

Production and Measurement of Low Temperatures.

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THIRTY years ago Prof. Kamerlingh Onnes, working in Leiden, with the help of Dr. W. H. Keesom and Mr. H. Filippo succeeded in liquefying helium for the first time on July 10, 1908. He¹ has given a graphic description of his experiments, and we shall quote here only a small part of it.

"The surface of the liquid was soon made clearly visible by reflection of light from below, and that unmistakably because it was clearly pierced by two wires of the thermo-element. This was at 7-30 p.m. when the surface had once been seen, it was no more lost sight of. It stood out sharply defined like the edge of a knife against the glass wall."

This article is written to commemorate the production of 'liquid helium', and gives the present position in the low temperature technique.

INTRODUCTION.^{2, 3}

It was Lavoisier, who suggested that if the earth were cooled sufficiently, even the gaseous air above it might take a liquid form. Sir Humphry Davy and his young assistant Faraday found that the gas chlorine could be condensed to a yellow liquid. Ammonia, sulphuretted hydrogen and hydrochloric acid gas also quickly yielded to their experimental skill. By 1823 Faraday had installed at the Royal Institution a liquefaction plant. Solid carbon dioxide was introduced in 1834 by Thilorier. Faraday was quick to turn to advantage the new discoveries; by mixing carbon dioxide snow with ether he obtained a freezing mixture, capable of cooling to -110° C.

Thomas Andrews, the Professor of Chemistry at Belfast, tried to liquefy air, and like the others before him failed, and yet made of his very failure a success. In a Bakerian lecture before the Royal Society he explained that unless the pressure exceeds a certain 'critical pressure' and the temperature is below a certain 'critical temperature' peculiar to the gas we can never hope to liquefy it; cold allied with compression succeeds where one alone fails.

The story then is one of triumph after triumph. Oxygen was liquefied by Olszewski in 1883, and two years later nitrogen and

carbon monoxide. The list of lowest temperatures as they were reached, reads like the records of athletic achievements; in both the next step is always harder to achieve than the one before. A new principle was applied to produce the cooling. If a gas under pressure, below the inversion temperature, is allowed to expand freely through a fine nozzle or if it is allowed to do mechanical work while expanding, it will cool, and may reach a temperature at which it liquefies. Thus we get two methods for liquefying the gases. One employs the Joule-Thomson effect, which allows the gas to expand suddenly and so produce the necessary cooling by the performance of internal work; the Linde and Hampson processes depend upon this principle. The other processes employ the reversible expansion of the gas with the performance of external work; the Claude and Heylandt processes are of this nature. In all these processes the regenerative method is used, the oncoming gas being cooled by that which has already passed through and been reduced in temperature, thus the oncoming gas on expansion reaches a still lower temperature until at last the liquid is produced. By such means, hydrogen was liquefied by Olszewski³⁶ in 1892. Hydrogen is a liquid at -253° C. and it solidifies at -259° C. Helium was liquefied by Kamerlingh Onnes for the first time in 1908. It is a long way from Michael Faraday's comparatively simple experiments to the operation of a modern liquid helium plant. By reducing the pressure over liquid helium, still lower temperatures can be reached; and it was in this way that Keesom succeeded in 1933 in cooling liquid helium to an estimated temperature of about 0.71° K. Liquid helium at present is available for research in such centres as Berkeley, Berlin, Breslau, California, Cambridge, Kharkow, Leiden, Oxford, Toronto and Washington.

Still lower temperatures can be obtained by the method of adiabatic demagnetisation of a paramagnetic salt, due to Debye⁴ and Giauque.⁵ The technique of this method has been developed by Giauque⁶⁻⁹ in California; de Haas¹⁰⁻¹⁴ in Leiden, and by Kürti and Simon¹⁵⁻¹⁸ at Oxford. The method consists in magnetising the

substance in a strong magnetic field and removing the heat so generated by cooling in liquid helium and then thermally isolating it. The magnetising field is then suddenly removed or reduced and the consequent demagnetisation results in further cooling. Using this method de Haas¹⁹ succeeded in obtaining a temperature of 0.005°K .

It is possible by means of observations and an application of gas laws to determine the equation of state for helium, that enables us to establish a temperature scale applicable over a range extending down to about 1.5°K . Below this temperature we are largely dependent on extrapolation. The vapour pressure of liquid helium enables us to reach the temperature 0.71°K ; and the magnetic susceptibilities of certain salts can be used to tell us when such temperatures as 0.05°K are reached.

THERMODYNAMICS APPLIED TO THE LIQUEFACTION OF GASES.²⁰⁻²²

It will be possible for us to liquefy a gas if and only if, we apply a pressure p to the gas which is greater than the critical pressure p_c , at a temperature T which is less than the critical temperature T_c . The critical temperature and the critical pressure is a property of the gas; and their numerical values can be calculated for any gas, if the equation of state for that gas is known. Thus assuming that van der Waals' equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \dots \dots (1)$$

is applicable to the gas, we get the critical temperature

$$T_c = \frac{8}{27} \cdot \frac{a}{bR}$$

and the critical pressure

$$p_c = \frac{1}{27} \cdot \frac{a}{b^2}$$

The following six processes are used in producing cooling and low temperatures.

(1) The solution of salts, acids or gases in water or ice.

(2) Evaporation.

(3) Adiabatic expansion of a gas with the performance of external work.

(4) Throttling of a gas and taking advantage of the Joule-Thomson effect.

(5) Using the heat of adsorption.

(6) Adiabatic demagnetisation.

(1) *Freezing Mixtures*.—If some salts or acids (whose heat of solution is negative

or is less than the amount of heat required to melt the ice mixed with them) are mixed with ice we get freezing mixtures. Table I gives a list of the freezing mixtures commonly employed.

TABLE I.

Quantity of salt per 100 grms. of ice	Approx. temperature of the mixture
10 grms. K_2SO_4	-1.9°C .
30 " KCl	-10.6°C .
25 " NH_4Cl	-15.0°C .
33 " NaCl	-21.2°C .
200 " CaCl_2	-35.0°C .

(2) *Evaporation*.—Latent heat is the amount of heat, we have to supply to a liquid, if the liquid is to be converted into vapour. If the liquid is thermally isolated and allowed to evaporate, the requisite heat for evaporation will be supplied by the liquid itself, and its temperature will be reduced. The space above the liquid will contain a definite amount of the liquid vapour, depending on the vapour pressure of the liquid. If the liquid vapour is carried away by a continuous stream of air,—as is done in the dew point experiment—the partial pressure of the vapour is reduced, more liquid evaporates and the temperature of the liquid is reduced. In certain experiments, the liquid is placed in a vacuum Dewar-flask, and the liquid vapour is continually pumped away, resulting again in the cooling of the liquid. This method is used with liquid helium to obtain still lower temperatures.

(3) *Adiabatic Expansion of a Gas*.—If a gas of mass M , and specific volume v , changes the pressure from p_1 to p_0 (where $p_1 > p_0$) then the external work done is given by

$$M \int_1^0 p dv; \text{ as the expansion is adiabatic the}$$

amount of energy of the gas is reduced by

$$M \int_1^0 p dv. \text{ Let } u \text{ be the energy per unit}$$

mass of the gas, then

$$p dv = -du = -\left(\frac{\partial u}{\partial T}\right)_v dT - \left(\frac{\partial u}{\partial v}\right)_T dv \dots (2)$$

but $(\partial u/\partial T)_v = C_v$ the specific heat at constant volume, and the second law of thermodynamics gives the relation

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p \quad \dots \quad (3)$$

$$\therefore dT = - \frac{T \left(\frac{\partial p}{\partial T}\right)_v}{C_v} dv \quad \dots \quad (4)$$

In the case of a perfect gas this reduces to

$$dT = - T \frac{C_p - C_v}{C_v} \frac{dv}{v} = - T (\gamma - 1) \frac{dv}{v}$$

$$\text{or } \frac{T_0}{T_1} = \left(\frac{v_1}{v_0}\right)^{\gamma-1} \quad \dots \quad (5)$$

This method was first used by Cailletet,²³ to liquefy air, hydrogen, etc. This theory forms the basis of the Claude and Heylandt method of liquefying air.

(4) *The Joule-Thomson Effect.*—The Joule-Thomson effect is the change of temperature produced in a current of gas, when it expands adiabatically, through a porous plug. The effect of the porous plug is to keep the kinetic energy of the gaseous atoms unaltered. Let u be the internal energy, v the volume per gram and i the total amount of heat in the gas. Then

$$\begin{aligned} du + d(pv) &= 0 \\ i = u + pv &= \text{constant} \end{aligned}$$

and

$$dS = \frac{du + pdv}{T}; \quad dS = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp.$$

Eliminating du we get

$$\begin{aligned} \left(\frac{\partial T}{\partial p}\right)_i &= \left[T \left(\frac{\partial v}{\partial T}\right)_p - v \right] \frac{1}{C_p} \\ &= \frac{T^2}{C_p} \frac{\partial}{\partial T} \left(\frac{v}{T}\right)_p \quad \dots \quad (6) \end{aligned}$$

where S is the entropy, C_p is the specific heat at constant pressure, and the suffix i indicates that i remains constant even when the pressure changes. Equation (6) gives the change of temperature produced by the passage through the porous plug and is called the 'Differential' Joule-Thomson effect. If we change the pressure from p_2 to p_1 , keeping i constant, and integrate 6 over this range, we get the 'Integral' Joule-Thomson effect ΔT_i .

$$\Delta T_i = \int_{p_1}^{p_2} \frac{T^2}{C_p} \frac{\partial}{\partial T} \left(\frac{v}{T}\right)_p dp_i \quad \dots \quad (7)$$

It is the integral Joule-Thomson effect which can be experimentally observed.

The differential Joule-Thomson effect can be calculated from the observed integral effect if the rate of variation of the integral effect with respect to pressure and temperature is known. For a given pressure, we have a given temperature, the so-called inversion temperature, at which the Joule-Thomson effect changes its sign. Thus the Joule-Thomson effect tells us that if a gas is allowed to expand, under suitable conditions, it can perform internal work and produce the necessary cooling. Joule-Thomson effect was used by Linde and Hampson to liquefy air; it was also used by Kamerlingh Onnes to liquefy helium.

(5) *Adsorption and Desorption.*²⁴⁻²⁷.—In Simon's process of liquefying helium, helium is allowed to come in contact with an adsorbing substance, kept at the temperature of liquid hydrogen. The adsorbing substance is either charcoal or chabasit (a calcium-aluminium silicate, hydrate). The heat of adsorption of helium is carried away by the liquid hydrogen bath. The system is now thermally isolated, and the adsorbed helium is made to leave the adsorbing material by pumping out the system. This results in a desorption—a negative heat of adsorption, and the system is cooled to a temperature which is below the critical temperature of helium. The expansion of the gas now results in liquefaction.

(6) *Adiabatic Demagnetisation*²⁸⁻³⁰.—Weiss and Piccard³¹ found that nickel is cooled, when quickly demagnetised in the neighbourhood of the Curie point. Debye⁴ and Giauque⁵ suggested that if gadolinium sulphate, which is at the temperature of liquid helium, is demagnetised adiabatically, it may be possible to obtain temperatures below 1° K.

Debye and Giauque calculated and predicted the effect for gadolinium sulphate. Their calculation was based on the following considerations: a magnetisable body contains a great number of small elementary magnets. When such a body is magnetised these magnets are directed in the direction of the field. The part of the entropy belonging to this order is decreased and the process being supposed isentropic, the part of the entropy connected with the statistical movement must necessarily increase. When, on the contrary, the disorder of the elementary magnets is increased by demagnetisation, the part of the entropy connected with magnetisation is increased and the

part belonging to the statistical movement is decreased, so that the body is cooled down.

If we wish to obtain easily seen results the following points require special attention :

(1) the elementary magnets shall not exert a directing influence upon each other (the substance used should not be ferromagnetic); (2) the elementary magnet shall have a moment as large as possible, subject to the restriction 1; (3) at low temperatures the effect will be greatest, as here the part of the entropy belonging to the magnetisation becomes comparable with the other part, while at the same time the order strongly increases.

During the adiabatic demagnetisation the entropy S remains constant, further as the substance is kept in vacuum the pressure p is also constant. The entropy S is thus a function of the temperature T , and the magnetising field H .

$$dS = 0 = \left(\frac{\partial S}{\partial H}\right)_{p,T} dH + \left(\frac{\partial S}{\partial T}\right)_{p,H} dT \dots (8)$$

$$\text{or } dT = - \frac{\left(\frac{\partial S}{\partial H}\right)_{p,T}}{\left(\frac{\partial S}{\partial T}\right)_{p,H}} dH \dots (9)$$

But since the process is reversible, we can write $dS = dQ/T$, where dQ is the quantity of heat added to the substance.

$$dQ = dU + p dV + HVX dH$$

U is the internal energy, V the mol. volume, and X the susceptibility of the material per cm.³

Writing $J = U + pV$ we get

$$dS = \frac{dQ}{T} = \frac{dJ - V dp + HVX dH}{T} \dots (10)$$

and hence

$$\left(\frac{\partial S}{\partial T}\right)_{p,H} = \frac{1}{T} \left(\frac{\partial J}{\partial T}\right)_{p,H} = \frac{C_{p,H}}{T} \dots (11)$$

$$\left(\frac{\partial S}{\partial H}\right)_{p,T} = \frac{1}{T} \left\{ \left(\frac{\partial J}{\partial H}\right)_{p,T} + HVX \right\} \dots (12)$$

This means that C_p the specific heat per mol is also a function of H . As dS is a perfect differential,

$$\frac{\partial^2 S}{\partial T \partial H} = \frac{\partial^2 S}{\partial H \partial T}, \text{ and we get}$$

$$\left(\frac{\partial J}{\partial H}\right)_{p,T} + HVX = TH \left[\frac{\partial}{\partial T} (VX) \right]_{p,H} \dots (13)$$

$$\text{and } \left(\frac{\partial S}{\partial H}\right)_{p,T} = H \left[\frac{\partial}{\partial T} (VX) \right]_{p,H} \dots (14)$$

This leads to

$$dT = - \frac{TH \left[\frac{\partial}{\partial T} (VX) \right]_{p,H}}{C_{p,H}} dH \dots (15)$$

Thus to make dT as large as possible $\frac{\partial}{\partial T} (VX)$ must be as large as possible, and $C_{p,H}$ as small as possible. Giauque found that in the case of gadolinium sulphate, although C_p obeys the Debye's T^3 law upto fairly low temperatures³²; yet at still lower temperatures C_p increases rapidly^{6,7}; and therefore gadolinium sulphate is not the most suitable substance for the magneto-calorific effect.

The substances which obey the law of Curie and Langevin, $\chi = c/T$, even at the lowest temperatures, are more suitable for the magneto-calorific effect. In such substances the magnetic atoms are widely separated from one another so that their mutual interaction is very small.

THE TECHNIQUE OF THE LIQUEFACTION OF GASES.

The low temperatures may be divided into five different groups :

(1) The region of refrigeration and cold storage, upto about -50°C . using NH_3 , SO_2 , etc.

(2) The region of solid CO_2 , and of solid CO_2 mixed with acetone, and other substances to form freezing mixtures.

(3) The region of liquid air upto -200°C .

(4) The region of liquid hydrogen (-252°C .) and liquid helium (-269°C .).

(5) The region of Debye and Giauque of isothermal magnetisation and adiabatic demagnetisation.

In this article we shall describe only 3, 4 and 5. For a description of the methods 1 and 2, please refer to articles like the 'Kältetechnik' by Meissner.³³

THE LIQUEFACTION OF AIR.^{20 22}

Cailletet²³ was the first to liquefy nitrogen, oxygen, air and hydrogen. He allowed them to expand suddenly from a pressure of 200 to 300 atmospheres. The presence of the liquid was manifested in the form of small drops or spray. In practice, however, it is always necessary to use multiple expansion as well as previous cooling.

Carl von Linde³⁴ was able to produce liquid air for the first time on a commercial scale. He used the heat exchangers where

the gas cooled by expansion was made to cool the incoming gas, he also made use of the Joule-Thomson effect to produce the cooling.

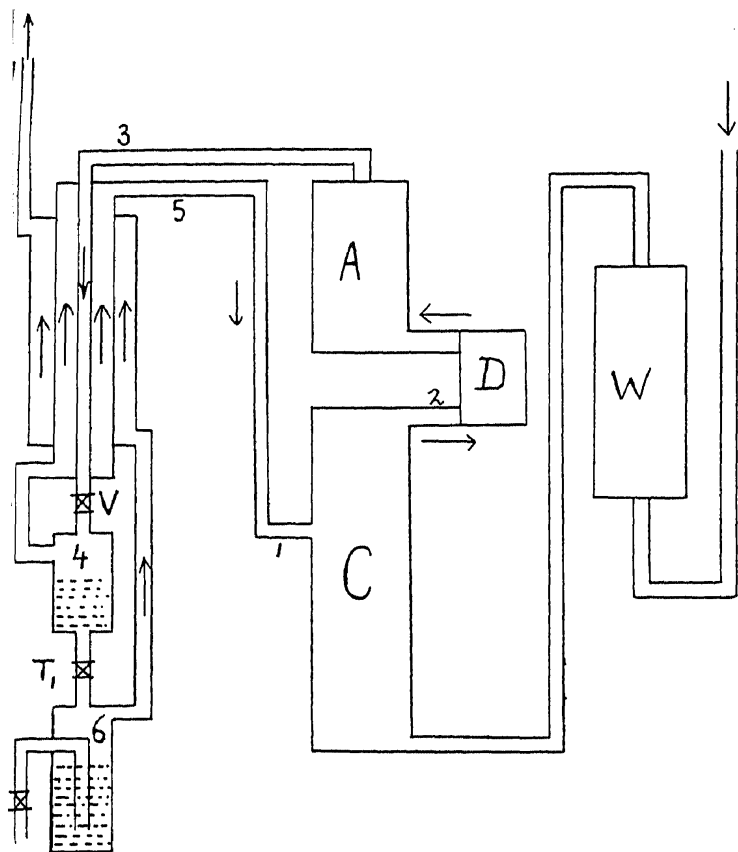


Fig. 1.

Scheme of Linde's liquid air plant.

Linde's Liquid Air-Plant.—The air is sucked in at 0 at atmospheric pressure. It is then purified in W, *i.e.*, the dust particles and carbon dioxide are removed. The purified air goes into the compressor C, where it is compressed to 200 atmospheres. Then it goes through 2, the drying tube D, and the chamber A, which is surrounded by an ammonia freezing mixture, where the compressed air is cooled to -50°C . This cooled, compressed air enters the heat exchanger E through the tube 3. After that it passes through the valve V, which reduces the pressure to 20–50 atmospheres. A large portion of the air which is thus allowed to expand goes back to the compressor through 4, 5 and 1; while a small part of it is liquefied and is allowed to fall in 6 through the tap T_1 . The liquefied air from 6 can be removed by the tap T_2 , while the air above the liquid air, is allowed to pass through the exchanger, and escapes into the atmosphere at 7. Thus after the machine has started, only just sufficient quantity of air to replace

the liquefied air will be sucked up in the machine.

Claude³⁵ and Heylandt Liquid Air-Plant.—Purified air is admitted through 0 into the compressor C, and is compressed to 200 atmospheres. Then it goes through 1 and the drying tube D. At 2 the current of air branches itself, a part of it going through 4 into an engine A, where it performs external work, is expanded to one atmosphere and is cooled; this cooled air goes through 5 into the heat exchanger E_1 . The other branch of the current goes through the exchanger E_1 and is cooled; then it goes through the valve V and expands to 1 atmosphere. Thus a part of the air that escapes through the valve V is liquefied. The not liquefied air goes through the exchanger E_2 and escapes into the atmosphere at 7.

Thus Heylandt has substituted for the ammonia freezing mixture of Linde, a cold current of air, which is cooled by allowing it to do some external work. The efficiency of the machine appears to be 25%, *i.e.*, 25% of the air compressed in the compressor will be liquefied.

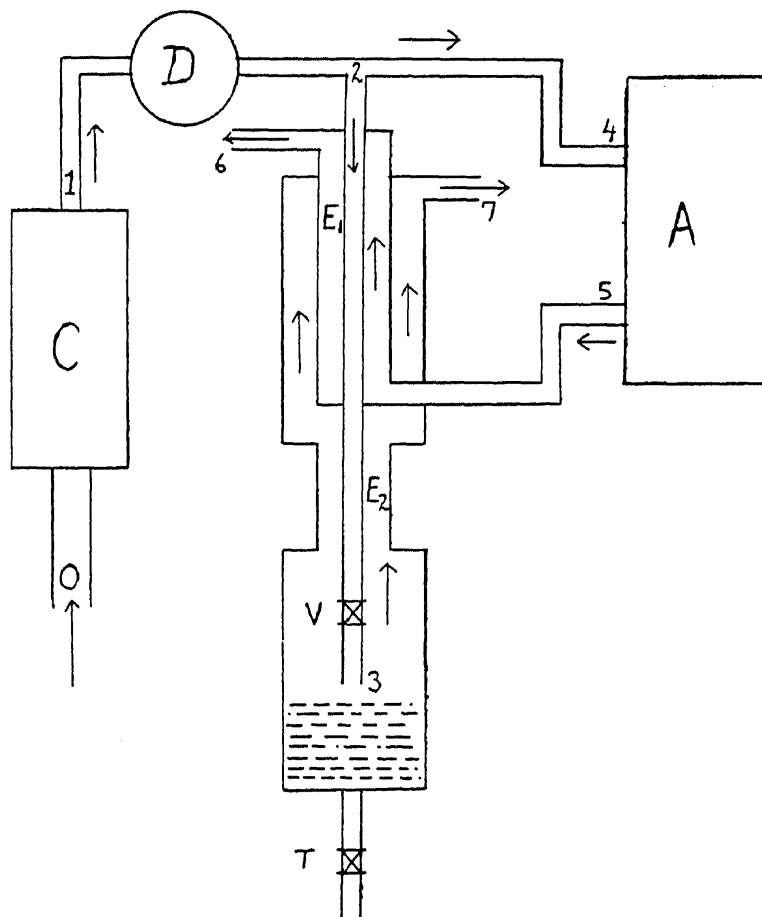


Fig. 2.

Diagram of the Claude and Heylandt liquid air machine.

LIQUEFACTION OF HYDROGEN AND HELIUM.

At present two principal methods are used for cooling and liquefying gases. The first method is based on cooling produced by adiabatic expansion where the expanding gas is cooled by doing external work. Olszewski³⁶ applied this method to the liquefaction of hydrogen. This method has also been used by Simon for liquefying helium³⁷ and hydrogen.³⁸ This method can however be only conveniently applied for obtaining small amounts of liquid hydrogen and helium. Further the method is also complicated by the fact that high pressures are required, and that pre-cooling either with liquid nitrogen or hydrogen boiling at reduced pressure is necessary.

The alternative method of cooling, which was the only method used for the production of liquid hydrogen and helium on a large scale till 1934, consists in allowing the gas which is to be liquefied to expand and do internal work. The phenomena is known as the Joule-Thomson effect and was first employed by Dewar^{39,40} to produce liquid hydrogen. But there is always the danger of explosion when we are working with large quantities of hydrogen. And Dewar's method was improved by Kamerlingh Onnes⁴¹ and Lilienfeld who introduced a large number of safety devices. Meissner^{42,43} has also designed a hydrogen liquefier for the Physikalisch-Technische Reichsanstalt, which works on the same principle. The Joule-Thomson effect was also employed by Kamerlingh Onnes⁴⁴ for the liquefaction of helium. But since helium approaches very closely to the requirements for an ideal gas, the Joule-Thomson effect is very small, and it is only by pre-cooling the helium to the temperature of liquid hydrogen boiling at reduced pressure, that we reach a stage where the magnitude of the effect is sufficient to liquefy the gas. The efficiency of this method is very low. Meissner⁴⁵ estimates that it is only 1% of the efficiency which would be obtained by the use of the adiabatic method.

The great advantage of liquefying gases by making them do direct work on a mechanical system has long been recognised, and this method is now commonly employed for the liquefaction of most gases. Due, however, to the technical difficulty of constructing an expansion engine, which will operate at very low temperatures, this

method could not be easily applied to helium and hydrogen. Kapitza⁴⁶ succeeded in developing an expansion engine which will work continuously at low temperature, and was able to use the more efficient method to liquefy helium.

The liquefier is pre-cooled by liquid nitrogen only, and further cooling of the helium is done in two stages; down to 10° K by means of the expansion engine, and finally down to liquefaction point by using the Joule-Thomson effect. The starting time of the liquefier is 1½ hours, and the output is 2 litres per hour, using 1½ litres of liquid nitrogen to produce 1 litre of liquid helium.

The most important part of the liquefier is the reciprocating engine. The piston of the engine is loosely fitted in the cylinder with a definite clearance, and when the gas is introduced into the cylinder at high pressure, it is allowed to escape freely through the gap between the cylinder and the piston. The piston moves very rapidly on the expanding stroke and the expansion takes place in a fraction of a second, so that the amount of gas escaping through the gap is very small, and does not appreciably affect the efficiency of the machine, which is about 60%. The expansion engine works at the rate of 100 to 120 strokes per minute and treats about 30 cubic metres of helium at N.T.P. per hour. The diameter of the piston is 31 mm. and the stroke between 35 and 50 mm. The inlet and the outlet pressures are 30 and 2.2 atmospheres respectively, while the inlet temperature of the gas is 19° K and the exhaust temperature is 10° K. The mechanism which allows the piston to move quickly on the expanding stroke and do work, and then move slowly, back again, is a hydraulic mechanism. The piston is made of Firth's 'Staybrite' steel and the cylinder of phosphor-bronze.

This liquefier of Kapitza represents a very notable advance in the design of apparatus for the production of liquid hydrogen and liquid helium.

It is possible to obtain still lower temperatures, by allowing liquid helium to boil under reduced pressure. Kamerlingh Onnes used a series of diffusion pumps and obtained in 1921 a temperature of 0.85° K. Keesom⁴⁷ used two Gaede-pumps with a capacity of 670 litres/second, and reached the temperature of 0.71° K in 1933. Table II gives the

temperature and the corresponding vapour pressure of helium.

TABLE II.

Vapour Pressure of Liquid Helium.⁴⁸

Temperature on the Kelvin scale	Pressure in mm. of mercury
4.219	760.0
1.714	10.0
1.237	1.0
1.00	1.5×10^{-1}
0.50	2.5×10^{-5}
0.30	7×10^{-10}
0.10	3×10^{-31}
0.03	6×10^{-103}

In this connection it may be pointed out that the temperature of a body in the interstellar space cannot fall below 2 or 3° K as it always has to be in equilibrium with stellar radiation. Further the vacuum in the interstellar space is of about 10^{-22} cm. Hg. Thus in the direction of low temperature and low density we can surpass the conditions found in nature.

THE METHOD OF ADIABATIC DEMAGNETISATION.

To obtain much lower temperatures than 0.71° K, the method of adiabatic demagnetisation of paramagnetic salts, with the initial temperatures sufficiently low, suggested by Debye and Giauque is used. This method is based on the possibility of diminishing considerably the entropy of some paramagnetic salts by isothermal magnetisation. The subsequent demagnetisation, if carried out adiabatically, then results in a lowering of the temperature. A suitable substance for this method will be one with magnetic dipoles which are relatively free, *i.e.*, one in which the possible orientations of the dipoles all have nearly the same energy. In this case an external magnetic field will be able to produce a big change in the order of the dipoles, thus diminishing the entropy. Such a substance can be recognised by the fact that it follows the Curie-Langevin law very closely, since this law is derived on the assumption of perfectly free elementary magnets. A substance possessing perfectly free dipoles, and therefore following the Curie-Langevin

law at all temperatures cannot exist, because for such a substance $S_{T=0^{\circ}K} \neq 0$, and this, that is, the entropy not vanishing at absolute zero is contradictory to the Nernst's law. To measure these low temperatures we establish a thermodynamic scale of temperature; we shall consider this scale in the next section.

Now we shall give the results of the experiments performed by various people. Here T_i and H_i are the initial temperatures and initial magnetic fields; while T_f and H_f are the final temperatures and the fields; when the value of H_f is not specially mentioned it is nearly zero or negligible. The thermodynamical considerations tell us that

$$T_f = \text{constant} \frac{T_i}{H_i}$$

Kürti and Simon¹⁷ used five different substances and the results they obtained are given in Table III.

TABLE III.

Substance	$T_i^{\circ}K$	H_i in gauss	$T_f^{\circ}K$
FeNH ₄ (SO ₄) ₂ , 12H ₂ O } ironammonium alum	1.23	14,100	0.038
	1.23	2,900	0.187
	2.23	10,300	0.099
MnSO ₄ (NH ₄) ₂ SO ₄ ·6H ₂ O ..	1.23	8,000	0.09
$\frac{1}{2}$ Gd ₂ (SO ₄) ₃ , 8H ₂ O ..	1.15	5,400	0.35
KCr(SO ₄) ₂ , 12H ₂ O ..	1.16	24,600	0.031
1[MnSO ₄ (NH ₄) ₂ SO ₄ ·6H ₂ O]+ 20[MgSO ₄ (NH ₄) ₂ SO ₄ ·6H ₂ O] }	?	?	0.05 to 0.08

Giauque and McDougall⁸ start with 50 grms. of gadolinium sulphate and a field of 8000 gauss; if the starting temperatures are 3.4, 2.0 and 1.5° K the final temperatures are 0.53, 0.34 and 0.25° K respectively.

de Haas^{13,14} and others, using only a few hundred milligrams of the substance obtained the results given in Table IV.

ON THE POSSIBILITY OF OBTAINING STILL LOWER TEMPERATURES.^{49,50}

Heat motion consists in the unordered motion of the smallest particles. The intensity of this irregular motion rises with increasing temperature. There is no upper limit to the intensity of this motion, and

TABLE IV.

Substance	H_i in gauss	H_f	$T_i^\circ \text{K}$	T_f
CeF ₃	27,600	4,500	1.314	0.27
CeF ₃	"	2,200	"	0.19
CeF ₃	"	850	"	0.13
Ds (C ₂ H ₅ SO ₄) ₃ , 9H ₂ O	19,500	200	"	0.12
Ce (C ₂ H ₅ SO ₄) ₃ , 9H ₂ O	27,600	850	"	0.09
K ₂ SO ₄ Cr ₂ (SO ₄) ₃ , 24H ₂ O	19,500	350	"	0.05
Cs ₂ SO ₄ Ti ₂ (SO ₄) ₃ , 24H ₂ O	25,075	1.0	"	0.0055
1 [K ₂ SO ₄ Cr ₂ (SO ₄) ₃ , 24H ₂ O] + } 14.4 [K ₂ SO ₄ Al ₂ (SO ₄) ₃ , 24H ₂ O] }	24,075	"	1.92	0.0044

thus there can be no limit to the high temperatures. But there will be a lower limit to the temperature scale, at the point where the thermal motion stops altogether. This point is called the absolute zero, and although it is impossible to reach it, its position is given with great accuracy as -273.1°C . Nernst's theorem postulates that at absolute zero all substances are in a state of perfect order, which means that it will be impossible to reach the absolute zero of temperature. This, however, does not mean that it will be impossible to reach any finite temperature, be it as small as you like.

To heat a substance means to increase its energy, but still more to increase the internal disorder of its particles. To cool a substance means to diminish its energy, and to increase the internal order of its particles. A gas will liquefy if it is cooled sufficiently and will solidify if it is cooled still further. The solidified gas is a system which is in a state of nearly perfect order. The thermal vibrations of the atoms about their mean positions, are the source of some disorder. On cooling still further this disorder tends to vanish and at these temperatures the disorder, if any, is likely to be due to the interaction forces between the nuclear moments and their surroundings.

Thus if we start with the room temperature and go to lower and lower temperatures, we observe that the gaseous disorder is the first to vanish. This happens when we reach a temperature at which there are no

more gases available. The crystalline disorder due to the forces between the atoms is the next to pass over into a state of order. The only disorder available at this stage appears to be due to the interaction between the nuclear moments and their surroundings. And the method which suggests itself is to try to work with a substance that exhibits nuclear paramagnetism.

The part played by the nuclear paramagnetism in producing still lower temperatures, can be better understood if we consider the time effects in the magnetic cooling method.⁵⁰ Suppose we have a paramagnetic salt, the ions of which carry a magnetic moment μ . We assume that the interaction of these spins with the lattice and with one another is small, so that the spins can be considered as relatively free, but not completely free. These properties are realised in salts of those ions of the iron group or the rare earths which have a multiple S-state as the ground state. In the absence of a magnetic field the spins are distributed at random. If now we switch on a magnetic field isothermally, the spins will be orientated in the direction of the field. The entropy will decrease, which means that the heat of magnetisation must be conducted away or that the magnetic energy $2H\mu$ of the spins must be transferred to the lattice vibrations. According to Heitler, in the case of paramagnetic salts normally employed, the time required for the transfer of this energy is short enough for temperatures above about $0.1 - 0.2^\circ \text{K}$

and magnetic fields higher than about 1500 gauss, but rather long for lower temperatures and lower magnetic fields.

Now we shall discuss the question whether the use of the nuclear spins offers any hope of attaining still lower temperatures.

Consider first the case of a diamagnetic insulating crystal the nuclei of which carry a magnetic moment μ_n . μ_n is about one thousandth that for an electron. This gives rise to a very small interaction between the crystalline field and the nuclei. And as a result the time required for the exchange of energy in the present case is at least 10^{12} times the time of exchange for electrons. This time is of the order of magnitude of 10^6 years. Thus we cannot expect that the use of nuclear spins will lead to any further progress in approaching the absolute zero, if we start with a diamagnetic insulating crystal.

The nuclear spins of the metals, however, present an entirely different case. Here the magnetic energy $2H\mu_n$ can also be transferred to the conduction electrons, and the time required for an exchange of energy between the nuclear spins and the conduction electrons is about one second; this time is short enough to allow a further application of the magnetic cooling method.

MEASUREMENT OF LOW TEMPERATURES.

The conception of absolute temperature is based upon the properties of an ideal gas. This conception was first introduced by Lord Kelvin, and temperatures measured from the absolute zero of temperature are said to be measured on the Kelvin or the thermodynamic scale of temperatures.

Let⁵¹ Q be the quantity of heat given to a system at the temperature $T^\circ\text{C.}$ and the system undergoes a reversible isothermal change, then we can write

$$T = \frac{Q}{Q_{100^\circ\text{C.}} - Q_{0^\circ\text{C.}}} \cdot 100 \quad \dots \quad (16)$$

If further we assume that the equation of state of the gas is given by $pv = A$, where A is a function of the temperature alone, then the gas is known as an Avogadro gas and the temperature T_A on the Avogadro scale is given by

$$T_A = \frac{A}{A_{100^\circ\text{C.}} - A_{0^\circ\text{C.}}} \cdot 100 \quad \dots \quad (17)$$

The Avogadro scale and the Kelvin scale are identical so that $T = T_A$.

But no gas at our disposal is an ideal, or an Avogadro gas which obeys the law $pv = A$, where A is a function of the temperature, at all temperatures. We must therefore use only such gases, as hydrogen and helium. In the case of hydrogen and helium the deviations from the ideal gas relation are very small. The difference between the readings of an ideal gas thermometer and the helium thermometer are no longer negligible when we approach the boiling point of liquid helium. Within the limits of the experimental accuracy, the helium gas thermometer, gives us the temperatures on the Kelvin scale, in all regions of temperature except the liquid helium region.

The constant volume helium thermometer with an initial pressure of 100/76 atmosphere at 0°C. , is called the international helium thermometer. The temperature on this scale is denoted by $T_{i\text{He}}$ (temperature international helium),

$$T_{i\text{He}} = \frac{p}{p_{100^\circ\text{C.}} - p_{0^\circ\text{C.}}} \cdot 100 \quad \dots \quad (18)$$

If we write for the mean coefficient of expansion $\alpha_{i\text{He}}$ then

$$\alpha_{i\text{He}} = \frac{p_{100^\circ\text{C.}} - p_{0^\circ\text{C.}}}{p_{0^\circ\text{C.}} \cdot 100}$$

and the temperature $T_{i\text{He}}$ can be written as

$$T_{i\text{He}} = \frac{1}{\alpha_{i\text{He}}} \cdot \frac{p}{p_{0^\circ\text{C.}}} \quad \dots \quad (19)$$

$\alpha_{i\text{He}} = 0.0036609$, while the corresponding coefficient of expansion⁵² for an ideal gas is $\alpha_A = 0.0036611$.

Thus the general way of determining the absolute temperature consists in measuring the pressure-volume relation of helium, extrapolating it to density zero, and getting the absolute value of T by applying the law for an ideal gas.

In the liquid helium region (0.7°K to 5.0°K) where the temperatures are reached by allowing helium to boil under different pressures; the measurement of the vapour pressures itself will give us the corresponding temperatures. Various empirical formulæ were suggested by Keesom⁵³ and his results are given in Table II.

To measure still lower temperature we construct a thermodynamic scale of temperatures,^{8, 54, 55} on which the magnetic

susceptibilities of certain salts can tell us the temperature reached. The first two laws of thermodynamics yield the equation

$$TdS = dE + pdV - HdI.$$

It is convenient to define the heat content $Q = E + pv - HI$, and since the pressure effects are negligible in the present connection, we shall drop the pv term. For a process at constant entropy $dE = HdI$ and

$$\Delta E = \int_H \left(\frac{\partial I}{\partial H} \right)_S dH$$

also

$$\Delta I = \int \left(\frac{\partial I}{\partial H} \right)_S dH$$

$$Q = E_{H=0} + \int_0^H H \left(\frac{\partial I}{\partial H} \right)_S dH - H \int_0^H \left(\frac{\partial I}{\partial H} \right)_S dH$$

and

$$T = \frac{dE - HdI}{dS} = \left(\frac{\partial Q}{\partial S} \right)_H \quad \dots (20)$$

It is evident from the equation (20) that the measurements of energy, entropy and differential susceptibility determine the temperature on the thermodynamic scale.

According to Kúrti and others,⁵⁵ if T_a is the temperature on some arbitrary scale, if dS is the change of entropy between the temperatures T_a and $T_a + dT_a$, and if dQ is the corresponding change in total heat; then assuming that the rates of variation of S and Q with respect to T_a are known, the temperature T on the absolute scale is given by the formula (21)

$$T = \left(\frac{\partial Q}{\partial T_a} \right)_H / \left(\frac{\partial S}{\partial T_a} \right)_H \quad \dots \quad \dots (21)$$

To determine the variation of Q with respect to T_a we heat the specimen by a constant source of heat like the γ rays, and measure the rate of change of T_a with time; this enables us to calculate $\partial Q / \partial T_a$ to an accuracy of about 10%. The variation of S with respect to T_a can be obtained from the variation of S with respect to H . This last variation is determined by carrying out the adiabatic demagnetisation starting with various fields, and applying the law of Langevin and Brillouin.

In the magnetic method of cooling, we use substances for which $\chi = \text{constant}/T$.

For such paramagnetic substances it is easy to construct a thermometer, using its susceptibility as a measure for the temperature. Simon⁴⁹ measures the susceptibility by bringing a system of two coils around the place where the salt is situated, and sending an alternating current through the primary coil, the induced e.m.f. in the secondary depends on the susceptibility of the salt. The induced e.m.f. is amplified and sent to a galvanometer. The system is so compensated that the deflections on the scale are proportional to the susceptibility and hence $1/T$.

In the method of Giauque and Mc Dougall,⁸⁹ the temperature is measured by putting a coil round the paramagnetic substance. The coil is connected with a ballistic galvanometer. The deflections of the galvanometer are calibrated from the vapour pressure of helium, to as low temperatures as possible. Lower temperatures than this are measured by extrapolation, and Giauque and Mc Dougall believe that the actual temperatures were probably lower than those determined by extrapolation.

de Haas and others¹³ make the paramagnetic substance itself read its own temperature. They do not use a coil and a ballistic galvanometer, but measure the force acting on the substance in a non-homogeneous field, and calculate the susceptibility and the temperatures from this. The substance is suspended in vacuum from one arm of a balance, and this enables them to balance the force exerted upon the substance in a non-homogeneous field. The vacuum enclosure itself is placed in a Dewar flask filled with liquid helium under a reduced pressure and a temperature of 1.3°K . The Dewar flask is placed between the pole pieces of a powerful electromagnet. The force F exerted on the substance is given by $F = MV\chi H \partial H / \partial x$, where M is the Mol number. But as H and $\partial H / \partial x$ are constant in the experiment, and as Curie law is obeyed

$$\text{we get } \frac{T_2}{T_1} = \frac{F_1}{F_2}.$$

For several measurements, e.g., the measurements of specific heat, it is desirable to have at one's disposal a secondary thermometer that indicates quickly. For this purpose the resistance thermometer appears to be very useful. Keesom and Bijl⁵⁶ compared the platinum resistance thermometer with helium thermometer and found

values for the constants in the formula suggested by Henning and Otto.⁵⁷ This formula gives R/R_0 as a function of the temperature.

$$\frac{R}{R_0} = a + (bT + cT^2) D \left(\frac{100}{T} \right) + (d + eT + fT^2) D \left(\frac{230}{T} \right) \quad \dots (22)$$

where D's are the Debye function.

The temperature coefficient of resistance of most metals is practically zero in the liquid helium range. A large number of experiments were made to find out substances which can be used for resistance thermometry in this range. Babbit and Mendelssohn⁵⁸ find that a wire of 5% lead in silver is convenient in the range 7° K to 3° K. According to Keesom and Ende⁵⁹ phosphor-bronze that has not been annealed is extremely suitable in the range 4.2° K to 1° K.

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