evaporators

Inside this heat exchanger, the liquid refrigerant absorbs heat from the air in the cold room and vaporises. Depending on their design, evaporators can be classified into two types: direct expansion and indirect expansion evaporators. In the first type, the refrigerant vaporises inside the coils which are in direct contact with either the atmosphere or the object being cooled. In contrast, indirect contact evaporators use a carrier fluid (secondary refrigerant) that transfers heat from the atmosphere or the object that is being refrigerated to the evaporator coils. Although this type of evaporator costs more, it is useful when several locations are to be refrigerated with a single refrigeration system.

The most common type of industrial evaporator is that in which the air is forced through a row of fins. This air absorbs heat from food and returns to the evaporator where it rejects the heat gained. The heat transfer within such an evaporator can be described as a typical multilayer heat transfer with resistances in series. Heat must move from the air to the outer wall of the coil (convective resistance), then to the inner wall of the coil (conductive resistance) and finally to the refrigerant (convective resistance). These resistances can be defined as follows:

$$R_{cv} = \frac{1}{HA_o} \tag{4.1}$$

$$R_{cd} = \frac{\Delta x}{KA_{mean}} \tag{4.2}$$

where R_{cv} and R_{cd} are the convection and conduction resistances, respectively, H and K are heat transfer coefficient for convection and thermal conductivity and A is the related heat transfer area. It is clear from these equations that an increase in the heat transfer area will reduce the resistances, which is desirable. Additionally, it is known that the higher resistance is found in the outer layer of the coils and therefore it is common to see fins installed in the evaporator, in order to extend the contact area and decrease the resistance to heat transfer.

4.3.2.2 **Condensers**

Three main types of condensers can be found in refrigeration systems (see Fig. 4.5):

- air cooled
- water cooled
- evaporative

The purpose of each piece of equipment is to reject the heat absorbed by the refrigerant and transfer it to another medium such as air or water.

Similar to evaporators, air cooled condensers also use fins or plates to increase heat transfer efficiency. It is common to find fans attached to the condenser in order to increase air flow and therefore heat transfer rate. This type of equipment is easy and inexpensive to maintain and is therefore found in household appliances.

In water cooled condensers, the refrigerant flows inside tubes. Double pipe condensers have been used for many years in the food industry, however shell and tube condensers are more common nowadays.

Evaporative condensers operate like cooling towers. Water is pumped from a reservoir at the base of the condenser and sprayed onto the coils. Water evaporation extracts heat from the coils and a fast flowing air stream takes away the va-

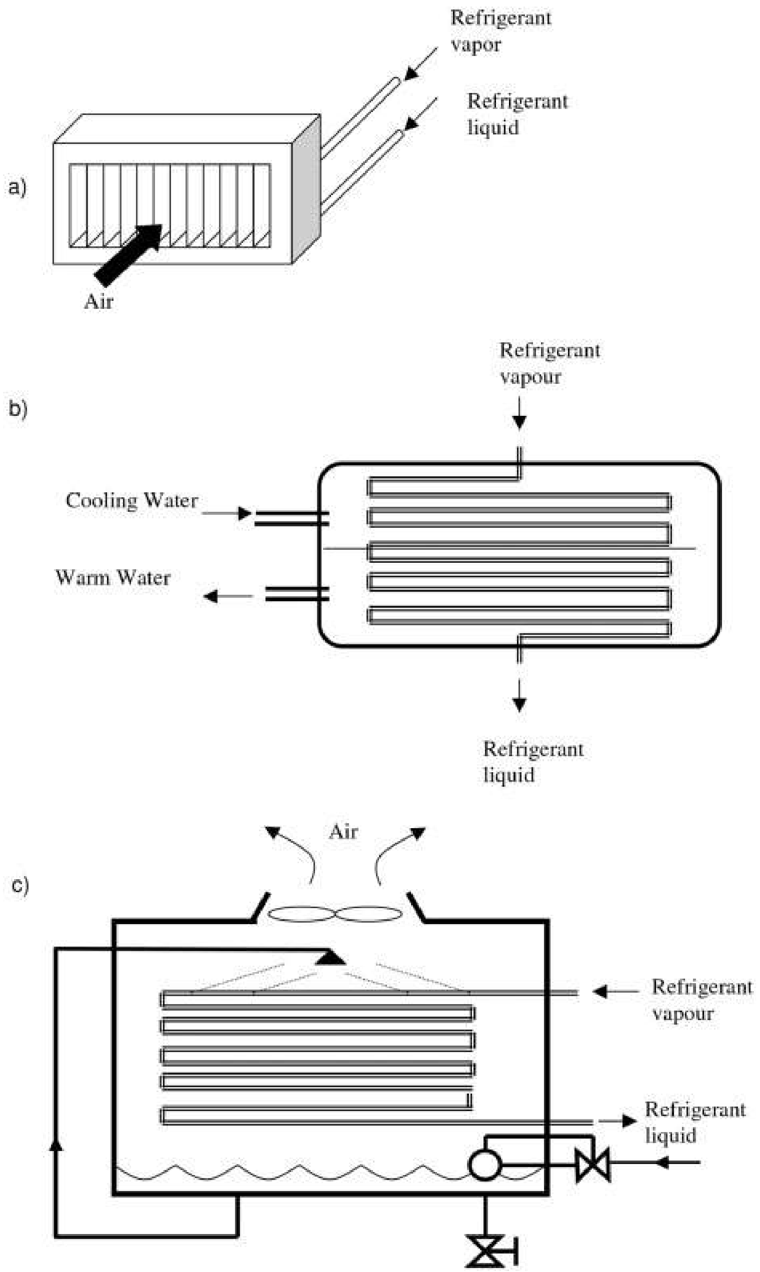

Fig. 4.5 Three different types of condensers: (a) air cooling, (b) water cooling, (c) evaporative.

pour, favouring heat and mass transfer. The water which failes to evaporate returns to the pan and is recycled with the pump. These types of systems are very efficient, although they require a lot of space.

4.3.2.3 **Compressors**

Refrigeration systems can be classified into three types depending on the method employed for compression:

- Mechanical compression. The most widely used system is the mechanical compression system, which is described in detail below.
- Thermal compression (absorption-desorption). This method is preferred when low cost/low pressure steam or waste heat is available. It is usually used to chill water (7–10 °C) and for capacities in the range from 300 kW to 5 MW.
- Pressure difference (or ejectors). These systems are used for similar applications as thermal compression systems and have lower initial and maintenance costs. However, they are not as common as thermal compression systems.

Mechanical Compression Compressors can be divided into two groups: positive displacement compressors (PDC) and dynamic compressors. PDC increase the pressure by reducing the volume. Typical compressors in this group are the reciprocating compressors, which dominate in the range up to 300 kW applications and tend to be the first choice due to their lower costs. Rotary compressors also belong to the PDC group. Screw type rotary compressors are found in the range 300–500 kW. Other rotary compressors such as the Vane [9] are found in applications in low capacity equipment.

In contrast, centrifugal compressors, which belong to the dynamic group, are found in equipment in the range 200–10 000 kW. These compressors have impellers turning at high speed and impart energy to the refrigerant. Some of this kinetic energy gained by the refrigerant is converted to pressure energy. These types of devices are more expensive than the reciprocating variety. However, they tend to be more economical to maintain. Further, they are generally small in size and are recommended when space is limited and long running periods are desired with minimum maintenance.

4.3.2.4 **Expansion Valves**

They are essentially flow controlling devices that separate the high pressure zone from the low pressure zone in a refrigeration system. Common types are:

- Manually operated. These are used to set the volume of refrigerant flowing from the high to the low pressure side.
- Automatic valves. This group can be divided into float, thermostatic and constant pressure valves. The float valve is the most cost effective of the three due to its simplicity and low maintenance costs, although it can only be used in flooded type condensers. However, thermostatic valves are the most widely used in the refrigeration industry.

4.3.2.5 **Refrigerants**

These can be classified into two groups: primary and secondary refrigerants. In the primary group belong those that vaporise and condense as they absorb and reject heat. Secondary refrigerants, in contrast, are heat transfer fluids commonly known as carriers. The choice of refrigerant is not easy, and there is a long list of commercial options. Desirable characteristics of these fluids are summarised in Table 4.2.

The refrigerants used in earlier days tended to be easily and naturally found: air, ammonia, CO_2, SO_2, ether, etc. Ammonia is the only refrigerant from this list that is still being used by the industry, however recent interests have been shown in CO_2 [10]. Ammonia shows several thermodynamically desirable properties, such as a high latent heat of vaporisation. Additionally, it has economic and environmental advantages; however, its irritating and intoxicating effects are major drawbacks. Other types of refrigerants became important in the 20th century due to efficiency and safety considerations. Halocarbons such as R12 (Freon, dichorofluormethane), R22 (cholodifluormethane), R30 (methylene chloride) and others are still being used in air conditioning (building and car) and small refrigeration systems. During the 1970s, it was postulated that chorofluorcarbons (CFCs) have damaging effects on the ozone layer. Due to their high stability in the lower atmosphere, they tend to migrate to the upper atmosphere where the chlorine portion splits and reacts with the ozone. The use of this kind of refrigerants started to decline in the 1990s due to the influence of global environmental agreements such as the Montreal treaty [11].

Hydrofluorocarbons (HFCs) are compounds containing carbon, hydrogen and fluorine. Some of these chemicals are accepted by industry and scientists as alternatives to CFCs and hydrochlorofluorocarbons. The most commonly used HFCs are HFC 134a and HFC 152a. Because HFCs contain no chlorine, they do not directly affect stratospheric ozone and are therefore classified as substances with low ozone depletion potential. Although it is believed that HFCs do not deplete ozone, these compounds have other adverse environmental effects, such as infrared absorptive capacity. Concern over these effects may make

Table 4.2 Desirable characteristics of modern refrigerants.

Safe	**Nontoxic; not explosive; nonflammable**
Environmentally friendly	Ozone friendly; no greenhouse potential; leaks should be easily detected; easily disposable
Low cost	Low cost per unit of mass; high latent heat/cost ratio
System compatible	Chemical stability; noncorrosive
Good thermodynamic and physical properties	High latent heat; low freezing temperature; high critical temperature (higher than ambient); low viscosity

it necessary to regulate the production and use of these compounds at some point in the future. Such restrictions have been proposed in the Kyoto protocol [12].

4.3.3
Common Terms Used in Refrigeration System Design

There are some useful expressions to define the capacity and efficiency of a refrigeration system and its components. Some of them are based on the variation of refrigerant energy and therefore show how pressure-enthalpy diagrams are useful tools for the design of refrigeration systems.

4.3.3.1 **Cooling Load**

This is defined as the rate of heat removal from a given space. As pointed out earlier in this chapter, ice was the main source of low temperatures when refrigeration was first commercialised; and therefore a typical unit for cooling load – known as a tonne of refrigeration – is equivalent to the latent heat of fusion of 1 t of ice in 24 h, which is equivalent to 3.52 kW. In designing a refrigeration system, several other sources of heat, in addition to the demand by the food itself, should be considered. Table 4.3 summarises some of the most relevant factors.

4.3.3.2 **Coefficient of Performance (COP)**

This is expressed as the ratio of the refrigeration effect obtained to the work done in order to achieve it. It is calculated by dividing the amount of heat absorbed by the refrigerant as it flows through the evaporator by the heat equivalent of the work done by the compressor. Thus in enthalpy values:

Table 4.3 Basic sources of heat to be considered in a cold room design.

Source of heat	Conside rations
Heat introduced through ceiling, floor and walls	Conduction of heat through walls and insulation materials
Heat transferred by the food material	Sensible heat; respiration heat (applied to refrigerated vegetables); latent heat (when freezing occurs)
Heat transferred by people	Working time; number of people
Heat transferred by engines working inside the cold room	Working time; number of engines; total power
Heat transferred by illumination bulbs	Working time; number of bulbs; total power
Heat introduced by air renewal	Number of times the door is opened; other programmed changes of air

$$COP = \frac{h_2 - h_1}{h_2 - h_3} \tag{4.3}$$

The COP value in a real refrigeration cycle is always less than that for the Carnot cycle. Therefore, industry is constantly striving to improve COP. It should be pointed out that methods to increase COP should be studied for every refrigerant separately.

4.3.3.3 **Refrigerant Flow Rate**

This quantity is useful for design purposes and depends on the cooling load in the following way:

$$\dot{m} = \frac{Q}{h_1 - h_4} \tag{4.4}$$

where $\dot{m}$ is the refrigerant flow rate (kg s^{-1}) and Q is the total cooling load (kW).

4.3.3.4 **Work Done by the Compressor**

The energy used for using the rise in enthalpy of the refrigerant is:

$$Wc = \dot{m}\,(h_2 - h_1) \tag{4.5}$$

An efficiency term should be introduced into the above equation when calculating the work done by the compressor.

4.3.3.5 **Heat Exchanged in the Condenser and Evaporator**

As heat exchange in both condenser and evaporator occur at constant pressure and temperature, the amount of heat rejected or gained by the refrigerant in each process can be estimated as follows:

$$Q_c = \dot{m}\,(h_2 - h_3) \tag{4.6}$$

$$Q_e = \dot{m}\,(h_1 - h_4) \tag{4.7}$$

4.4 Freezing Kinetics

As explained earlier, from a thermodynamic point of view, freezing is a more complex process than cooling due to the phase change involved:

- cooling and undercooling of the liquid sample
- nucleation
- growth
- further cooling of the frozen material.

The state diagram shown in Fig. 4.6 is useful to describe a typical water freezing process which follows the cooling path A-B-C-D-E.

Starting at room temperature (point A), the sample is taken to point B without phase change (undercooling) due to an energy barrier that must be surmounted before nucleation starts. The formation of stable nuclei is governed by the net free energy of formation, which is the summation of the surface and volume energy terms. Higher undercooling favours the formation of a higher number of nuclei, which could have an effect on the final crystal size distribution. Due to the latent heat liberated, a temperature shift would be expected (points B-C in Fig. 4.6). Once stable ice nuclei are formed, they continue to grow. Progress in crystal growth (points C-D in Fig. 4.6) depend on the supply of water molecules from the liquid phase to the nuclei (mass transfer) and the removal of latent heat (heat transfer). After all of the water is frozen, the temperature decreases again (points D-E in Fig. 4.6).

There are some differences between the phase diagrams of food and water. Due to the interaction of water with solutes present in the food, a freezing point depression occurs. Additionally, ice crystallisation causes a progressive concentration of the solution that remains unfrozen. Thus, as more ice is formed, the amorphous matrix increases its solid content and viscosity and reduces its freezing point, as seen from the path C′-E′. This concentration and ice formation continues until a temperature is reached at which no more water will freeze; this temperature is known as the glass transition temperature of the amorphous concentrated solution (T_g' [13], point E in Fig. 4.6). At this temperature, the concentrated solution vitrifies due to the high viscosity of this matrix (10^{12} Pa s); and molecular movement is negligible (diffusion rates fall to a few microns per year) and therefore in food materials a fraction of unfrozen water is unavoidable.

Both water and temperature affect molecular mobility, due to their plasticising capacity. Therefore, diffusion coefficients increase when water content or

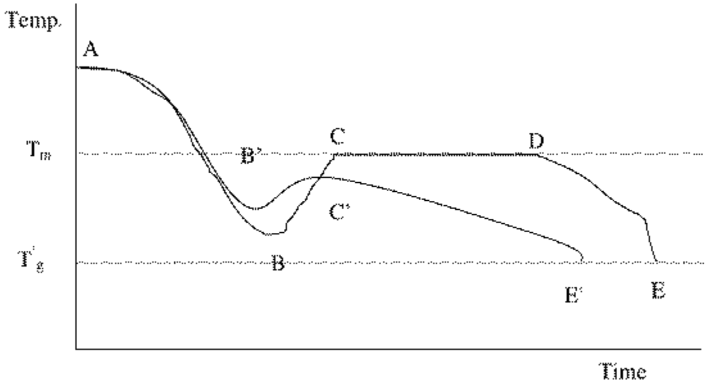

Fig. 4.6 A time-temperature curve during typical freezing. Path A-B-C-D-E corresponds to the freezing of water; and path A-B′-C′-E′ corresponds to that for a solution.

temperature is increased. William et al. [14] observed that the decrease in viscosity above T_g for various glassforming substances could be modelled with what became the well known WLF equation:

$$\log\frac{\mu}{\mu_o} = \frac{c_1(T - T_o)}{c_2 + T - T_o} \tag{4.8}$$

where μ and μ_o are the viscosities at temperatures T and T_o, and the so called universal constants c_1 and c_2 are equal to 17.44 and 51.6, respectively. The validity of this equation over a temperature range of $T_g < T < (T_g+100)$ has been tested and related to other physical changes such as collapse, crispiness, crystallisation, ice formation and deteriorative reactions [15]. However, the validity of the so called universal constants has been questioned.

4.4.1
Formation of the Microstructure During Solidification

The overall driving force for solidification is a complex balance of thermodynamic and mass transfer factors, which dominate in different parts of the process [16]. Crystal growth tends to be parallel and opposite to the direction of heat transfer; and therefore finger-like dendrites can be formed if unidirectional heat transfer is imposed [17].

Under unidirectional freezing, the most important crystal form is the dendrite [17]. Under directional cooling, cell-like structures can grow (see Fig. 4.7).

However, anisotropy in heat and mass transfer properties tends to favour dendritic cells and dendrite growth (Fig. 4.7 b, c). The formation of a dendrite begins with the breakdown of the planar solid-liquid interface. Dendritic tips reject solute in all directions and therefore spaces between dendrites accumulate the rejected solute, favouring the formation of cell-type dendrites (Fig. 4.7 a). Secondary branches form afterwards if the conditions of the media allow.

A combination of heat and mass transfer governs the movement of the freezing front. During unidirectional cooling, heat transfer tends to be faster than mass transfer due to the high thermal conductivity of ice and low mass diffusion coefficients. Therefore, solute diffusion will be the limiting factor of growth and an undercooling in the tip region will be observed. This supercooling is known as constitutional undercooling and has been used to develop models on the primary spacing between dendrites, i.e. the space between the tips of two dendrites [18–22]. All these models have, in common, the following general expression that correlates interdendritic spacing with freezing kinetics:

$$L \propto R^a G^b \tag{4.9}$$

where L is the mean interdendritic distance R is the freezing front rate, G is the temperature gradient between the ice front and the freezing plate and a, b are constants.

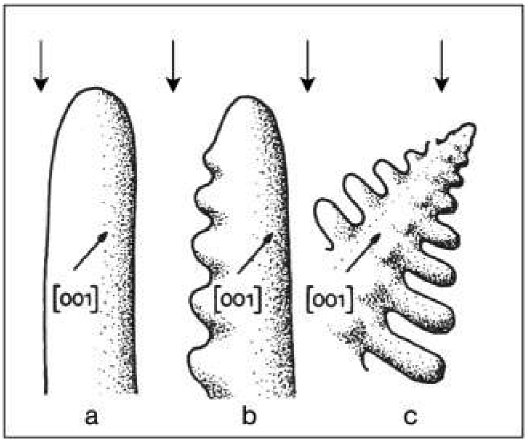

Fig. 4.7 Different ice crystal shapes: (a) represents a cell which is only possible in unidirectional freezing, (b) this shape is known as dendritic cell and (c) this shape is described as dendrite; after [17].

4.4.2
Mathematical Models for Freezing Kinetics

The kinetics of freezing has been widely studied and mathematically defined as a heat conduction process with phase change. The estimation of freezing times requires analysis of conductive heat flow through frozen and unfrozen layers, in addition to the heat transfer from the sample to the environment. The most common analyses are based on either Plank's or Neumann's models, which are exact solutions valid for unidirectional freezing under the assumption of an isothermal phase change [23, 24]. While Plank's model assumes quasi-steady state heat transfer, the Neumann's model is more generally applicable and is based on unsteady state conduction through frozen and unfrozen layers. In addition to analytical methods, approximate analytical procedures are reviewed by Singh and Mannapperuma [25].

4.4.2.1 **Neumann's Model**

Under conditions of unidirectional freezing, it has been established that the position of the freezing front varies with time as follows [17, 22, 26]:

$$x = c\sqrt{t} \tag{4.10}$$

where x is the position of the ice front, t is time and c is a kinetic constant. This equation is valid under the assumption of a planar freezing front.

The equations following from Neumann's model are listed in Table 4.4. They can be solved analytically to result in a relationship similar to Eq. (4.10):

$$x = 2\delta\sqrt{a_1 t} \tag{4.11}$$

where a_1 is the thermal diffusivity of the frozen zone, and δ represents the Neumman dimensionless characteristic number.

Table 4.4 Basic heat equations involved in Neumman's model.

	Frozen layer	**Liquid layer**
Conservation equation	$\frac{\partial T_1}{\partial t} = a_1 \frac{\partial^2 T_1}{\partial x^2} 0 < x < s$	$\frac{\partial T_2}{\partial t} = a_2 \frac{\partial^2 T_2}{\partial x^2} \; s < x < x_t$
Initial conditions and boundary conditions	$T_1 = T_f, \; x = 0, \; t > 0$ $T_1 = T_m, \; x = s, \; t > 0$	$T_2 = T_0$ for all $x, \; t = 0$ $T_2 = T_0, x \to \infty, \; t > 0$ $T_2 = Tm, x = s, \quad t > 0$
At the ice front	$-K_1 \frac{\partial T_1}{\partial x} + K_2 \frac{\partial T_2}{\partial x} + \rho_1 \Delta H_f \frac{ds}{dt}, \; x = s$	

4.4.2.2 **Plank's Model**

Plank's analytical solution is recognised as the first equation proposed for predicting freezing times. It is based on two assumptions: (a) the sample is initially at its freezing point and (b) there is constant temperature in the unfrozen region. These assumptions imply that each layer in the unfrozen region remains at a constant temperature until the freezing front reaches it. In addition, Plank's model uses convective heat transfer as a boundary condition. Plank's model has been applied to different basic geometries and the general solution is as follows:

$$t = \frac{\rho \Delta H}{T_f - T_a} \left(\frac{PD}{h} + \frac{RD^2}{K} \right) \tag{4.12}$$

where P and R are geometric constants with values which change according to the shape of the sample. For a slab $P = \frac{1}{2}, \; R = \frac{1}{8}$; for a cylinder $P = \frac{1}{4}, \; R = \frac{1}{8}$; and for a sphere $P = \frac{1}{6}, \; R = \frac{1}{24}$.

Pham [27] extended Plank's solution to account for sensible heat removal. He divided the freezing process into three stages: precooling, freezing and subcooling.

4.4.2.3 **Cleland's Model**

This model [28] estimates freezing times of food samples based on the following assumptions: (a) the conditions of the surrounding are constant, (b) the sample is found initially at a uniform temperature, (c) the final temperature has a fixed value and (d) Newton's cooling law describes the heat transfer at the surface.

Freezing time can be estimated using the following equation:

$$t_{slab} = \frac{R}{h} \left[\frac{\Delta H_1}{\Delta T_1} + \frac{\Delta H_2}{\Delta T_2} \right] \left(1 + \frac{N_{Bi}}{2} \right) \tag{4.13}$$

This equation is valid for Biot numbers between 0.02 and 11, Stefan numbers between 0.11 and 0.36 and Plank numbers between 0.03 and 0.61. Table 4.5 contains the equations used to estimate ΔH_1, ΔH_2, ΔT_1, ΔT_2.

Table 4.5 Equations and variables involved in Cleland's model.

$\Delta H_1 = C_u\,(T_i - T_3)$

$\Delta H_2 = H_L + C_f\,(T_3 - T_f)$

$\Delta T_1 = \dfrac{(T_i + T_3)}{2} - T_a$

$T_3 = 1.8 + 0.263\ T_f + 0.105\ T_a$

$\Delta T_2 = T_3 - T_a$

C_u: unfrozen volumetric specific heat capacity $\dfrac{J}{m^3 K}$

C_f: frozen volumetric heat capacity $\dfrac{J}{m^3 K}$

H_L: latent heat of fusion $\dfrac{kJ}{kg}$

T_i: initial temperature

T_a: chamber temperature

The basic model is defined for a slab, but freezing times for samples with various geometrical shapes can be estimated by approximating these shapes to an ellipsoid. A shape factor E is used to relate the estimated freezing time for the slab to that of the ellipsoid as seen from the following equations:

$$t_{ellipsoid} = \frac{t_{slab}}{E} \tag{4.14}$$

$$E = 1 + \frac{\left(1 + \frac{2}{N_{Bi}}\right)}{\left(\beta_1^2 + \frac{2\beta_1}{N_{Bi}}\right)} + \frac{\left(1 + \frac{2}{N_{Bi}}\right)}{\left(\beta_2^2 + \frac{2\beta_2}{N_{Bi}}\right)} \tag{4.15}$$

$$\beta_1 = \frac{A}{\pi R^2} \tag{4.16}$$

4.5 Effects of Refrigeration on Food Quality

Market trends show that consumers are paying more attention to flavour and nutritional attributes of food rather than to texture and colour characteristics; and therefore refrigerated products are gaining more importance in the marketplace due to the ability of this technology to maintain the two abovementioned quality factors [29]. Foods gain from refrigerated storage (frozen and chilled) due to the positive effect of low temperatures on molecular movement, microbial growth and chemical reaction rates. At temperatures marginally above zero, quality is well preserved for short periods (days or weeks). However, for longer periods, frozen storage is well suited because reactions continue at very low rates and microbial growth is virtually stopped to a point where the microbial population can be reduced [1].

During freezing, ice crystals can be formed in the space between cells and intracellular water can migrate, provided the cooling rate is slow enough [20]. This movement of water can produce irreversible changes in cell size. Additionally, it can damage membranes, causing the loss of water and enzymes that are responsible for colour and odour changes during thawing. Therefore rapid freezing, the use of cryoprotectants such as sugar and pretreatments such as blanching can improve the quality of the frozen product because cell wall damage and enzyme activity can both be reduced. Reid [30] suggests four processes that can help to explain the damages of vegetable tissue during freezing: cold (temperatures above 0 °C), solute concentration, dehydration and ice crystal injuries. These injuries also apply to animal tissues. However, their relative importance is different: while solute concentration causes more damage to the latter, crystal injuries have a bigger effect on texture and therefore are more important in vegetable tissues.

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