

THE GENERATION AND UTILISATION OF COLD.

A GENERAL DISCUSSION.

OPENING REMARKS BY THE PRESIDENT OF THE FARADAY SOCIETY,
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We have met together to discuss the questions of the production and utilisation of cold. This is the thirty-second General Discussion which has been arranged under the auspices of the Faraday Society, often in conjunction with others. On this occasion we have associated with us the British Cold Storage and Ice Association, and as President of the Faraday Society I welcome its members to our meeting.

We had looked forward to having with us Professor Kamerlingh Onnes and Professor J. P. Kuenen of Leyden. On the eve of the completion of the arrangements for the meeting, however, science suffered a great loss by the sudden and unexpected death of Professor Kuenen.

He was well known to many in England, and therefore his loss is the more personal. I remember him when he worked at University College with Sir William Ramsay. He was afterwards appointed to be Professor of Physics at Dundee University, and in these connections he made many friends in England. He was best known scientifically for his work on binary mixtures of liquids and vapours. He was taking an active interest in the preparations for this meeting when his untimely death occurred. Professor Onnes, owing to delicate health, is also prevented from coming.

The duty of representing the Leyden Cryogenic Laboratory has therefore fallen upon Professor Crommelin whom we are delighted and honoured in welcoming here. M. Georges Claude of Paris was also expected, but is unable to be present. He has, however, sent a communication which is in print and this will be read for him.

This is not the place to go into detail in regard to the principles of mechanical refrigeration. They are all based upon the fundamental fact that heat will not flow spontaneously from a cold to a hot body: the transference can be effected only by the performance of mechanical work. The most theoretically perfect way of doing this is by a contrivance which passes the working substance through a reversed Carnot cycle of changes. In such a cycle the heat Q_2 can be removed from a refrigerated material at temperature T_2 , and the amount Q_1 passed out of the system into a condenser at a higher temperature T_1 by the aid of the work, W , required to effect the changes, where

$$Q_1 - Q_2 = W,$$

and

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}.$$

So that the coefficient of performance =

$$\frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}.$$

This value of the coefficient of performance represents, however, the un-attainable limit: in practice, even if the Carnot cycle is aimed at, additional work has to be done owing to frictional and other losses and the coefficient of performance is always reduced thereby.

The Carnot cycle requires that the compression and expansion shall take place in a cylinder in much the same way as in a steam engine; but in the reversed sense. In mechanical refrigeration it is found to be more convenient to replace the cylinder expansion by expansion through a throttle or valve. In this expansion less external work is done by the system than in cylinder expansion, and therefore to effect the same change in other respects there is a greater call for supply of external work from elsewhere. If the pressure and volume change from p_1 and v_1 to p_2 and v_2 in the expansion the work done is only $p_2v_2 - p_1v_1$, whereas in a cylinder expansion it would have been $\int_1^2 p dv$.

The difference is

$$p_2v_2 - p_1v_1 - \int_1^2 p dv = \int_1^2 v dp.$$

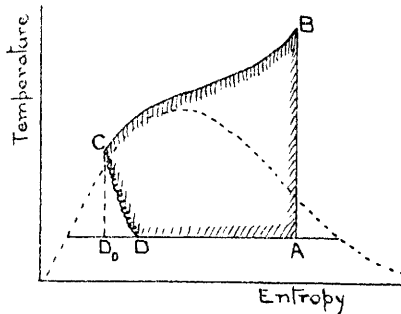


FIG. 1.

I am accustomed to give the name "shirk" to this work that fails to be done; that is,

work actually done + shirk = work that might have been done.

The equation characteristic of the expansion through a throttle is that

$$\begin{aligned} \text{internal energy} + pv &= \text{constant,} \\ \text{or } E + pv &= \text{constant.} \end{aligned}$$

The quantity $E + pv$ is what is usually known in England as Total Heat or Heat Contents. I submit that these names are not satisfactory, because the quantity is not heat in general; and the presence here of a member of the Leyden Laboratory encourages me to press the claims of the name proposed by Kamerlingh Onnes, *viz.*, Enthalpy—a name which I have used for some years. We can denote it by H , which can stand either for capital h (Heat Contents) or for Greek E (Enthalpy) at the option of the reader.

The outline scheme in a CO_2 or NH_3 machine is as seen in the

diagram. The fluid is kept circulating by a compressor pump. The expansion in the throttle is from C to D. The enthalpy does not change in this expansion; neither does it change in any complete cycle. We can write down the following specification of the various changes:—

WITH THROTTLE EXPANSION.

Path.	Change of Enthalpy.	Heat Entry.	Characteristics.
AB	$H_B - H_A$	0	Cylinder compression.
BC	$H_C - H_B$	$H_C - H_B$	Constant pressure cooling.
CD	0	0	Throttle expansion (adiabatic).
DA	$H_A - H_D$	$H_A - H_D$	Refrigerating evaporation.

$$\begin{aligned} \text{Hence, Total work done on system} &= - \text{Total heat entry} \\ &= - H_A + H_D - H_C + H_B \\ &= H_B - H_A \text{ [because } H_C = H_D\text{]}. \end{aligned}$$

The heat removed from the refrigerated material at the low temperature is $H_A - H_D$. Hence the coefficient of performance is—

$$\frac{H_A - H_D}{H_B - H_A}$$

With cylinder expansion the data are:—

WITH CYLINDER EXPANSION.

Path.	Change of Enthalpy.	Heat Entry.	Characteristics.
AB	$H_B - H_A$	0	Cylinder compression (const. entropy).
BC	$H_C - H_B$	$H_C - H_B$	Const. press. cooling.
CD ₀	$H_{D_0} - H_C$	0	Cylinder expansion (const. entropy).
D ₀ A	$H_A - H_{D_0}$	$H_A - H_{D_0} = Q_2$	Refrigerating evaporation.

The coefficient of performance is:—

$$\frac{Q_2}{W} = \frac{H_A - H_{D_0}}{H_B - H_A + H_{D_0} - H_D}$$

Because $H_D > H_{D_0}$ and $Q_2 > W$ this expression is greater than for throttle expansion. The adoption of the latter is governed by convenience. I have given these results to show the importance of enthalpy in dealing with refrigeration problems.

Throttle expansion is adopted for convenience, but it is well known that at sufficiently high temperatures it produces heating instead of cooling. This is so for hydrogen and helium at moderate pressures at ordinary temperatures. In such cases pre-cooling is necessary. In the following account we will suppose that the flow is strictly adiabatic. I wish to emphasise, what is not so generally known, that there is in most cases, and probably in all cases, also a *minimum* temperature at which cooling takes place. Such a point has already been experimentally determined

for CO_2 by Professors Jenkin and Pye.¹ The position found directly lay between -20.7° and -31° C. By plotting their data for volume and temperature I calculated in 1913² that its value must lie at a temperature not much removed from -24° C. when the pressure is about half the critical. This result is remarkable, not only owing to its bearing upon the possible use of a throttle at low temperatures but also because it shows that *liquid* CO_2 is, in this region, behaving very nearly as a perfect gas—its volume being nearly proportional to the absolute temperature.

Moreover, I had previously shown³ that all the well-known equations of state concur in indicating that such points should exist. The conclusions to be derived from the various equations are that at any one pressure there are two inversion temperatures if any at all; but that above a certain pressure heating in passing through a throttle is the universal rule at all temperatures. These results are shown in Fig. 2 on which

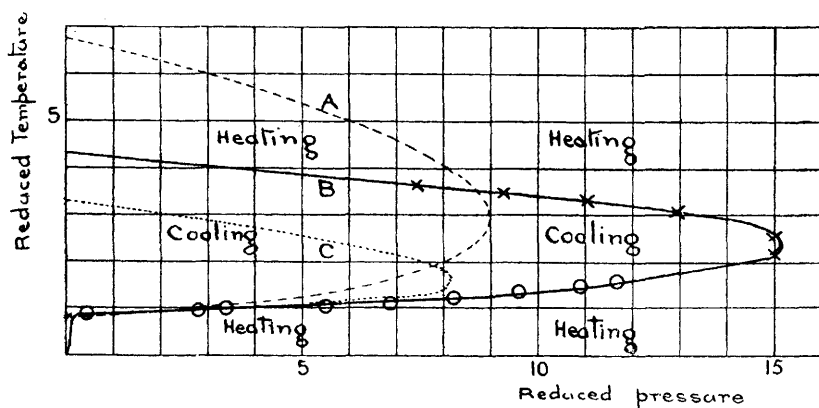


FIG. 2.

- Curve A. van der Waals.
 „ B. Dieterici (modified).
 „ C. Clausius.
 × × × Inversion points for Nitrogen } from experiment.
 o o o „ „ „ CO_2

the ordinates are reduced temperatures and the abscissæ are reduced pressures. The curves shown represent the boundary between the heating and cooling regions on various assumptions and from experiment. The change of pressure in going through the throttle is supposed to be small. Curve A is according to van der Waals' equation of state. It would indicate that for a pressure greater than nine times the critical the gas would undergo heating at all temperatures; also that for a reduced pressure of 5 (for example) the gas would cool *only* if the temperature lay between 5.4 and 1.3 times the critical. It does not appear that any substance follows van der Waals' equation however.

Curve C is, according to Clausius' equation,

$$\left(a + \frac{3}{\gamma\beta^2}\right)(3\beta - 1) = 8\gamma.$$

¹ *Phil. Trans.*, 1913, A, No. 499.

² *Proc. Roy. Soc.*, A, Vol. LXXXIX., 377.

³ *Phil. Mag.*, April, 1906, June, 1910.

where α , β , γ are the reduced pressure, volume and temperature respectively. Curve B is, according to Dieterici's form of equation, modified as regards the power of γ in the index as follows:—

$$\alpha = \frac{\gamma}{2\beta - 1} \exp. \left[2 \left(1 - \frac{1}{\gamma^n \beta} \right) \right].$$

where n is taken as $5/3$. On the same curve are shown inversion points for nitrogen (crosses) and for carbon dioxide (small circles) obtained from Amagat's data of $p_1 v_1 T$ for these gases by making use of the fact that at an inversion temperature (at which heating changes to cooling or *vice versa*) $T \frac{\partial v}{\partial T} - v = 0$. These experimental values lie *almost precisely on the curve calculated from Dieterici's equation with its modified index*. The cooling and heating regions for these real cases are labelled in the diagram. These results can be trusted for points above the critical point, but for lower temperatures and high pressures, Dieterici's equation is not valid.

It will be perfectly clear from the above that no such law as the inverse square temperature law for the cooling coefficient can possibly be valid in general. The true law may change sign twice or not at all.

These facts may not have any importance in connection with food refrigeration, because the working substances selected will always be such as at ordinary temperatures are either below or at least in the neighbourhood of their critical temperatures; but they do impose a limit to the lowest temperature attainable by throttle expansion.

A further word of explanation may be useful. The fall of temperature in throttle expansion is to be reckoned between any two points (one on each side of the throttle) at which the velocity of flow is small. In the throttle valve itself very high velocities may be reached, and since a considerable amount of energy is then present as kinetic energy the temperature may fall *in the throttle* below the final temperature. Ordinary hydrodynamics shows that if there were no friction in the gas the quantity $-\int v dp$ would be transformed into kinetic energy, ultimately being re-transformed as the passage gets wider and the kinetic energy disappears. In the actual fluid, friction is never absent, and is continually generating heat at the expense of the kinetic energy; and the temperature *even in the narrows* never falls as low as it otherwise would. There may be condensation into the liquid or even the solid phase in the narrows, but unless the liquid or solid can be trapped it will pass on with the current as a mist or sleet, gradually melting by the friction it experiences until in the wider part of the passage it will have a temperature greater or less than at start as indicated in the above considerations and shown in Fig. 2.