CRYOPHYSICS

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Broadly speaking, the physics of low temperatures is the physics of energy quantization in aggregate matter. Even if it be argued that such generalization might include the processes of liquefaction and solidification, it has to be remembered that many aspects of these, as for instance the law of corresponding states, are based on low temperature measurements. Indeed, towards the end of the nineteenth century, investigations of this nature led to the liquefaction of the "permanent" gases and with it to the approach of absolute zero. Thus, the problems to be solved by low temperature work at that time were mainly of interest to the physico-chemist, and it was from this quarter that the most fundamental contribution to the subject was made. The object of Nernst's work, which ultimately led to the third law of thermodynamics, was to find a reference point for the calculation of chemical equilibria. The absolute zero of temperature was clearly the most suitable condition in which different substances might be compared with each other since, already two hundred years earlier, Amontons had visualized it as an ultimate state of rest. This concept of absolute zero as the end of all kinetic motion remained unchallenged throughout this time and it appeared strange when Nernst concluded that it was the entropy, and not the energy, which vanished at $T = 0$.

While the zero of entropy served Nernst's purpose as a starting point from which to measure specific heats and free energies, its true significance remained hidden at first. The existence of zero point energies which are a direct consequence of the quantum principle could not be understood as long as the classical law of equipartition of energy was believed to

hold. Einstein's application of Planck's formula to the specific heats of solids at low temperatures indicated that quantization of the lattice vibrations was the correct explanation, but many questions remained open. In particular, the limitation of the third law to condensed systems had to be considered as most unsatisfactory. Nernst, in order to avoid the dilemma produced by the finite entropy of an ideal gas at $T = 0$, postulated a hypothetical "gas degeneracy". However, more than twenty years had to elapse before its existence could be demonstrated and physical meaning given to it by quantum statistics and the principle of indeterminacy.

The realization that the phenomena observed at low temperatures were due to energy quantization, shifted the centre of gravity of research from physical chemistry to pure physics. Problems of the validity of the third law and its applicability to "frozen in" systems have become of historical interest and have been replaced by the investigation of entropy changes predicted by it. These, such as the alignment of paramagnetic and nuclear spins, have led to the opening up of new low ranges of temperature. At the same time, they have answered the question of whether the attainment of increasingly lower temperatures can be of interest. Low temperature research is also playing a large part in the investigation of solid state problems through determination of specific heats, electrical and thermal conductivities and through various types of magnetic measurement. Here, too, directly or indirectly, the third law provides the guiding principle. Theory has often been able to predict these quantization phenomena at low temperatures or at least to provide an explanation for them.

It is different with the strange phenomena of superconductivity and superfluidity. Some of their effects were first observed nearly fifty years ago but they would be equally unexpected and almost equally inexplicable if they were discovered to-day. The superfluids provide the most fascinating aspect of low temperature research because they seem

to be completely divorced from any other manifestation of the laws of physics. Confined to the last few degrees above absolute zero, the pattern exhibited by them has as yet offered no link with the behaviour of matter at higher temperatures. While Nernst's theorem does not seem to require the existence of superfluids, it is noteworthy that the appearance of these phenomena is accompanied by a very rapid drop in the entropy. In view of their non-crystalline nature which seems to preclude the establishment of order in co-ordinate space, the superfluids present a unique problem in the statistical interpretation of entropy. It has thus become clear that we are not dealing with extreme cases of normal electrical conduction or of viscosity but that the study of low temperatures is revealing an entirely new aspect of physics. Indeed, the strangeness of the observed phenomena suggests that this new aspect is a fundamental one which has so far been missing in our concepts of condensed matter. Quite possibly the order pattern in velocities, exhibited by the superfluids, presents a new form of aggregation, equal in importance to that of the crystal.

The temperature region where the thermal energy is reduced to the same or to a lower order than the quantum-mechanical zero point energy presents unique physical conditions, both for the handling of problems and for the design of experiments. The contributions to knowledge by those laboratories which have specialized in cryophysical work is not due to particularly ample supplies of refrigerants but to the creation of research schools which think in terms of low temperature physics.

Cryogenics

The production of low temperatures can conveniently be grouped into methods based on gas liquefaction and magnetic methods. The former provide cooling between room temperature and 1°K or somewhat lower, while the magnetic methods are used for obtaining temperatures below 1°K. Liquefaction of air and hydrogen have been developed on an industrial scale by a variety of methods which lie outside the scope of this book. Only a brief account will therefore be given of the basic principles without going into questions of efficiency or liquefier construction. A number of devices for the liquefaction of helium, which still to some extent is a laboratory technique, are, however, described.

1.1 Gas Liquefaction

The component parts of any liquefaction apparatus consist of (a) a compressor, (b) a cooling device and, in the case of a continuous cycle, (c) a heat exchanger in which the incoming gas is cooled by that issuing from the cooling process. The compressor is in most cases a reciprocating engine in which the heat of compression is removed by water cooling.

One obvious cooling device consists of another reciprocating engine in which the compressed gas is allowed to expand adiabatically by doing external work. This engine might be replaced by a turbine, serving the same purpose. A single expansion stroke, in which part of the gas is lost, led to Cailletet's first (accidental) liquefaction of oxygen and has since been employed in a discontinuous method for

helium liquefaction. Let the initial pressure and temperature of the gas in an expansion engine be p_i and T_i and those after expansion be p_f and T_f, then the final temperature is given as

$$T_f = T_i(p_f/p_i)(C_p - C_v)/C_p \qquad (1\text{-}1)$$

where C_p and C_v are the specific heats of the gas at constant pressure and volume.

The other most important cooling device is the expansion of a gas without doing external work, as for instance by passage through a porous plug or through a valve. For small temperature differences this isenthalpic expansion leads to

$$T_f = T_i - [T(\delta v/\delta T)_p - v](p_i - p_f)/C_p \qquad (1\text{-}2)$$

Since for an ideal gas $T(\delta v/\delta T)_p = v$, no change in temperature can be expected but Joule and Thomson (later Lord Kelvin) observed a small cooling when performing the experiment with air, carbon dioxide, oxygen or nitrogen and a heating in hydrogen. The work $W = p_f v_f - p_i v_i$ is done "internally", i.e. against the interaction forces between the molecules and the sign of the differential Joule-Thomson effect (dT/dp) depends on $[T(\delta v/\delta T)_p - v]$ which may be positive (cooling) or negative (heating). Plotting the values for which this quantity is zero against pressure and temperature results in the "inversion curve" which separates the regions of heating and cooling (Fig. 1-1). By dividing P and T through the critical values P_c and T_c, we obtain a reduced diagram which, owing to the law of corresponding states, is in first approximation applicable to all gases. Similar inversion curves can be plotted for the integral Joule-Thomson effect in which the temperature changes are related to large finite drops in pressure.

The cooling obtained with this method is small compared with that achieved by doing external work but in many cases the absence of moving parts at low temperatures is considered ample compensation for the lack in efficiency. A more serious drawback is the need for cooling hydrogen gas to the

temperature of liquid air and helium gas to the temperature
of liquid hydrogen in order to make the Joule-Thomson
coefficient positive. In industrial plant as well as in labora-
tory equipment the two methods are often combined in cycles
in which an initial reduction of temperature through an
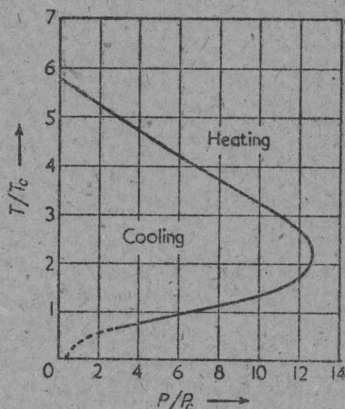expansion engine is followed by Joule-Thomson cooling.

Fig. 1–1. Inversion curve of the Joule-Thomson effect (after M. and
B. Ruhemann.)

A third cooling device, now mainly of historical interest,
is the liquefaction of a vapour by, effectively isothermal,
compression and a subsequent cooling of the liquid by allow-
ing it to boil under reduced pressure. This is the process used
in domestic refrigerators and its range is obviously limited
by the critical temperature at the upper and the triple point
at the lower end. However, by combining a series of cycles
employing different coolants a liquefaction "cascade" can be
operated. Oxygen which boils at 90°K, can thus be liquefied
by precooling with CH_3Cl to 200°K and then with C_2H_4 to
125°K. Since there are no substances with overlapping
liquid regions between liquid air and hydrogen or between
hydrogen and helium, liquefaction of these gases cannot be
achieved by the cascade method but a variation of it has been

used successfully in bridging the gap between the triple point of hydrogen (14°K) and the critical point of helium (5.2°K). At the former temperature helium gas is adsorbed under pressure on charcoal, in the pores of which it is held by capillary condensation (cf. Fig. 1–4, a). When subsequently the pressure over the charcoal is reduced adiabatically, temperatures well below 5.2°K are obtained. The function of the adsorbent is thus effectively an extension of the liquid range above the normal critical temperature.

The use of a heat exchanger greatly increases the efficiency of liquefaction or, as in the case of Joule-Thomson cooling, makes it altogether possible. The gas leaves the cooling device at a lower temperature than that at which it enters and the function of the heat exchanger is to pre-cool the entering warm gas by transferring heat from it to the cold returning gas. Heat exchangers may be of the counterflow or of the capacity (often called regenerator) type. The former, which is more commonly used, consists in its simplest form of two concentric tubes (Fig. 1–2, a). The compressed gas passes through the inner tube into the cooling device and is cooled by the expanded gas returning through the outer tube. Heat is transferred by conduction through the wall of the inner tube. In actual design a large variety of tube profiles and coiling patterns have been employed for which the assessment of efficiency remains semi-empirical. In the capacity exchangers the heat of the incoming gas is transferred to a solid substance which has previously been cooled by the returning gas. The regenerator consists of twin vessels 1 and 2 (Fig. 1–2, b), usually packed with large amounts of thin metal strip, through which the gas flow is alternated. With valves A, B, C, and D open, the entering gas is cooled in 1 while the cold gas coming from the cooling device cools the metal strip in 2. After a while, valves A, B, C, and D are closed and A', B', C' and D' are opened, thereby reversing the functions of 1 and 2. Capacity exchangers are mainly used in large low pressure (turbine) liquefaction plant but they have recently also been incorpo-

rated in a small air liquefier designed by Köhler and
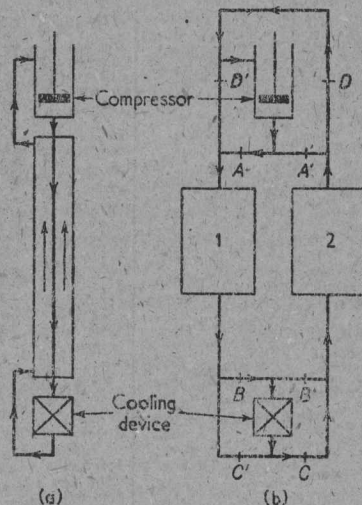Jonkers which operates at a reversal rate of about 1,500
per minute.

Fig. 1-2. Heat exchangers; (a) counterflow, (b) regenerator. (schematic)

Liquid oxygen is an important industrial product and
very large liquefiers using air as raw material and embodying
rectification equipment for the separation of O_2 and N_2 have
been built. Hydrogen liquefaction has been up to now mainly
a laboratory technique but liquefiers with a capacity of 300
litres of liquid per hour have been operated. Joule-Thomson
cooling, using counter-current heat exchangers, is generally
employed because engines operated with hydrogen as a
working substance might lead to accidents. However, a
hydrogen liquefier with a reciprocating engine, but using
helium as working substance, has been successfully operated.
Hydrogen gas at room temperature consists of 75 % ortho
and 25 % para modification while the equilibrium concentra-
tion at the boiling point (20°K) is 100 % para. The ortho-
para conversion is a slow exothermic process, leading to a

large excess evaporation of freshly liquefied hydrogen of normal concentration. Modern liquefiers therefore incorporate a catalyst, charcoal or chrome alumina, at the low temperature end which ensures a high para concentration of the liquid. Because of the low inversion temperature of the Joule-Thomson effect, the hydrogen gas has to be pre-cooled with liquid air or, for reasons of safety, liquid N_2. Interest in hydrogen liquefaction has recently been stimulated by the possibility of separating, by low temperature distillation, the heavy isotope which has slightly different critical data. Liquid hydrogen is further gaining importance for use in bubble chambers (cf. Chapter 8), as neutron moderator and as target in nuclear bombardment. Future uses of liquid hydrogen may include rocket propulsion and magnet cooling for bunched discharges in thermo-nuclear reactions. In connection with the missile development programme, a 6,000 litre transport vessel for liquid hydrogen has been
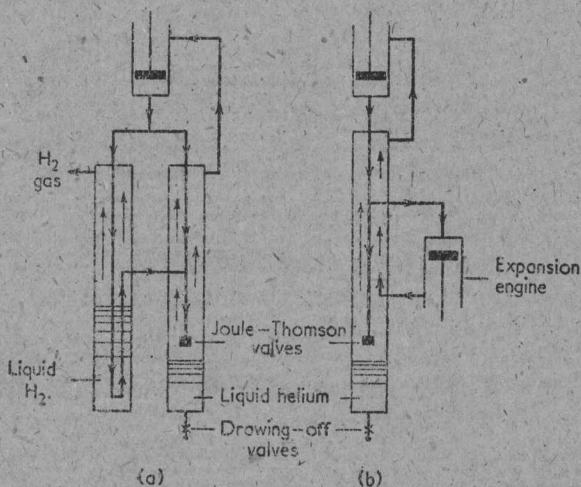

Fig. 1-3. Helium liquefiers; (a) with Joule-Thomson cooling only, (b) with expansion engine. (Schematic; for the sake of clarity the liquid air pre-cooling stage is omitted).

operated. For the same purpose fluorine, which owing to its chemical activity presents particular difficulties, is being liquefied and transported in considerable quantities.

The first helium liquefiers, too, operated by Joule-Thomson cooling and the flow diagram of a typical apparatus of this kind is shown in Fig. 1–3, a. Liquid H_2 is required for pre-cooling. In 1934 Kapitza introduced a helium liquefier embodying a reciprocating expansion engine (Fig. 1–3, b) and this type of machine has since been improved by Collins and is being produced commercially. The lack of a lubricant has been overcome by the use of a hardened nitrided nitralloy as construction material for a close fitting cylinder and piston. These machines have the great advantage not to require liquid H_2 pre-cooling and can even be operated with the warm end at room temperature, although for greater efficiency liquid air is normally used as pre-coolant.

The amount produced by the usual types of helium liquefiers varies from 2 to 20 litres per hour and the liquid is syphoned from the liquefaction apparatus into a Dewar vessel containing the research equipment to be cooled. However, this temperature range is peculiar in that, owing to energy quantization, the specific heats have become very small, and the latent heat of helium is in comparison extremely large. For instance, evaporation of 1 gm of liquid helium is sufficient to cool 0.5 kg of copper from 14°K to 4°K. This means that, when liquid H_2 is available in the laboratory, only small quantities of liquid He are required for most experiments. Making use of these peculiar conditions, Simon and his school have developed the so-called "small scale technique" in which the experiments are carried out in a combined liquefier-cryostat. The experimental equipment is attached to a miniature helium liquefier, the whole unit being arranged in a vacuum case inside a Dewar vessel filled with liquid H_2. The total quantity of liquid helium is sometimes not greater than a few cc. but the small heat influx from the surrounding liquid H_2 will nevertheless permit several hours of experimentation. Joule-Thomson cooling has been used in these small

units, particularly where investigations on liquid helium
itself are undertaken. Besides this, the discontinuous cooling
devices such as desorption (Fig. 1–4, a) and single stroke
expansion (Fig. 1–4, b) are particularly suited for small scale
liquefaction. In the latter method which is distinguished by
its great simplicity, helium gas is compressed into a strong-
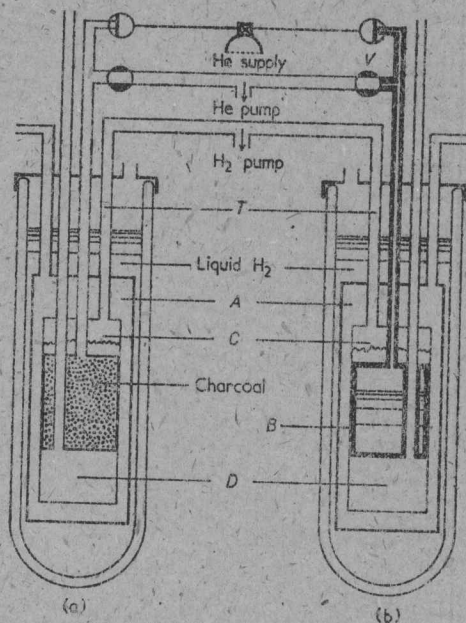walled bomb B which is cooled in liquid hydrogen. Since a

Fig. 1–4. Small scale helium liquefier-cryostats, using: (a) desorption,
(b) single stroke expansion. (Schematic). D, space for experiments.

low starting temperature is desirable, a container C with a
small amount of liquid hydrogen, which can be cooled to
below the triple point by pumping off the vapour through T,
is directly attached to B. After the apparatus has been
cooled to the boiling point of hydrogen, the vacuum case A
is exhausted and the hydrogen in C is pumped off vigorously
so that a temperature of 10°K to 11°K is reached. Then the

valve V is opened and the compressed gas is allowed to
expand into a gas holder, doing external work against
atmospheric pressure. Some gas remains in B and cools
until part of it liquefies, the degree of filling being plotted for
different initial temperatures and pressures in Fig. 1–5. It
may appear strange that, although much gas is lost through
V, filling degrees of 100 % can be obtained. This is explained
by the fact that the compressed helium gas at 10°K has a
much higher density than the liquid at its boiling point.
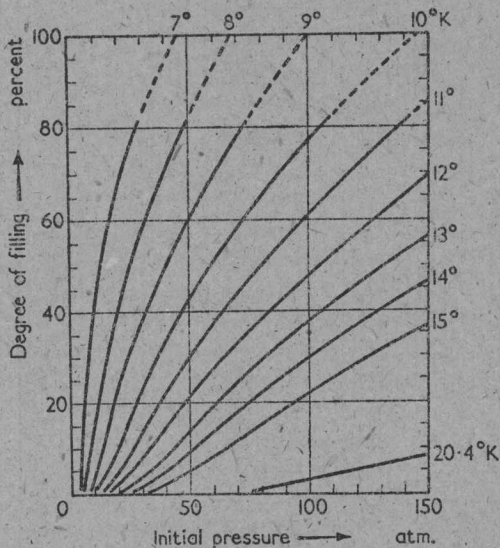Moreover, the heat capacity of the bomb is negligible at these
low temperatures.

Fig. 1–5. Degree of filling for a single stroke expansion liquefier as
function of initial temperatures and pressures. (Pickard and Simon).

The way in which experiments can be carried out in such
a liquefier-cryostat is illustrated in Fig. 1–6 where an
arrangement for measuring the heat conductivity of a rod
shaped specimen is shown. The rod is thermally attached to
the He expansion chamber which serves as a heat sink. Heat

is supplied by a heater and the temperature gradient is measured with the thermometers. The temperature of the heat sink cannot only be varied conveniently in the liquid range of helium by changing the vapour pressure, but also between its critical point and the temperatures of liquid hydrogen. This is done by expanding the gas only partially to the temperature at which observations are to be made.
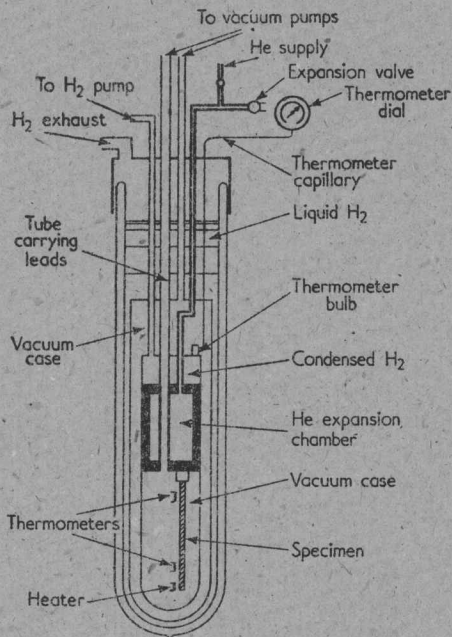

Fig. 1–6. Single stroke expansion liquefier-cryostat for the measurement of heat conductivity between 2°K and 90°K.

Since the bomb now contains more helium than if it were completely filled with liquid, its heat capacity is very large and it acts as a thermostat. Small temperature drifts can be compensated for by gradual expansion.

Future development will probably see a compromise

between small and large scale technique by filling helium, liquified in a large machine, into small and thermally well protected cryostats. In this way the simplicity of large scale work can be combined with the greater versatility of small installations.

Thermostating of cryogenic liquids is obtained by keeping the vapour pressure constant at a pre-set value. Stirring is usually necessary unless the liquid boils vigorously. By placing into the cryostat a resistance thermometer and a heater which are connected by a feed-back system, very high temperature constancy can be achieved. In the case of liquid He II which has a high heat conductivity, the temperature can in this way be kept within less than 10^{-5} deg.

Large Dewar vessels of metal construction are now generally employed for the storage and transport of liquid hydrogen and helium. These follow the well known pattern of storage flasks for liquid air, except that the inner vessel is surrounded with a mantle of liquid air or nitrogen. The vessels are carefully exhausted and then sealed off permanently. The pockets P (Fig. 1-7) contain charcoal which, when cooled, will adsorb any residue of gas remaining in the vacuum spaces. Transfer of cryogenic liquids is effected through double-walled syphons whose inter-space is permanently evacuated.

Litre quantities (at n.t.p.) of the extremely rare isotope He^3 have now become available from nuclear reactions and owing to its lower critical data (cf. Chapter 7.) temperatures down to 0.3°K can be obtained by pumping off the vapour above the liquid. Thanks to the relatively large latent heat, a fraction of a cc. of liquid He^3 is sufficient to cool an apparatus of fairly big heat capacity from 1°K to 0.8°K and to maintain it at this temperature for several hours. For experimental arrangements involving a large heat influx, such as an open container with liquid He^4, Peshkov has designed an ingenious cryostat (Fig. 1-8) in which He^3 is circulated. The He^3 cryostat is surrounded by a bath of liquid He^4 and consists of a boiler B in which liquid He^3 is