

LOW-TEMPERATURE TECHNIQUES

F. DIN AND A. H. COCKETT

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by

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PREFACE

THIS book has been written to provide a source of up-to-date information about the principles and practice of low-temperature techniques. The emphasis throughout has been on the practical aspects of these techniques, which are becoming of increasing importance for many experimental and industrial applications.

Mathematical symbolism and theoretical jargon have been kept to a minimum. There are no references; instead, recommendations are made for further reading. Where exact figures are quoted, e.g. for the triple points, boiling points, etc., of gases, these figures have been selected with care in the belief that they are the best available at the time of writing.

It is hoped that the book will prove of real value to students, laboratory workers and technologists in all scientific and industrial fields.

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CHAPTER 1

GEOGRAPHICAL AND HISTORICAL

Fahrenheit's Ice-Salt Mixture. Causes of Variation in Temperature. Other Refrigerant Mixtures. Academic Research into Low Temperatures.

Meteorological Temperatures

It is said that when the eighteenth-century German scientist Fahrenheit invented his temperature scale he chose the human body temperature to represent one hundred degrees, whilst zero on his scale was the temperature of a mixture of snow and salt which he considered to be the coldest possible. This, however, is difficult to believe. In Germany, and even in England and Holland where Fahrenheit worked, winter temperatures below 0°F are often reached, and one can scarcely credit that Fahrenheit failed to observe this. Further east in Russia and in North America, winter temperatures of 'forty below'—minus 40° is the same temperature on both the Fahrenheit and Celsius scales—are common. It is probable that the coldest temperature anywhere on the earth's surface is reached in the centre of the land mass around the south pole, but as yet there are no well-authenticated records of the temperatures in this region. The coldest place on the surface of the earth is generally considered to be north-eastern Siberia where a winter temperature of -80°F is not uncommon.

The temperature at the surface of the earth varies enormously with the locality. Quite apart from the effect of latitude, proximity to the sea has a considerable effect in tempering extremes of heat and cold. Thus, tropical islands in the Pacific Ocean have remarkably close temperatures at all seasons while places in the centre of the great land masses, such as Asia, have great heat in the summer season and extreme cold in the winter.

The U.S. Armed Forces have developed a portable refrigerated warehouse designed for service in various parts of the world on the basis of a record of extreme temperatures which includes the figures given in Table 1. It is not clear to what extent the figures are

authentic, or whether the temperatures refer to sea level, because, as already stated, lower temperatures than -61°F have certainly been recorded in the Soviet Union.

TABLE 1.—EXTREMES OF TEMPERATURE IN VARIOUS LOCALITIES

<i>Locality</i>	<i>Maximum ° F</i>	<i>Minimum ° F</i>
U.S.A.	134	— 78
Italy	114	4
U.S.S.R.	110	— 61
India	120	— 19
Iraq	123	19
Libya	136	33
Solomon Islands .	97	70

That the temperature of the atmosphere falls with increasing altitude is well known. This is because gases do not absorb radiation, and the atmosphere is not therefore warmed directly by the sun. The air attains its temperature through contact with land or water. When air has been thus warmed, there is a tendency for it to rise by convection, but in doing so it becomes rarified and its pressure falls. Theoretically this fall in pressure takes place under adiabatic conditions since the entire atmosphere of the earth must be regarded as an isolated system. Consequently, according to elementary physical principles, the temperature falls. The reverse conditions apply for winds that have risen to great heights in crossing ice-covered mountains. On descending to the land below, they are compressed and warmed. The 'Chinook' wind of Canada, a westerly wind that crosses the ice-capped Rocky Mountains and descends into the central provinces, is a well-known example.

Temperatures lower than any at the surface of the earth are therefore encountered by modern high-flying aircraft which may have to operate at temperatures as low as -100°F . Flying at these low temperatures introduces special problems, some of which are occasioned by the extreme dryness of the atmosphere under these conditions. To study these problems, aircraft companies have installed huge refrigerated chambers inside which whole experimental aircraft can be investigated.

The theoretical falling-off in temperature with altitude is readily calculable as follows.

Assume that the atmosphere behaves as a perfect gas and obeys the two well-known relationships:

$$\text{For adiabatic expansion } pV^\gamma = \text{constant} \quad (1)$$

$$\text{Perfect gas law } pV = nRT \quad (2)$$

p is the pressure, V the volume, γ the ratio of the specific heats at constant pressure and constant volume, n the number of moles and R the gas constant per mole.

Taking logarithms of these two equations and differentiating:

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0 \quad (3)$$

$$\frac{dp}{p} + \frac{dV}{V} = \frac{dT}{T} \quad (4)$$

Equation (2) can be written:

$$p = \frac{mRT}{MV} = \rho \frac{RT}{M} \quad (5)$$

where m is the mass of air considered, M the molecular weight and ρ the density.

Eliminate $\frac{dV}{V}$ from equations (3) and (4):

$$\frac{dT}{T} = \frac{\gamma - 1}{\gamma} \frac{dp}{p} \quad (6)$$

At height h above the surface of the earth the differential diminution of pressure, $-dp$, with increase of height, dh , is given by:

$$-dp = \rho g dh \quad (7)$$

where g is the acceleration due to gravity, and may be regarded as constant over the range of altitude considered.

Combining equations (5) and (7):

$$-\frac{dp}{p} = \frac{Mg dh}{RT} \quad (8)$$

Combining equations (6) and (8):

$$\frac{dT}{dh} = -\frac{\gamma - 1}{\gamma} \frac{Mg}{R}$$

Putting $g = 981 \text{ cm/sec}^2$; $\gamma = 1.40$; $R = 8.31 \times 10^7 \text{ ergs/mole, } ^\circ\text{C}$;
 $M = 28.9$

$$\begin{aligned} \frac{dT}{dh} &= -9.8 \times 10^{-5} \text{ } ^\circ\text{C/cm} \\ &= -9.8 \text{ } ^\circ\text{C/km} \end{aligned}$$

In actual fact, the rate of decrease of temperature with increasing height is somewhat less than the theoretical figure worked out above. This is due to the condensation of water vapour as the air gets colder which adds the latent heat of vaporization and makes the atmosphere less cold than it otherwise would be.

Refrigerant Mixtures

Returning to Fahrenheit's ice and salt mixture, temperatures lower than 0°F or -17.8°C can be obtained with mixtures of ice and other quite common chemicals. According to well-known principles of physical chemistry, a constant low temperature is reached at the 'eutectic point' where the ice and the other solid are

TABLE 2.—EUTECTIC MIXTURES WITH ICE

<i>Substance</i>	<i>% by Weight of Substance on Anhydrous Basis</i>	<i>Actual Solid Phase with Ice</i>	<i>Eutectic Temperature $^{\circ}\text{C}$</i>
Magnesium sulphate	19.0	$\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$	— 3.9
Zinc sulphate	27.2	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	— 6.55
Sodium thiosulphate	30.0	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	— 11
Ammonium nitrate	41.2	NH_4NO_3	— 17.35
Sodium nitrate	37	NaNO_3	— 18.5
Sodium chloride	22.4	$\text{NaCl} \cdot 2\text{H}_2\text{O}$	— 21.2
Sodium hydroxide	19	$\text{NaOH} \cdot 7\text{H}_2\text{O}$	— 28
Magnesium chloride	21.6	$\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$	— 33.6
Potassium carbonate	39.5	$\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O} (?)$	— 36.5
Ferric chloride	33.1	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	— 55
Calcium chloride	29.8	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	— 55
Zinc chloride	51.0	$\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$	ca. — 62
Potassium hydroxide	ca. 31.5	$\text{KOH} \cdot 4\text{H}_2\text{O}$	ca. — 65
Hydrogen chloride	24.8	$\text{HCl} \cdot 3\text{H}_2\text{O}$	— 86

both in equilibrium with the saturated solution. In general, the more soluble the second substance is in water the lower will be the eutectic temperature, although the formation of solid hydrates often complicates the behaviour of the system. The eutectic temperatures with ice as one of the solid phases, shown in Table 2, are taken from the Landolt-Bornstein tables.

With the aid of freezing mixtures of the type just described, Faraday was able to liquefy some of the more readily condensable

gases. His method was to generate the gases under pressure by heating suitable chemicals in one limb of a sealed stout-walled glass tube bent into the form of an inverted letter V. The empty limb of the tube was immersed in the freezing mixture and the combination of the elevated pressure with the low temperature was sufficient in many cases for the gas to condense in the cold part of the tube as a liquid. In this way he succeeded in liquefying chlorine, sulphur dioxide, hydrogen sulphide, cyanogen, ammonia and other gases.

Thermodynamic Approach to Refrigeration

After Faraday's experiments, attempts were made to liquefy air, hydrogen, methane and other gases by subjecting them to very high pressures, but with no apparent success. That is to say, in no circumstances was it possible to see at the bottom of the apparatus a liquid phase separated by a clearly visible meniscus from a vapour phase above. Hence these gases became known as the 'permanent gases' because it was believed that they could not be liquefied under any circumstances. It was not until after the work of Andrews with carbon dioxide in 1869 that the significance of a low temperature rather than a high pressure was appreciated. Andrews' method was to confine a quantity of carbon dioxide in a calibrated glass tube with mercury. By forcing the mercury into the tube the gas was compressed and its volume correspondingly reduced. Andrews noted the volume and the prevailing pressure at a series of constant temperatures or isotherms. The observations showed quite clearly that there was a well-defined region of pressure, volume and, more particularly, temperature where liquid and vapour phases could exist

TABLE 3.—CRITICAL CONSTANTS OF GASES

Gas	Critical Temperature ° C	Critical Pressure Atmospheres	Critical Density g/cm ³
Ammonia	132.45	111.5	0.235
Carbon dioxide	31.04	72.85	0.4679
Ethylene	9.5	49.98	0.2198
Oxygen	— 118.38	50.14	0.4299
Nitrogen	— 146.95	33.5	0.3110
Hydrogen	— 239.9	12.80	0.03102
Helium	— 267.9	2.26	0.0693

together. In particular, above 31°C a liquid phase never appeared under any conditions of volume and pressure; 31°C is thus the critical temperature of carbon dioxide, and any gas has to be cooled below its critical temperature, which is characteristic of the gas, if it is to be liquefied. The pressure and density, or the specific volume, at the critical point are also characteristic of the gas, and with the temperature they constitute the critical constants. The critical constants of some common gases are given in Table 3. The values have been carefully selected, and represent the best data available at the time of writing.

It will be noticed that as the critical temperature diminishes, the pressure necessary to bring about liquefaction also diminishes.

At low pressures and temperatures well above the critical temperature gases obey the laws of Boyle and Charles, which can be derived theoretically from the kinetic theory of gases on the assumption that the molecules are elastic points without action on each other. Due to a fortuitous compensation of errors, nitrogen is the gas which obeys the perfect gas laws best at normal ambient temperatures and one atmosphere pressure. Very sensitive apparatus is needed to detect the departure from Boyle's law with nitrogen or with air.

At low temperatures and in the critical region, gases show considerable deviations from the perfect gas laws. By allowing for the attractive forces between the molecules, as well as their finite volume, van der Waals derived for the relationship between pressure, volume and temperature of real gases the equation:

$$\left[p + \frac{a}{V^2}\right] [V - b] = RT$$

in which a and b are constants, the latter being equal to approximately four times the volume of the molecules themselves.

Qualitatively, this equation agrees with the results obtained by Andrews for carbon dioxide, and provides, therefore, a theoretical reason for the departure of real gases from the simple ideal laws. These departures are of practical significance in the processes of gas liquefaction as will be seen later.

It is interesting to note that Andrews' work on carbon dioxide was undertaken at a time when the population was increasing rapidly as a result of industrial expansion. The demand for increased food supplies to satisfy the needs of growing urban populations was, therefore, reflected in an increased demand for refrigerated storage

and transport facilities. In Roman times and up to the time of the Industrial Revolution in Great Britain, ice had been used in appreciable quantities for preserving fish and other perishable foods during hot weather. For this purpose it was collected during the winter, often from relatively remote areas, and stored in domestic ice chests for use during warmer weather. In Great Britain it was quite common for ice rooms to be built in a pit in a sheltered part of the garden, using the excavated earth for thermal insulation on the outside. Real progress in food storage was made possible only by the development of the refrigeration industry, based on more accurate knowledge of the low-temperature properties of gases and the availability of improved mechanical equipment.

Once the significance of the critical temperature was appreciated, the liquefaction of the 'permanent gases' readily followed. After Cailletet had observed a thick mist when compressed oxygen at -30°C was suddenly expanded, Pictet liquefied oxygen in quantity in 1877 by the process which bears his name. It is also known as the cascade process because the low temperatures are reached not by a continuous falling-off but in distinct steps. A gas whose critical temperature is above normal ambient temperature, ammonia for instance, can be liquefied by compressing it. Liquid ammonia at normal ambient temperature exerts a vapour pressure of about 7 atm. If, however, the pressure above the liquid is allowed to fall to 1 atm, the liquid ammonia will at once start to boil, and the temperature will fall very rapidly to the normal boiling point at 1 atm, -33°C . This temperature will be low enough to liquefy a second gas by compression, say ethylene, critical temperature 10°C , and by reducing the pressure above liquid ethylene to a few millimetres of mercury a temperature as low as -160°C can be reached, and so on. All gases can be liquefied by the cascade process except three, namely, neon, hydrogen and helium. The critical temperature of neon is -229°C and at this temperature nitrogen is a solid, triple point -210°C , and cannot be circulated in a cascade process. Oxygen has a lower triple point than nitrogen, namely -219°C , but this is still above the critical temperature of neon.

Fortunately, there are other means of producing low temperatures in gases which can be applied to neon, hydrogen and helium. First may be mentioned the effect of forcing a gas under pressure past a constriction of some sort, which may be a partially-opened valve,

a very small orifice or a porous plug of felt, porcelain or similar material. It was observed by Joule and Thomson, later Lord Kelvin, in the late nineteenth century that by such a process gases suffer a temperature change which under the right conditions can be a cooling effect. Linde in Germany and Hampson in England both successfully applied this principle to produce liquid air, and in 1898 Dewar succeeded in liquefying hydrogen by this method. The last of the known gases to be liquefied was helium which yielded to Kamerlingh-Onnes in 1908, also by the use of the Joule-Thomson expansion. The processes by which gases are liquefied will be dealt with in greater detail in the next chapter.

At this stage mention should be made of one other method, Claude's method, of producing the necessary low temperature, in which the compressed gas is made to do external work in a suitable engine. The gas expands under adiabatic conditions and the energy represented by the external work done has to come, therefore, from the gas itself, so that it suffers a considerable drop in temperature.

The Joule-Thomson expansion, expansion with the performance of external work and, to a limited extent, the cascade process, are all used in modern large- and small-scale gas liquefiers.

Academic Research at Low Temperatures

The early pioneers in the low-temperature field were inspired by the natural desire to liquefy all the gases and to determine their fundamental physical properties, such as their melting and boiling points, their densities and so on. The earliest school devoted to these studies was that of Olszewski and Wroblewski at Cracow University in Poland. This school flourished between the year 1880 and the end of the century. Although their apparatus appears extremely crude by modern standards—they had no Dewar vessels—they nevertheless determined the boiling points and critical temperatures of all the then known gases except hydrogen. They were even able to freeze nitrogen, but not oxygen.

The most celebrated of the pioneer schools, however, was that founded by H. Kamerlingh-Onnes at the University of Leiden in Holland in 1895 and which is working at the present day with undiminished vigour. The Cryogenic Laboratory as it was then called—it now bears the name of its founder—was devoted exclusively to studies in the low-temperature field and the reports of its work were published from time to time as 'Communications from the Cryo-

genic Laboratory of the University of Leiden'. Communication No. 1 describes the foundation of the Laboratory by Kamerlingh-Onnes himself, and it appears that his principal interest at the time was to test van der Waals' law of corresponding states. The work soon extended, however, to other fields. Besides measuring the fundamental physical properties of substances at low temperatures, much attention was given to the actual measurement of temperature itself and to pressure and volume measurement as well. Some of the early Leiden Communications carry the general title 'Methods and Apparatus used in the Cryogenic Laboratory' and then go on to describe a new thermometer, manometer, dilatometer, cryostat, etc. In this connection it is interesting to note that this Laboratory became, and still is, a recognized school for the training of scientific glassblowers. As the reputation of the Laboratory grew it was asked to provide the thermodynamic diagrams needed by the refrigeration and air liquefaction industries. This it did by making use largely of the fundamental experimental data reported in its own Communications.

Naturally the Cryogenic Laboratory did not confine itself exclusively to this service work, so to speak. Inevitably after the first liquefaction of helium in 1908 they had an absorbing interest in reaching even lower temperatures. By pumping away the vapour above liquid helium, Onnes was able to reduce the temperature to 0.84° K. Acting on the suggestion of Debye and of Giauque that lower temperatures could be reached by the adiabatic demagnetization of a paramagnetic salt, Onnes' successors, Keesom and de Haas, were able, in common with other schools that had arisen in the low-temperature field, to reach temperatures of only a few thousandths of a degree Kelvin.

The early theoretical work at Leiden was directed towards testing the physical laws that applied at ordinary temperatures at the newly obtainable low temperatures. Thus in 1905, before helium was liquefied, we find Kamerlingh-Onnes discussing the magnetic properties of oxygen and the paramagnetic salts. Tests of the Quantum Theory and the Third Law of Thermodynamics called for measurements of the specific heats of substances and measurements of the electrical resistance of metals at low temperatures.

It was whilst engaged on a study of the electrical resistance of mercury in 1911 that Kamerlingh-Onnes discovered that the resistance became suddenly immeasurably small as the temperature was

reduced below a well-defined figure of 4.15°K . This was the first observation of the phenomenon of superconductivity which has since been one of the principal subjects of low-temperature research. A similar phenomenon connected with liquid helium, superfluidity, has subsequently been discovered, but to this day the precise nature of these phenomena is incompletely understood.

According to the Second Law of Thermodynamics, the absolute zero of temperature is unattainable, since as the zero is approached an infinite amount of work must be performed in pumping away the heat and rejecting it at a higher temperature; unless, of course, the Second Law should prove to be no longer valid at temperatures approaching the absolute zero. Indeed, as Simon and others have frequently pointed out, reducing the temperature from 1°K to 0.001°K is just as great a step as reducing it from 1000°K to 1°K . At these extremely low temperatures, a linear scale of degrees loses significance. A logarithmic scale is much more meaningful.

Before concluding this chapter, which is intended mainly as a brief historical review of pioneer work in the low-temperature field, mention should be made of some of the other schools that have made notable contributions. Eucken founded a low-temperature school in Berlin, about the year 1910, which was continued by his eminent pupil Clusius who is at present working in Zürich. In the United States, pride of place must be given to Giauque and his co-workers of the University of California whose low-temperature calorimetric and vapour-pressure measurements stand in a class of their own. In the attainment of extreme low temperatures, the school of Simon which was started in Breslau and is now continuing its work in Oxford, is pre-eminent.

Another early British school was founded at Cambridge by the Russian physicist Kapitza who had been one of Rutherford's pupils. In 1934 he designed and built the first expansion engine for the liquefaction of helium. Helium liquefiers with expansion engines have been so improved by Collins of the Massachusetts Institute of Technology and the U.S. firm of Arthur D. Little Inc. that they are now available commercially.

It is not possible to list all the modern schools working in low-temperature physics. In practically every physics department of every university in Europe and America there is a low-temperature laboratory. In these laboratories, the attainment of low temperatures is not now an end in itself as it was in the early years, but rather

a means to an end. Modern low-temperature studies are of an advanced theoretical character directed largely towards elucidating the properties of atoms and molecules in the solid state. As the temperature is reduced, the entropy of substances diminishes, that is to say, they assume a progressively more and more ordered state. It thus becomes possible to distinguish between the various modes of vibration that the atoms within the substance can assume and to study them individually. One can begin to understand why some metals become superconducting at low temperatures, why they show specific heat anomalies, why traces of impurities have such an enormous effect on the physical properties and so on.

It is often said of present times that we live in the 'atomic' age. Whatever this may mean, it is certain that low-temperature physics has no small part to play in it.

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CHAPTER 2

PRODUCING LOW TEMPERATURES

Elementary Thermodynamic Principles. Refrigeration by Various Methods. Heat Pumps. Liquefaction of Gases. Adiabatic Demagnetization.

The Principles of Refrigeration

Temperatures below that of the surroundings are produced in a refrigerator, which is simply a heat engine working in reverse. The working of a heat engine may be summarized as follows: a quantity of heat Q_1 is taken in by the engine at a temperature T_1 , above, usually well above, that of the surroundings. A portion of this heat is converted to useful work W by the engine. The remainder of the heat Q_2 which from the First Law of Thermodynamics must amount to $Q_1 - W$, is rejected at the temperature of the surroundings T_2 . The efficiency of a perfect heat engine, i.e. one in which all the operations are thermodynamically reversible, is defined as the ratio of the useful work performed W to the quantity of heat taken in at the high temperature. This is readily shown in textbooks on thermodynamics to be equal to:

$$\text{efficiency} = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} \quad (T_1 > T_2)$$

The temperatures T_1 and T_2 are absolute temperatures.

A refrigeration machine reverses everything. A quantity of heat Q_2 is taken in at the lower temperature T_2 which is not now the temperature of the surroundings but the low temperature in the refrigerator. External work W is done *on* the machine, not by it. This work is converted to heat which is added to the heat taken in at the low temperature. The total quantity of heat Q_1 which equals $W + Q_2$, is rejected at the higher temperature T_1 , which now becomes the temperature of the surroundings. The coefficient of performance of the refrigerator is defined as the ratio of the quantity