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General Editor: Douglas F. Brewer, M.A., D.Phil.,

REFRIGERATION AND
THERMOMETRY
BELOW
ONE KELVIN

D. S. BETTS

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PREFACE

This book, like the earlier volumes in the series, is intended primarily for postgraduate students and other beginners, in this case those in the field of research traditionally called low temperature physics. It is more specialised than, for instance, G.K. White's admirable Experimental Techniques in Low Temperature Physics (Oxford, 2nd edition, 1968) in that it concentrates exclusively on the range below one kelvin. However the level is somewhat similar, and it should be understandable as an introduction and a guide to more detailed sources.

I have been actively involved in experimental low temperature research since 1958, and many topics included are matters of personal experience. This is particularly true of the methods for refrigeration, while the wider range of thermometric techniques unavoidably includes a few which I know only through the work of others. References will be found to papers up to and including much of 1975, although the most recent ones have been in some cases only detected by luck, or because they appear in the Proceedings of the Fourteenth International Conference on Low Temperature Physics at Helsinki in August 1975 (eds. M. Krusius and M. Vuorio, North-Holland/American Elsevier 1975).

Some of the material presented here has its origins in earlier articles of mine in Contemporary Physics ("Helium Isotope Refrigeration", "Pomeranchuk Cooling by Adiabatic Solidification of Helium-3"), the Encyclopaedic Dictionary of Physics ("Helium Dilution Refrigeration") or in lecture notes prepared for various audiences ("Attainment and Measurement of Temperatures below One Kelvin" for Sussex postgraduates, "Techniques below 2 K" for research students attending an Institute of Physics course, "Thermometry below 80 K" and "Attainment of Temperatures below 1 K" for a Harwell course on low temperature technology, given many times over a period of several years.)

I have generally used SI units except where quoting results or tables in other units. Personally, I would prefer a world fully converted to SI, but in a period of transition it is sometimes convenient to be bilingual, particularly when I know that SI acts as a powerful irritant on many of my colleagues.

The first draft of the text was already complete when O. V. Lounasmaa's Experimental Principles and Methods below 1K (Academic Press, 1974) came into my hands. In my view there is plenty of room for both and, indeed, more books on this field which is currently undergoing a period of very rapid development.) There is, of course, a similarity and an overlap between the books, but also a considerable difference of selection, stress and bias, which may be found beneficial by readers of both.

Most of the typing of the early versions was the work of Deborah Evans, and the visual clarity of this final copy is due entirely to Nanette Kingan. I am extremely grateful to them for the painstaking business of converting scruffy sheets of handwriting into order. On matters of physical fact and felicities of expression, this would have been an appreciably lesser work but for the careful reading by Douglas Brewer, and the contributions of Colin Finn and John Plaskett.

Finally I hope, if this volume proves of value, that readers will let me know where improvements could be made. I am entirely responsible for the form and content of these pages and do not wish unknowingly to propagate error.

David Betts

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Chapter 1

FUNDAMENTAL PRINCIPLES OF REFRIGERATION

1.1 PREAMBLE

All processes of refrigeration involve in some way the conversion of a refrigerant material from one form or state to another with different values of thermodynamic properties. The process can be single-shot, in which the temperature is reduced isentropically, isenthalpically or otherwise from T_i to T_f , or continuous in which a thermal load is maintained at a base temperature T_o by the continuous extraction of heat at a rate \dot{Q} . Many examples might be given, but we offer only a representative few. In all cases, the basic idea hinges on the choice of a refrigerant whose entropy, enthalpy or other property depends not only on temperature but also on what we shall term here the manipulable cooling parameter which can be externally varied to cause cooling in the refrigerant. Some of our examples are well-known from standard books on thermodynamics, but we present them here as members of a closely linked family of methods. Some of the methods will be discussed in greater detail in appropriate later chapters.

(a) Isentropic (i. e. reversible adiabatic) expansion

Here we make use of the fact that the entropy of a material depends not only on temperature but also on volume (the manipulable cooling parameter in this example) or pressure. The initial and final states may be anywhere on the p - V - T surface. Taking helium-3 (^3He) as an appropriate example and using published tables,¹ we construct Fig. 1.1 showing a few isochores (i. e. paths of constant volume) in an entropy versus temperature plot including the two-phase region below the critical point. From such a chart we can see at a glance what the consequences of an expansion or compression would be. If the refrigerant material were a perfect monatomic gas,

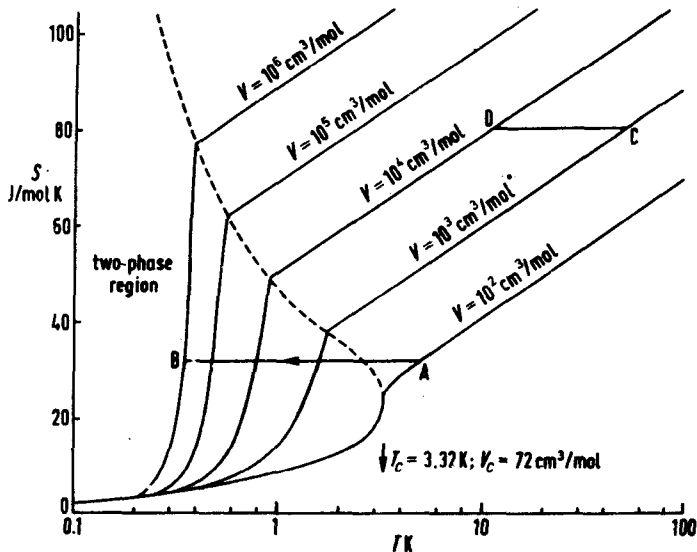


Fig. 1.1 The entropy of ^3He along several isochores (Ref. 1). Isentropic cooling on expansion is represented by a horizontal line joining points on the initial and final isochores. For example, an expansion from point A ($V = 10^2 \text{ cm}^3/\text{mol}$ at 5 K) to point B ($V = 10^6 \text{ cm}^3/\text{mol}$) reduces the temperature to 0.35 K. Since B is within the two-phase region, the final state has liquid in equilibrium with its vapour. In the single-phase gas region (e.g. C to D) equation (1.2) is appropriate.

there would be no phase transition and the entropy would be

$$S = \frac{3}{2}Nk + Nk \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{V}{N} \right] \quad (1.1)$$

so that, for a process in which S is kept constant,

$$T^{\frac{3}{2}}V = \text{constant.} \quad (1.2)$$

A more general thermodynamic formulation appropriate to any system is

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial T}{\partial S} \right)_V \left(\frac{\partial S}{\partial V} \right)_T \quad (1.3)$$

$$= - \frac{T}{C_V} \left(\frac{\partial P}{\partial T} \right)_V \quad (1.4)$$

using standard identities, where C_V is the constant-volume heat capacity

of the sample. This expression is often but not always negative and must in any case approach zero in the limit $T \rightarrow 0$. For an ideal gas with $pV = NkT$ and $C_V = \frac{3}{2}Nk$, equation (1.4) reduces to the form of (1.2) as expected. In general, the integration of equation (1.4) should be treated with care where phase changes are involved.

It would be possible, though inconvenient and inefficient, to incorporate such a process in a continuous cycle, involving either a cyclic sequence of processes, or actual circulation of the material (only really practicable for fluids).

(b) Joule expansion (free expansion)

This is usually described in terms of a gas as the working system. However, in principle, the effect could be produced starting with any single phase or any combination of phases. The process allows an irreversible expansion into a previously evacuated space, the whole volume being rigid (so that $\Delta W = 0$) and insulating (so that $\Delta Q = 0$). It follows from the first law that $\Delta U = \Delta Q - \Delta W = 0$, i. e. the free expansion is at constant internal energy. The resulting temperature change may be obtained graphically or expressed thermodynamically:

$$\left(\frac{\partial T}{\partial V}\right)_U = - \left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T \quad (1.5)$$

$$= - \frac{1}{C_V} \left[T \left(\frac{\partial S}{\partial V}\right)_T - p \right] \quad (1.6)$$

$$= - \frac{1}{C_V} \left[T \left(\frac{\partial p}{\partial T}\right)_V - p \right] \quad (1.7)$$

This is in general not zero (except for a perfect gas), and can be expressed in terms of the equation of state. However, the free expansion is never the basis of practical methods and will not be discussed further here.

(c) Isenthalpic expansion (also called Joule-Thomson or throttling process)

This is widely applied. An idealisation of a single-shot version of it is shown in Fig. 1.2, and it is readily proved that such a process is

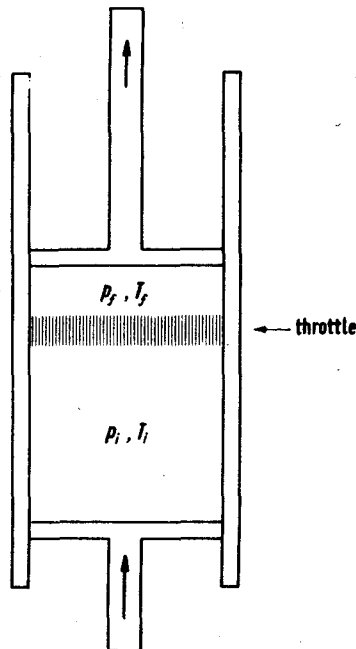


Fig. 1.2 Idealisation of the irreversible throttling process in which enthalpy is conserved. The movements of the two pistons are correlated in such a way that pressures p_i and p_f are maintained constant while fluid is pushed upwards through the throttle. There is a temperature change ($T_f - T_i$).

irreversible and isenthalpic. The starting point may be anywhere on the p - V - T surface, and it is not necessary for the system to be a single phase, although it is frequently so described. In Fig. 1.2 a sample of fluid initially at p_i is expanded through the plug, by a correlated control of the two pistons, being finally at p_f . The possible result of such an operation is shown on Fig. 1.3, an H versus T chart for ^3He (Ref. 2). The resulting cooling is not encouraging unless the transition from p_i to p_f involves a phase change, although the effect can be utilised in heat exchanger design. The temperature change may be expressed thermodynamically ;

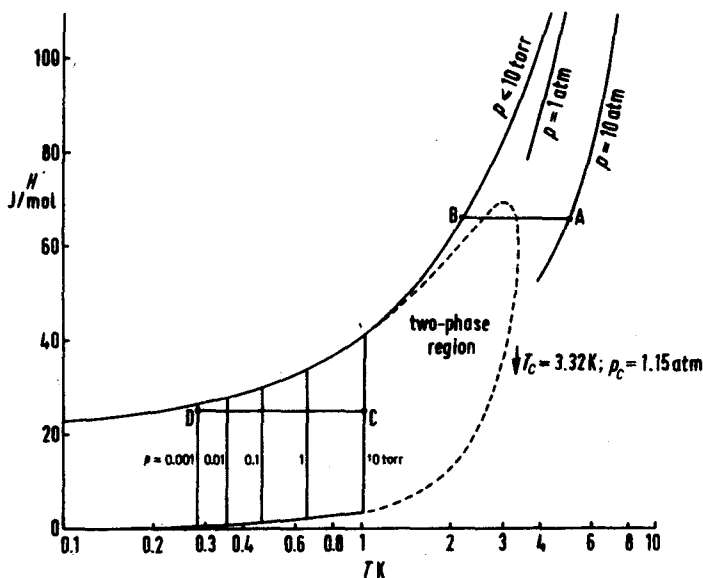


Fig. 1.3 The enthalpy of ^3He along several isobars (Ref. 1). Isentropic cooling (or heating) on reduction of pressure is represented by a horizontal line joining points on the initial and final isobars. For example, a decompression from point A ($p = 10$ atm at 5 K) to point B ($p \leq 10$ torr) reduces the temperature to 2.2 K, and a decompression from point C ($p = 10$ torr at 1.03 K) to point D ($p = 0.001$ torr) reduces the temperature to 0.28 K. (1 torr $\equiv 133.322$ Pa; 1 atm $\equiv 101.325$ kPa).

$$\left(\frac{\partial T}{\partial p}\right)_H = - \left(\frac{\partial T}{\partial H}\right)_p \left(\frac{\partial H}{\partial p}\right)_T \quad (1.8)$$

$$= - \frac{1}{C_p} \left[T \left(\frac{\partial S}{\partial T}\right)_T + V \right] \quad (1.9)$$

$$= + \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_p - V \right] , \quad (1.10)$$

where C_p is the constant-pressure heat capacity of the sample. As for the Joule expansion this is in general not zero except for a perfect gas, and can be positive or negative. Again, the integration of equation (1.10) should be treated with caution where phase changes are involved. We shall

deal in § 2.4 with the practicalities of ³He Joule-Thomson refrigerators.

(d) Evaporation cooling

In practice this is usually a rather non-ideal hybrid affair, in which vapour is drawn from the liquid surface and disposed of in an ill-defined way. The important thing is the latent heat of evaporation. Fig. 1.4 shows a plausible idealisation of a quasi-continuous process, in which a

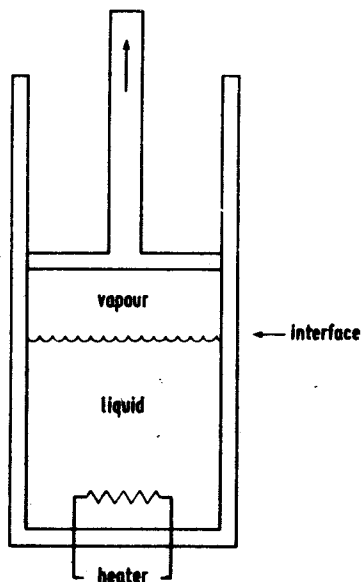


Fig. 1.4 Idealisation of the reversible evaporation process. With the heater switched off, withdrawal of the piston produces cooling by isentropic expansion (see Fig. 1.1). Alternatively, the heating rate can be correlated with the piston withdrawal rate so that the temperature remains constant. This can be seen as a special reversible case of the throttling process (see Fig. 1.2) in which the interface acts as the throttle but maintains a zero pressure difference.

cryostat maintains a constant base temperature T against a steady heat load \dot{Q} . There are two ways of viewing the process. It can be argued that the heater introduces entropy at a rate \dot{Q}/T , so that

$$\frac{\dot{Q}}{T} = h(s_v - s_l), \quad (1.11)$$

where \dot{h} is the molar rate of conversion of liquid to vapour and S_v and S_l are molar entropies of vapour and liquid under the vapour pressure. Alternatively it can be maintained that the heat introduced is enthalpy, since we are dealing with a constant pressure process, so that

$$dH = TdS + Vdp = TdS. \quad (1.12)$$

Thus

$$\dot{Q} = \dot{h}(H_v - H_l). \quad (1.13)$$

Equation (1.13) also shows the close similarity between evaporation cooling and the throttling process discussed in (c) above. A comparison of Figs. 1.2 and 1.4 suggests that the liquid-vapour interface plays the role of throttling valve, which, however, does not have to maintain a finite pressure difference. The heater provides enthalpy, and equation (1.13) simply expresses the conservation of enthalpy. Actually, equations (1.11) and (1.13) are interchangeable, a fact which can be seen by examining the definition of enthalpy;

$$H \equiv U + pV \quad (1.14)$$

$$= N_o \mu + TS, \quad (1.15)$$

where N_o is Avogadro's number and μ the chemical potential. Thus in the liquid

$$H_l = N_o \mu_l + TS_l \quad (1.16)$$

and in the vapour

$$H_v = N_o \mu_v + TS_v. \quad (1.17)$$

Therefore

$$H_v - H_l = N_o (\mu_v - \mu_l) + T(S_v - S_l). \quad (1.18)$$

But provided the vaporisation is reversible (usually assumed), the vapour is always in equilibrium with the liquid. Thus, from the usual condition of equilibrium,

$$\mu_v = \mu_1, \quad (1.19)$$

so that

$$H_v - H_1 = T(S_v - S_1), \quad (1.20)$$

and equations (1.11) and (1.13) are equivalent descriptions of the process.

We shall deal in Chapter 2 with the design and performance of ^3He evaporation cryostats, both quasi-continuous and recirculating and say no more about them here except to note that the lowest achievable temperature for a given heat load is determined solely by the speed of the pumping system.

(e) Adiabatic demagnetisation of a paramagnet

There are no obvious magnetic analogues to the free expansion or throttling processes. However, adiabatic (isentropic) demagnetisation of electronic or nuclear paramagnets is perfectly feasible and indeed until recent years it was the only available technique below about 250 mK. Fig. 1.5

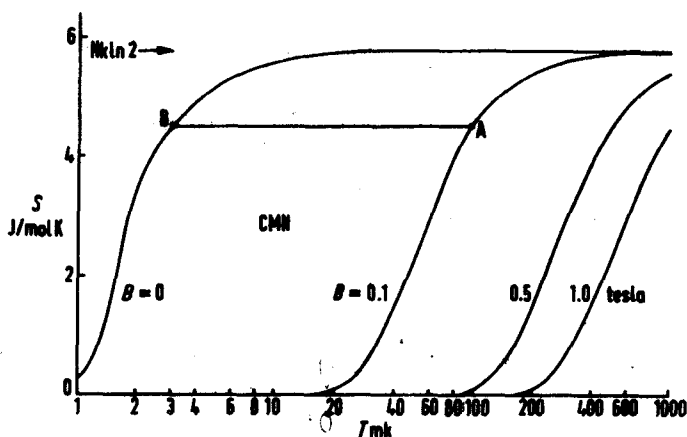


Fig. 1.5 The entropy of cerous magnesium nitrate (CMN) along several lines of constant magnetic field (Ref. 2). Isentropic cooling on reduction of the field is represented by a horizontal line joining points on the initial and final field curves. For example, a demagnetisation from point A ($B = 0.1$ tesla at 100 mK) to point B (zero field) reduces the temperature to 3 mK.