1 Introduction to refrigeration and thermometry

1.1 Preamble

It is useful when learning about the technicalities of low temperature physics to have ready access to some fundamental thermodynamic notions relating to refrigeration and thermometry. These can readily be summarised and that is the purpose of this chapter.

1.2 Refrigeration

The physical systems commonly exploited as refrigerants in low temperature research are fluids (specifically ^{3}He, ^{4}He, and ^{3}He–^{4}He mixtures), solids with electronic paramagnetism (for example, cerous magnesium nitrate (CMN)) or nuclear paramagnetism (for example, copper) or hyperfine-enhanced nuclear paramagnetism (for example, praesodymium nickel five (PrNi$_5$)), and solid/liquid ^{3}He at its melting pressure. For present illustrative purposes, however, we shall consider the thermodynamics of refrigeration using a monatomic van der Waals fluid; and using an idealised paramagnet.

1.2.1 Free expansion of a fluid

The fluid expands into a previously evacuated space and if the container has walls which are perfectly insulating and perfectly rigid then it is trivial to show that the internal energy U remains constant. The process is irreversible (entropy rises), and in the single-phase state the temperature change can conveniently be expressed in the following form:

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right].\tag{1.1}$$

This is in general not zero (except for a perfect gas) but can be

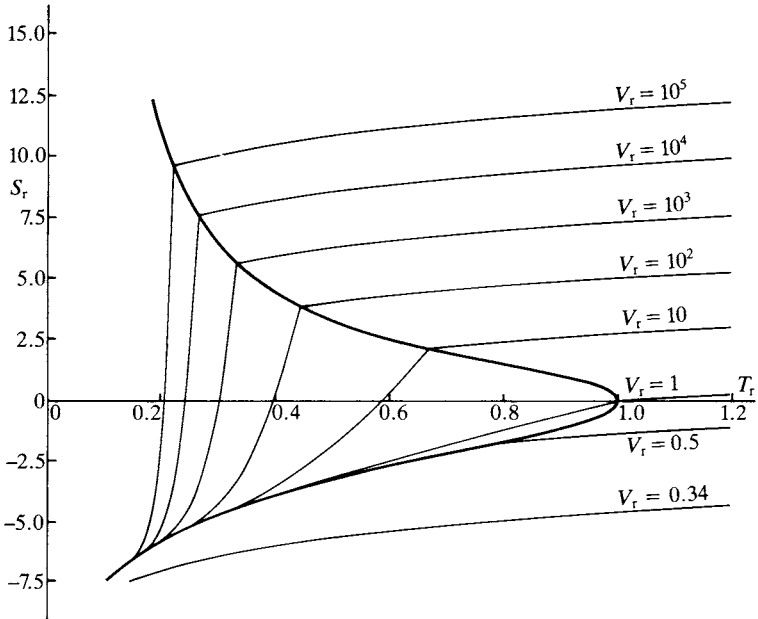2   *Introduction to refrigeration and thermometry*
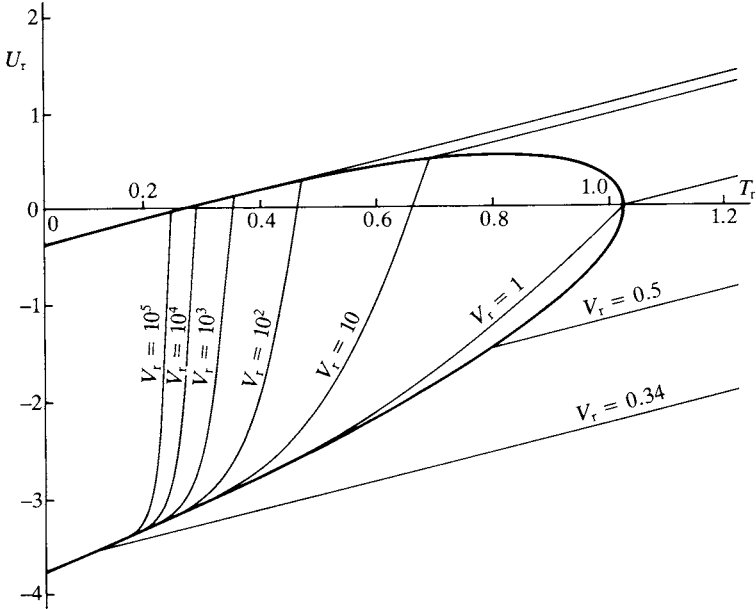
Figure 1.1. Internal energy U_r versus relative temperature $T_r = T/T_c$ (where the subscript c labels quantities at the critical point) for several fixed relative volumes $V_r = V/V_c$ for a van der Waals fluid, considered as an illustrative example. The relative internal energy is scaled to have the value 0 at the critical point; under the vapour pressure as $T_r \to 0$, $U_r(\text{liq}) \to (2\frac{1}{2}T_r - 3\frac{3}{4})$ and $U_r(\text{vap}) \to (1\frac{1}{2}T_r - \frac{3}{8})$. Temperature changes can be read off a horizontal line through and to the left of the point representing the initial state. I am grateful to Mr Erik Westerberg for writing the program which generated this figure.

expressed in terms of the fluid's equation of state, if known. Figure 1.1 shows the calculated results for a van der Waals fluid including both the single-phase and two-phase states. The free expansion is never used as a practical means of refrigeration and will not be discussed further here.

1.2.2   Isentropic expansion or compression of a fluid

The fluid is allowed to expand in a reversible and adiabatic way, performing external work in the process. One may visualise the fluid as being constrained in an insulated cylindrical container, one end of which is a frictionless piston whose motion against external pressure is kept to a very low speed to avoid irreversibility as far as possible. The process is

Figure 1.2. Entropy S_r versus relative temperature $T_r = T/T_c$ (where the subscript c labels quantities at the critical point) for several fixed relative volumes $V_r = V/V_c$ for a van der Waals fluid, considered as an illustrative example. The relative entropy is scaled to have the value 0 at the critical point (the van der Waals fluid does not obey the third law of thermodynamics); under the vapour pressure as $T_r \to 0$, S_r(liq) diverges towards minus infinity as $[2\frac{1}{2} \ln T_r - \ln(6\frac{3}{4})]$ and S_r(vap) diverges towards plus infinity as $[2\frac{1}{2} \ln T_r - \ln(6\frac{3}{4}) + 3\frac{3}{8}/T_r]$. Temperature changes can be read off a horizontal line through the point representing the initial state. I am grateful to Mr Erik Westerberg for writing the program which generated this figure.

quasistatic and in the single-phase state the temperature change can conveniently be expressed in the following form:
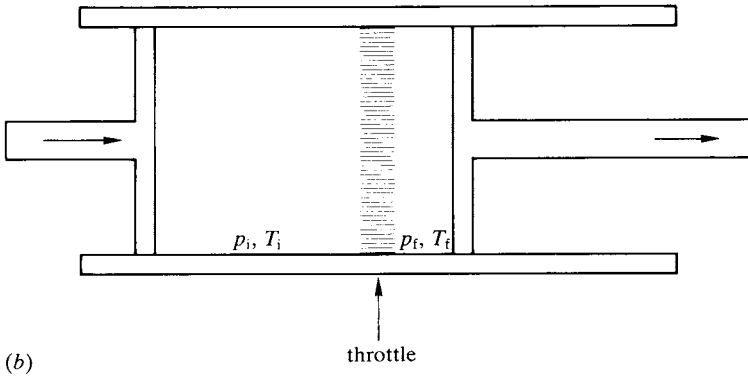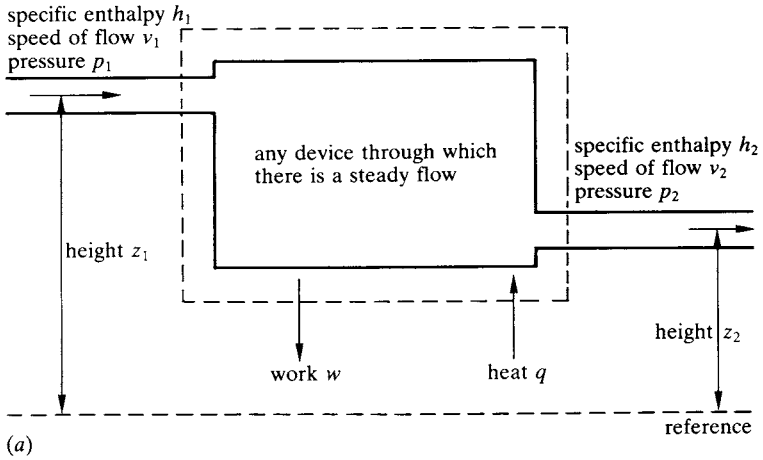
$$\left(\frac{\partial T}{\partial V}\right)_S = - \frac{T}{C_V}\left(\frac{\partial p}{\partial T}\right)_V. \tag{1.2}$$

This can be expressed in terms of the fluid's equation of state, if known, and for a monatomic perfect gas reduces to the familiar form

$$T_f = T_i(V_i/V_f)^{2/3}. \tag{1.3}$$

Figure 1.2 shows the calculated results for a van der Waals fluid including both the single-phase and two-phase states. This method, or a practical

4   *Introduction to refrigeration and thermometry*

Figure 1.3. (*a*) A general device through which there is a flow. The equation which relates the various quantities is

$$(h_2 - h_1) + \tfrac{1}{2}(v_2^2 - v_1^2) + g(z_2 - z_1) = q - w$$

where h_1, h_2, q, and w all refer to unit mass of flow. A special case of (*a*) is shown in (*b*) in which the device is a throttle whose effect is to render v_1, v_2, $(z_2 - z_1)$ negligible and in which q and w are zero. In this case the process is isenthalpic since $(h_2 - h_1) = 0$.

approximation to it, is used in low temperature refrigerators, most obviously in simple ^{3}He and ^{4}He 'pots'.

It is not practical to use a moving piston because of the large vapour volumes but the use of a vacuum pump to evaporate the liquid acts in a similar fashion. Also the basic principle of the Pomeranchuk refrigerator is recognisably the same, even though the two phases are in that case liquid and solid rather than vapour and liquid; moreover a movable piston *is* then used, usually in the form of bellows. See Chapter 4.

1.2.3 Isenthalpic expansion of a fluid

This takes place ideally in a device illustrated in texts on classical thermodynamics and in Figures 1.3(a) and 1.3(b). In Figure 1.3(b) the fluid is directed through a small orifice from a chamber maintained (by suitably controlled motion of a frictionless piston) at pressure p_1 into a second chamber maintained (by suitably controlled motion of another frictionless piston) at pressure p_2. All the walls are insulating and $p_1 \geqslant p_2$. It is trivial to show that the enthalpy H remains constant. The process is
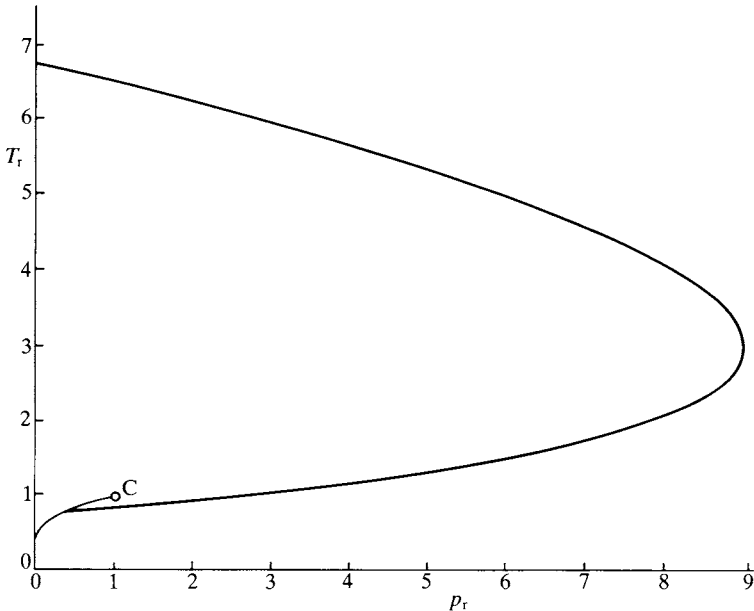
Figure 1.4. The inversion curve of a van der Waals fluid, considered as an illustrative example.

6   *Introduction to refrigeration and thermometry*
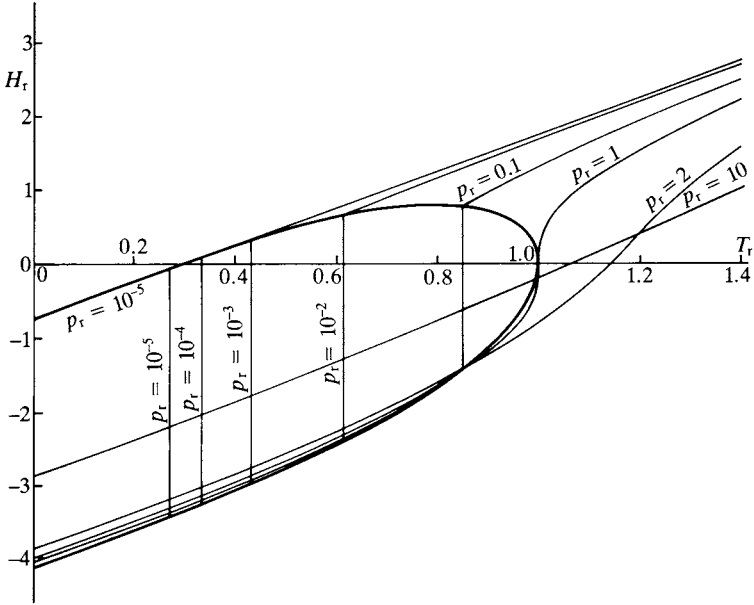
Figure 1.5. Relative enthalpy versus relative temperature $T_r = T/T_c$ (where the subscript c labels quantities at the critical point) for several fixed relative pressures $p_r = p/p_c$ for a van der Waals fluid, considered as an illustrative example. I am grateful to Mr Erik Westerberg for writing the program which generated this figure.

irreversible and entropy rises. In the single-phase state the temperature change can conveniently be expressed in the following form:

$$\left(\frac{\partial T}{\partial p}\right)_H = + \ \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]. \tag{1.4}$$

This is in general not zero (except for a perfect gas) and may be positive or negative depending on the pressures and initial temperature. In low temperature applications one is normally operating within the fluid's inversion curve and then the result is cooling. Figures 1.4 and 1.5 show respectively the inversion curve and calculated results for a van der Waals fluid including both the single-phase and two-phase states. In Figure 1.4 $T_r = T/T_c$ is plotted against $p_r = p/p_c$ where the subscript c labels quantities at the critical point. The critical point at $T_r = 1$ and $p_r = 1$ is labelled C in the figure and the curve which links it to the origin at $T_r = 0$ and $p_r = 0$ is the vapour pressure curve. All points in this figure, except those which lie on the vapour pressure curve, refer to the

single-phase state. All points within the enclosed area have a positive value of the quantity specified in equation (1.4), that is, cooling can be achieved by an isenthalpic process in which the fluid passes from a higher to a lower pressure. The maximum inversion temperature for a van der Waals fluid is exactly $T_r = 6\frac{3}{4}$ and the tip of the curve is exactly at $T_r = 3$ and $p_r = 9$.

In Figure 1.5 enthalpy is plotted against relative temperature for several fixed relative pressures. The relative enthalpy is scaled to have the value 0 at the critical point; under the vapour pressure as $T_r \rightarrow 0$, $H_r(\text{liq}) \rightarrow (2\frac{1}{2} T_r - 4\frac{1}{8})$ and $H_r(\text{vap}) \rightarrow (2\frac{1}{2} T_r - \frac{3}{4})$. Temperature changes can be read off a horizontal line through and to the left of the point representing the initial state.

This isenthalpic method, or a practical approximation to it, is used in low temperature refrigerators in that cooling and liquefaction can be achieved by forcing the fluid through a constriction into a lower pressure chamber. The ideal text-book case ignores changes in potential and kinetic energies between the two sides of the constriction; it is not difficult to incorporate these into the formulation but for the purposes of this book they can safely be neglected. In the cases of simple evaporation 'pots', in which the pressure difference across the liquid/vapour interface is zero, and the chemical potential is the same on both sides, one may equivalently describe the process (evaporation or condensation) as isentropic and as isenthalpic. Finally, real low-temperature refrigerators almost never have moving pistons (the exception mentioned above is the Pomeranchuk refrigerator) but vacuum pumps perform equivalent functions.

1.2.4   Adiabatic (isentropic) demagnetisation of a paramagnet

In this case one thinks of a solid array, not necessarily in the form of an ordered crystal, of atomic or nuclear magnetic moments. The most frequently used materials include CMN (cerous magnesium nitrate, an electronic paramagnet), copper (a nuclear paramagnet), and $PrNi_5$ (praesodymium nickel five, an intermetallic compound which is a hyperfine-enhanced nuclear paramagnet). Figure 1.6 shows the entropy of CMN as a function of temperature for several applied magnetic fields and illustrates the principle; for example, a demagnetisation from (A) 0.1 tesla at an initial temperature of 100 mK to (B) zero field reduces the temperature to about 3 mK.

The attainment of the initial state would normally require a fairly simple

8   *Introduction to refrigeration and thermometry*
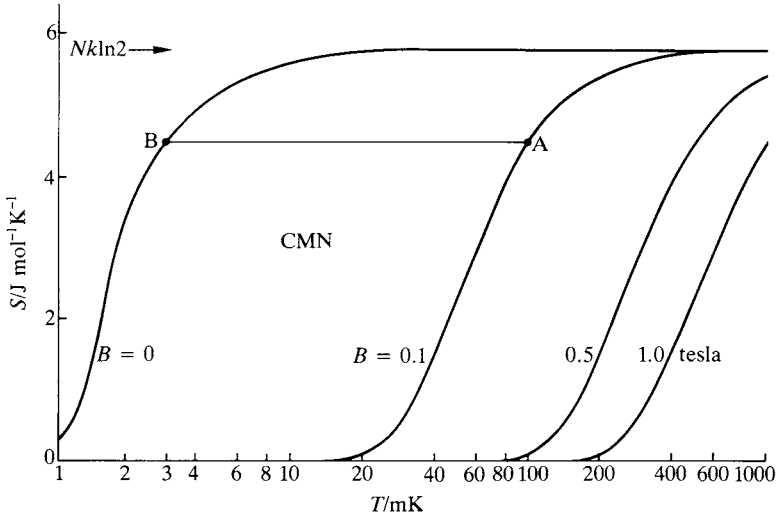
Figure 1.6. The entropy of crystalline CMN versus temperature for
several applied magnetic fields directed along the crystallographic
a-axis. From data given by Fisher *et al.* (1973).

dilution refrigerator (see Chapters 2 and 3) and some form of heat switch
to remove the heat of magnetisation which appears when the refrigerant
is magnetised. When the demagnetisation is made, the heat switch has to
be open to minimise heat leaks. The full cycle of magnetisation and
demagnetisation is indicated in Figure 1.7, and more detail is given in
Chapter 5.

  The thermodynamics of the processes can conveniently be summarised
in two equations. First, the heat of magnetisation released when the
applied field is increased from zero to B_i at T_i is (assuming reversibility):

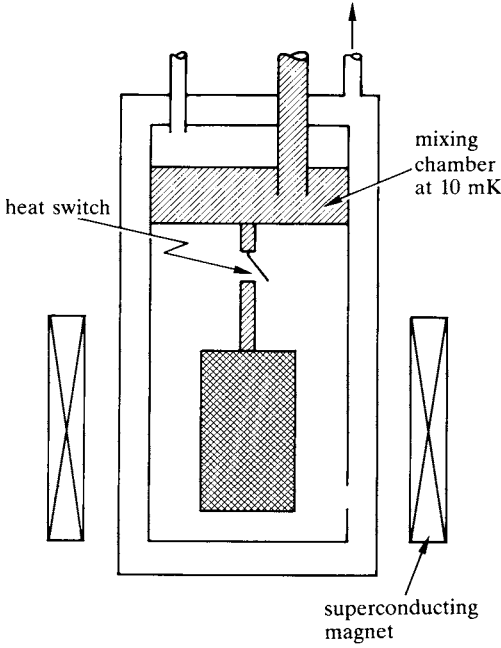$$Q_{\mathrm{mag}} = T_i[S(0,\ T_i) - S(B_i,\ T_i)]. \tag{1.5}$$

Second, the amount of cooling can be calculated in general by integrating
the following equation:

$$\left(\frac{\partial T}{\partial B}\right)_S = -\ \left(\frac{\partial T}{\delta S}\right)_B \left(\frac{\partial S}{\partial B}\right)_T \tag{1.6}$$

$$= -\ \frac{TV}{C_B}\left(\frac{\partial M}{\partial T}\right)_B \tag{1.7}$$

where C_B/V is the specific heat per unit volume at constant field B, and M
is the magnetisation (that is, the magnetic moment per unit volume). For

Figure 1.7. Diagram illustrating the full cycle of magnetisation and demagnetisation. The initial state may be taken as $T_i = 10$ mK (achievable by contact through a closed heat switch with the mixing chamber of a dilution refrigerator) with $B = 0$. The steps are as follows. (i) The field is raised from zero to B_i (typically using a superconducting solenoid), and the heat of magnetisation is conducted through the heat switch to the mixing chamber. (ii) The heat switch is opened so that the refrigerant is thermally isolated. (iii) The field is reduced slowly (ideally isentropically) to B_f and the temperature falls to T_f. The initial state is easily regained if required by closing the heat switch and reducing the field to zero.

a perfect paramagnet, that is, one in which interactions between the atomic or nuclear moments are ignored, it is a standard exercise in statistical mechanics to show that the entropy of N moments γ with quantum number J the entropy is given by

$$\frac{S}{Nk_B} = + \left[\ln \sinh \left(\frac{2J+1}{2J} \frac{\gamma B}{k_B T} \right) - \ln \sinh \left(\frac{1}{2J} \frac{\gamma B}{k_B T} \right) \right]$$

$$- \frac{\gamma B}{k_B T} \left[\left(\frac{2J+1}{2J} \right) \coth \left(\frac{2J+1}{2J} \frac{\gamma B}{k_B T} \right) - \left(\frac{1}{2J} \right) \coth \left(\frac{1}{2J} \frac{\gamma B}{k_B T} \right) \right]. \quad (1.8)$$

10   *Introduction to refrigeration and thermometry*

For the perfect paramagnet it can be seen by inspection of equation (1.8) that if B/T is constant then the process is isentropic, and vice versa. It follows that

$$T_f = (B_f/B_i)\,T_i.\qquad(1.9)$$

This form is often adequate but it cannot of course be accepted in the limiting case of demagnetisation to $B_r = 0$ because then the assumption of negligible interactions (compared with $k_B T$) between the moments breaks down. It is generally safer to think of the effective field B_{eff} on a moment being a combination of the applied field B and an internal field B_{int} characteristic of the actual paramagnet in use. A suitable combination is to take

$$B_{eff}^2 = B^2 + B_{int}^2\qquad(1.10)$$

and this leads to an improved version of equation (1.9):

$$T_f = \left(\frac{B_f^2 + B_{int}^2}{B_i^2 + B_{int}^2}\right)^{1/2} T_i.\qquad(1.11)$$

This correctly places $T_f = 0$ out of reach, consistently with the third law of thermodynamics in that even when $B_f = 0$ the predicted final temperature is not zero, and when in addition $B_i \gg B_{int}$ it reduces to the acceptable limit

$$T_f = (B_{int}/B_i)\,T_i.\qquad(1.12)$$

1.3 Thermometry

1.3.1 *The Kelvin scale*

The existence of temperature as a function of state is a direct consequence of the zeroth law of thermodynamics. At temperatures which are not too close to the absolute zero, the constant-volume gas thermometer serves as a fundamental thermometric device. According to this,

$$T = 273.16 \lim_{p_t \to 0} \left(\frac{p}{p_t}\right),\qquad(1.13)$$

where p is the gas pressure at temperature T, and p_t is the gas pressure at the triple-point temperature of water, defined as 273.16 K. This definition is found to provide a temperature scale which is independent of the properties of the particular gas used, but which of course depends on the properties of gases in general. Thus equation (1.13) cannot be used far below 1 K, simply because no uncondensed gases are available. It is