PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Thermal Properties of Carbonic Acid at Low Temperatures

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Phil. Trans. R. Soc. Lond. A 1914 **213**, 67-117
doi: 10.1098/rsta.1914.0003

III. *The Thermal Properties of Carbonic Acid at Low Temperatures.*

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Received January 27,—Read February 27, 1913.

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Published separately, July 23, 1913.

Part I.—Object, Scope, and Theory of Experiments.

The experiments described in the following paper were originally undertaken to determine the Latent Heat of Liquid CO_2 and the Specific Heats of the liquid and of the gas at temperatures below $-30°$ C., which is the lowest temperature for which Mollier has calculated them, and also to check Mollier's Entropy-Temperature diagram by direct experiment, as it appeared likely that the calculated results might be appreciably wrong near the limits of their range. The results of the first experiments confirmed this expectation, and it became apparent at the same time that Mollier's $\theta\phi$ diagram could not be modified to agree with the experimental results without some further data. The investigation was therefore extended so as to include the measurement of all the quantities required for the construction *de novo* of a $\theta\phi$ diagram for saturated gas at low temperatures. Finally, by Sir Alfred Ewing's suggestion, the range of the experiments was further extended to higher temperatures, to enable the diagram to be constructed nearly to the critical point.

The experiments made to carry out this programme were:—

1. The determination of the Pressure-Temperature Curve for Saturated Vapour;
2. Three series of heat measurements, called Series I., II., and III., to determine the Latent Heat L, the Total Heat I of the liquid, and the Specific Heat of the gas;
3. A series of throttling experiments, called Series IV., to determine the Joule-Thomson effect for liquid CO_2;
4. A series of direct volumetric measurements, called Series V., to determine the Dilatation and Elasticity of liquid CO_2.

The experiments also supply data from which may be calculated: Specific Volume of saturated vapour (or its reciprocal, the Density); relative Densities of liquid CO_2 at saturation pressures; Specific Heat of liquid CO_2 either at constant pressure or at saturation pressure.

The pressure-temperature curve has been often observed during the last 50 years; the specific volume of saturated vapour and the specific heat of the liquid at saturation pressure have not been observed before below $-25°$ C.; the latent heat, the specific heat of the gas, and the dilatation and elasticity of the liquid have not been observed before below 0° C. The total heat of the liquid, the specific heat of the liquid at constant pressure, and the Joule-Thomson effect have never been observed before. The latent heat has often been calculated, but the specific volume of the saturated vapour, on which the calculations are based, has not been observed below $-25°$ C., and only once below 0° C., so that all calculations below $-25°$ C. are based on extrapolations.

From the results of these six sets of experiments all* the data were calculated for constructing the $\theta\phi$ diagram from +20° C. to −50° C. The diagram is shown in fig. 12, p. 79, and some of the results are given in Table IX.

The experiments were carried out in the Engineering Laboratory at Oxford with a vapour-compression freezing machine, presented to the Laboratory by Brasenose College. In addition to the usual parts the apparatus includes a pair of suspended flasks by which the rate of flow of the CO_2 round the circuit can be measured. The following additional apparatus was made for these experiments:—Two electrically heated calorimeters, one of which always replaced the refrigerating tank of the freezing machine; several thermo-junctions for measuring the temperatures of the calorimeters and of the CO_2 at various points in the circuit; a graduated glass capillary tube, with regulating valves, for measuring the changes of volume of liquid CO_2 under varying pressures and temperatures in Series V. experiments; and a special throttle-valve for Series IV.

The gas used was commercial CO_2, supplied by Messrs. Barrett and Elers, Limited, of London, who have kindly informed the authors how it is made. Coke is burnt in a furnace and the products of combustion, after being washed with hot and cold water in scrubbers filled with fragments of limestone to eliminate any SO_2, are passed through absorbing towers filled with coke over which a stream of potash lye flows which absorbs the CO_2. The enriched lye is then heated in iron boilers and the CO_2, driven off by the heat, is compressed in compound pumps into the steel flasks in which it is sold. It is dried by passing over calcium chloride between the first and second stage of compression. The gas made in this way is said by the makers to contain no impurities, except possibly $\frac{1}{4}$ per cent. to $\frac{1}{2}$ per cent. of air and traces of SO_2. These traces of SO_2 were probably eliminated with the moisture in the special drying appliances used in these experiments, so that the only impurity left was air.

To estimate the amount of air present the gas was analysed in a modified form of HEMPEL'S apparatus specially arranged for this test. About 100 c.c. of gas was measured over mercury in a burette and then passed into the potash absorption bulb. The residue of undissolved gas (air) was then drawn back into a small burette and measured over potash solution. The apparatus was arranged so that the test could be repeated as often as desired while the residue accumulated in the small burette. In this way a sufficient quantity could be analysed to allow of an accurate determination of the small amount of air. The amount of air found was only 0·11 per cent. by volume (·073 per cent. by weight). ANDREWS,† in his classical experiments, never was able to reduce the air in the gas he used to less than $\frac{1}{500}$ to $\frac{1}{1000}$. The

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* This is not strictly accurate. In working out Series V. the density of liquid CO_2 at one temperature is needed. BEHN'S result has been used. Any possible error in this has no appreciable effect on the result. With this exception every quantity needed has been measured.

† 'Phil. Trans.,' 1869, p. 581.

presence of this small amount of air has introduced a small error into the pressure-temperature curve, but does not appreciably affect the results of any of the other experiments.

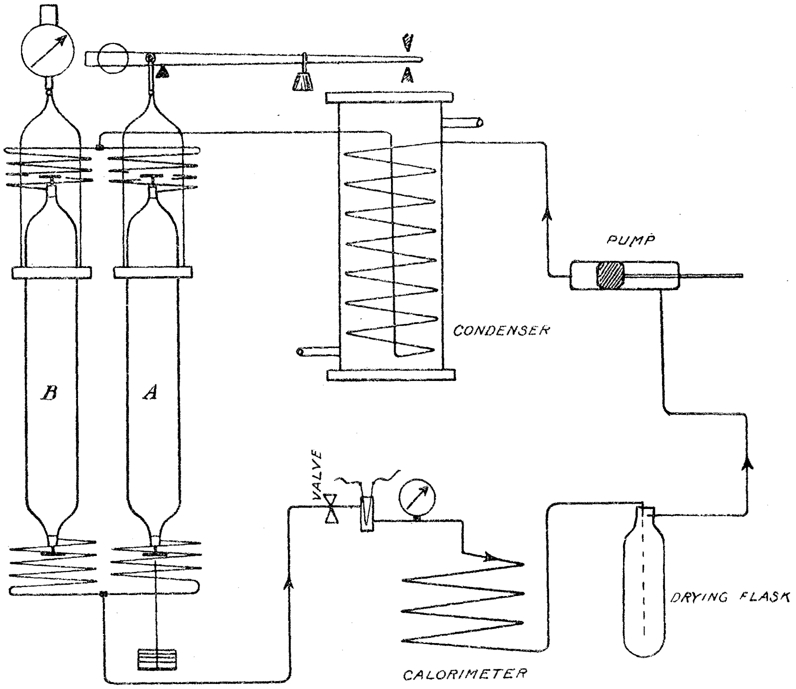

Fig. 1.

The general arrangement of the apparatus connected for normal working is shown diagrammatically in fig. 1. The gas enters the pump at pressure p_2 and is compressed to a higher pressure p_1. It is then condensed in the condenser at the corresponding saturation temperature θ_1. From the condenser it flows as liquid through the weighing flasks to the throttle valve on the calorimeter. In passing the throttle valve the pressure falls to p_2, some of the liquid evaporates and the temperature falls to θ_2. The mixture of liquid and gas then enters the calorimeter, where the rest of the liquid evaporates, taking up heat at the constant temperature θ_2. From the calorimeter the gas passes back to the pump. In order to make sure that all the liquid has evaporated, the gas is warmed (superheated) a few degrees above θ_2 before it leaves the calorimeter. The approximate $\theta\phi$ diagram* for this cycle is shown in fig. 2.

The line AB represents the expansion of the liquid through the throttle valve from $p_1\theta_1$ to $p_2\theta_2$. AB is a line of constant total heat I. The line BE represents the evaporation of the liquid at constant pressure p_2 and temperature θ_2. The line EC represents the small amount of superheating from θ_2 to θ_3 at constant pressure p_2. The line CD represents the adiabatic compression in the pump from p_2 to p_1. The

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* *Cf.* EWING (4), p. 80.

line DFA represents the cooling and condensation in the condenser, both at constant pressure p_1.

The pressure-temperature curve was determined with the apparatus working in this way : A pressure gauge was connected to the pipe immediately after the throttle valve and a thermo-junction inserted at the same place, as shown in fig. 1. The gas is always saturated at this point so that the temperature is unaffected by radiation or conduction along the pipes. By varying the adjustment of the throttle valve a series of readings of corresponding pressures and temperatures was obtained; a summary of the observations is given in Table I. The observations were plotted and a smooth curve drawn through them. Figures taken from the smooth curve are given in Table IX. The smooth curve is copied in fig. 18, p. 95, for comparison with previous observations.

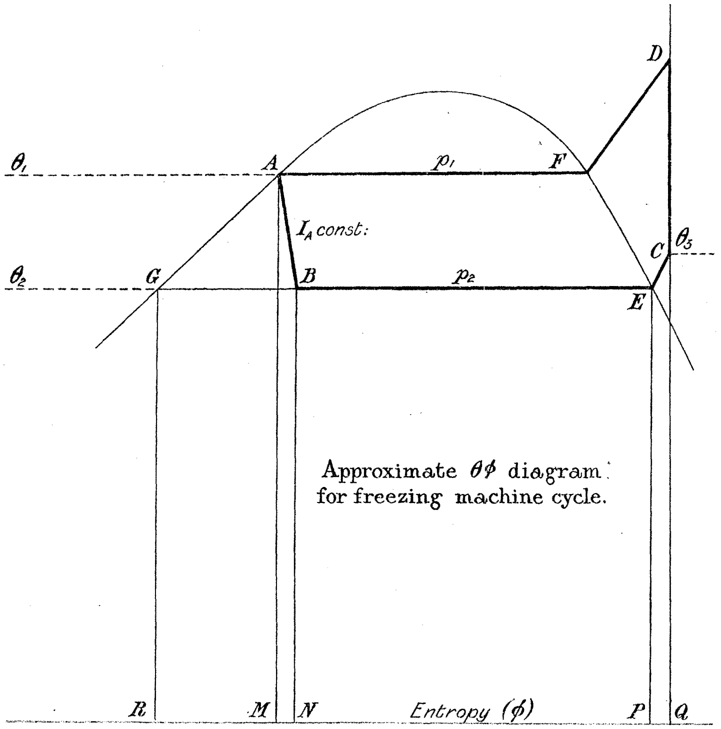

Fig. 2.

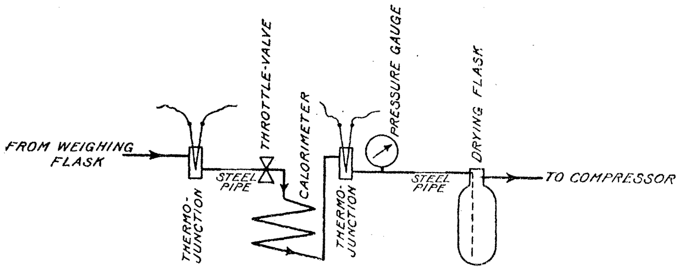

Fig. 3.

Series I. measurements were also made with the apparatus working in the normal way described above, two thermo-junctions and a pressure gauge being connected as shown in fig. 3. In this series the principal quantities measured were the rate of flow of CO_2 and the electrical power supplied to the calorimeter to balance the refrigeration. From these data the refrigeration, *i.e.*, the heat absorbed per lb., represented by the area NBECQ (fig. 2) was calculated. This is the heat required to evaporate the liquid part of the CO_2 and to superheat it all from θ_2 to θ_3, the heat used in superheating being represented by the area PECQ. A series of experiments was made with different values of θ_2. A summary of the observations is given in Table II.; the results are also given in column α, Table VI.

Experiments were not made at temperatures above 20° C. owing to the increasing difficulties of manipulation. At the higher temperatures the weighing flask had to be heated to keep the pressure above the evaporation pressure. At the same time its capacity fell off rapidly owing to the great expansion of the liquid. The condenser and pump had to be run at correspondingly higher temperatures and great care exercised lest the condenser and flasks got over-full of the expanded liquid.

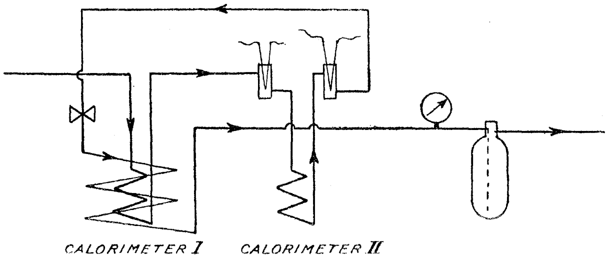

Fig. 4.

Series II.—For this series the normal arrangement of the apparatus was slightly modified, as shown in fig. 4. The liquid CO_2, before reaching the throttle valve, was led first through the second coil in calorimeter I., so that its temperature was reduced to any required temperature θ_x, and then through calorimeter II., in which it was warmed again at constant pressure to any desired temperature θ_y. The quantities measured were the rate of flow, the rise of temperature of the liquid, $\theta_y - \theta_x$, and the electric power supplied to calorimeter II. From these data the change of total heat I of the liquid at constant pressure for the range θ_x to θ_y was calculated. Two sets of experiments were made, one at 700 lbs. per sq. in. pressure and one at 900 lbs. per sq. in. pressure. A summary of the observations is given in Table III. The observations were plotted and smooth curves drawn through them. Figures taken from the smooth curves are given in Table VII. This series of experiments does not determine the absolute values of I, but only differences; the zero of the I scale was determined later, see p. 80. The slope of the I curve is the specific heat of the liquid at constant pressure. Values of the specific heat deduced from the slope of the curves are given in Table VII.

Series III.—For this series the normal arrangement of the apparatus was again slightly modified, as is shown in fig. 5, by inserting calorimeter II. between calorimeter I. and the pump. The gas leaving calorimeter I. at a temperature θ_3 was warmed to any desired extent in calorimeter II. The quantities measured in this series were the rate of flow of CO_2, the rise of temperature of the gas in calorimeter II., and the electrical power supplied to calorimeter II. From these data the specific heat of the gas at constant pressure was calculated. A series of measurements was made with different values of θ_2. The results are shown in fig. 6, where the specific heat of the gas near the limit curve* is plotted against the pressure.

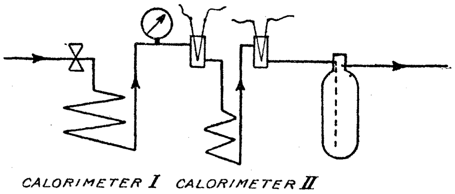

Fig. 5.

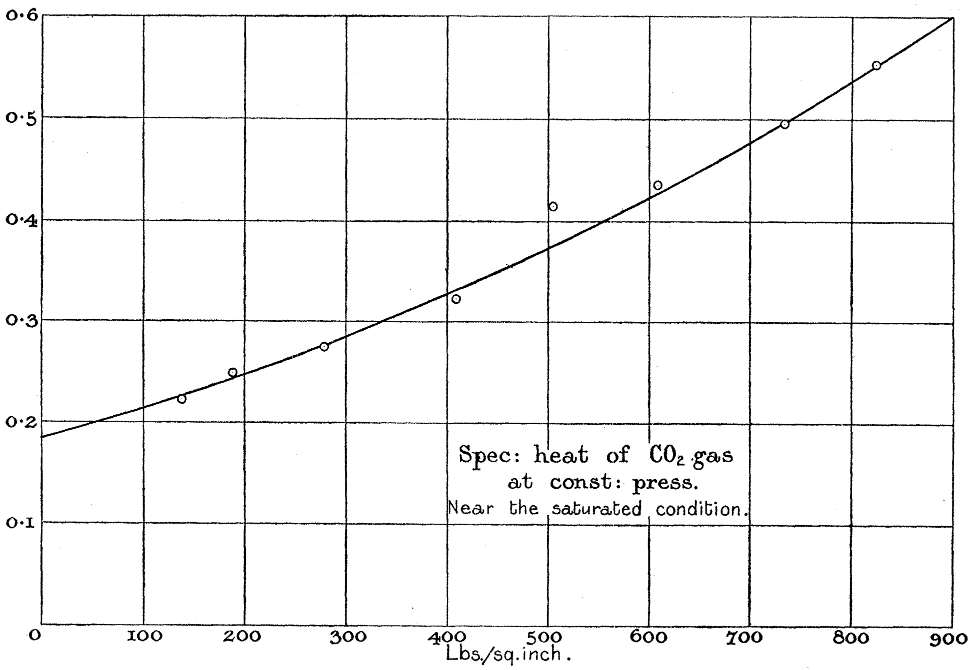

Fig. 6.

Combining the results of Series I., II., and III., an approximate value of the latent heat may now be calculated. If we neglect the complications introduced by the changes of volume of liquid CO_2 (or what is equivalent, if we assume, as a first approximation, that the limit curve coincides with the constant-pressure curves) then the difference of total heat I_2-I_1 from θ_2 to θ_1 is represented in fig. 2, p. 71, by the area RGAM.

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* The limit curve is the boundary of the area on the diagram representing saturated vapour, separating it on the one side from the area representing liquid and on the other from the area representing superheated gas. The two sides of the curve are called the "liquid-limit curve" and the "gas-limit curve"; they meet at the critical point.

Also, by a well-known property of constant-pressure lines,

$$\text{Area RGBN} = \text{RGAM}$$
$$= \text{I}_2 - \text{I}_1,$$

which can be read off the I curves.

Taking any experiment of Series I., we have

Area BQ, given by Series I. (column α, Table VI.);
,, EQ, which may be calculated from the specific heat of the gas obtained by Series III. (column γ, Table VI.);
,, GN $= \text{I}_2 - \text{I}_1$, read off the I curves obtained by Series II. (column δ, Table VI.).

Whence the latent heat, $\text{L} = \text{BQ} - \text{EQ} + \text{GN}$, may be found.

On the same assumptions an approximate $\theta\phi$ diagram may be constructed. Starting at the zero-point on the $\theta\phi$ diagram ($\theta = 273°$ C. abs., $\phi = 0$) plot, step by step, the constant-pressure line corresponding to the curve of I, remembering that on the $\theta\phi$ diagram the area under each element of the curve is equal to the corresponding difference of I; this is quickly done since the curve is almost straight. Since we are neglecting changes of volume of the liquid, this curve will coincide with the liquid limit curve (as it practically does in the Steam diagram). To obtain the gas-limit curve, mark off the values of L/θ for various temperatures, starting at the liquid-limit curve and measuring to the right; joining up the points

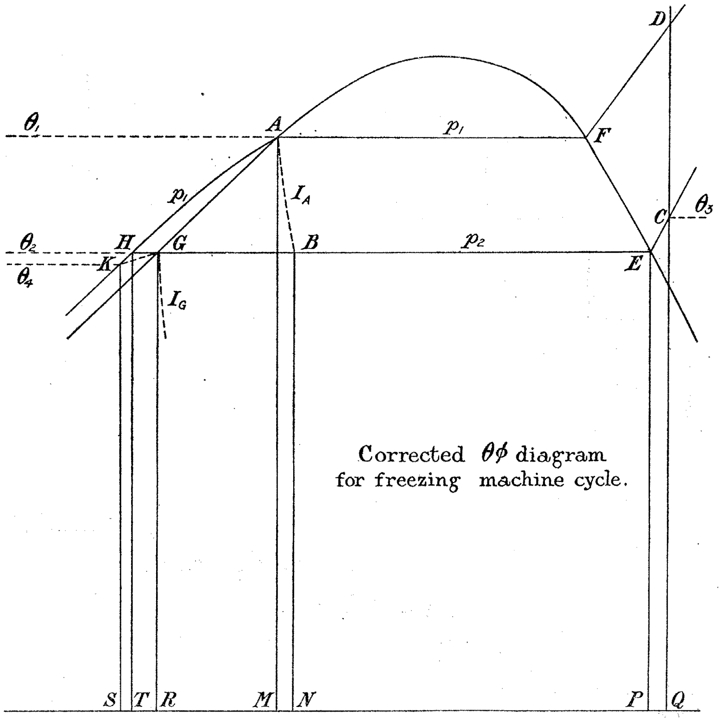

Fig. 7.

so found we have the gas-limit curve. The diagram might be completed by adding the I lines, &c., but it will be convenient to consider first the modifications required to allow for the changes of volume of the liquid CO_2 which have so far been neglected.

Fig. 7 represents the same diagram as fig. 2 with the addition of some lines to show the effects of the dilatation and elasticity of the liquid.

Let AHK be the constant-pressure line through A, in the liquid area,
Let GA represent the limit curve as before,
Let GK be the constant I line through G, meeting AHK in K.

The heating of the liquid CO_2 in Series II. experiments is now represented by the line KA, instead of by GA.

The true value of L is found as follows:—

$L = GN + BQ - EQ$ as before; also BQ and EQ are given, as before, by Series I. and III. experiments, but GN is no longer $I_2 - I_1$. We now have

$$\begin{aligned} GN &= I_B - I_G, \\ &= I_A - I_K, \text{ since AB and GK are constant I lines,} \\ &= (I_A - I_H) + (I_H - I_K), \\ &= (I_1 - I_2) + (I_2 - I_4), \text{ using suffixes to refer to the temperatures } \theta_1,\ \theta_2, \text{ and } \theta_4. \end{aligned}$$

$I_1 - I_2$ is read off the I curve as before, but $I_2 - I_4$ can only be read off the curve when θ_4 is known. The quantity $I_2 - I_4$ may be regarded as a small correction to be applied to the approximate value of L to allow for the elasticity and dilatation of the liquid.

Series IV. experiments were made to determine the difference of temperature $\theta_2 - \theta_4$ between H and K, *i.e.*, the Joule-Thomson effect for the pressure drop $p_1 - p_2$. It was observed directly by measuring the change of temperature as the liquid passed through a throttle valve. The arrangement of the apparatus is shown in fig. 8.

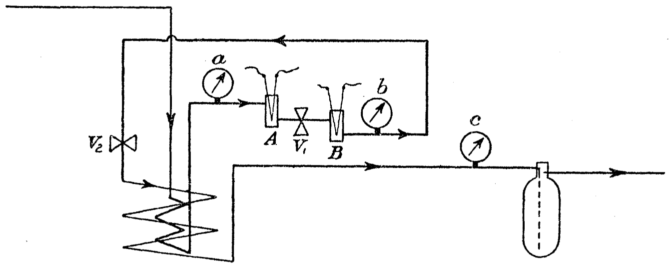

Fig. 8.

A summary of the observations is given in Table V. The observations are plotted in fig. 9 and a smooth curve drawn through them. The values of $I_2 - I_4$ calculated from this curve for each of Series I. experiments are given in column δ of Table VI., and the corrected values of L in the last column. These values of L were plotted and values taken from the smooth curve are given in column 5 of Table IX.

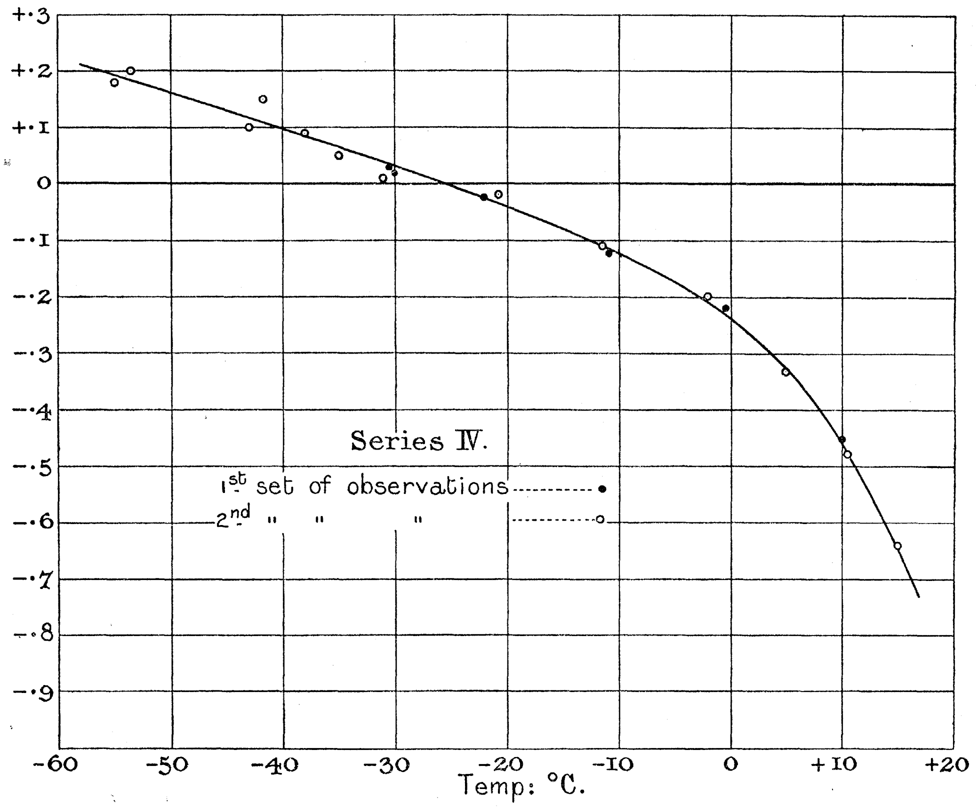

Fig. 9.

If we proceed now to the construction of the true $\theta\phi$ diagram a further difficulty is met with. If a constant-pressure curve is drawn as before, using the values of I already obtained, the result is the curve KA. The difficulty is to draw the true limit curve GA, which was previously assumed to coincide with KA. The authors have been unable to devise any direct experiment to fix the position of the limit curve relatively to the constant-pressure curve KA, and an indirect method had to be used. The fundamental thermodynamic equations give the well-known equation*

$$\left(\frac{d\phi}{dp}\right)_\theta = -\left(\frac{dv}{d\theta}\right)_p.$$

Let H, fig. 7, be the point $p_1\theta_2$; then

$$\mathrm{HG} = \delta\phi = \int_{p_1}^{p_2}\left(\frac{dv}{d\theta}\right)_p dp.$$

Thus the distance $\delta\phi$ between the limit curve and the constant-pressure curve can

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* *Cf.* PRESTON'S 'Theory of Heat,' p. 740, 2nd edition.

be calculated from the temperature coefficient of the liquid. This coefficient* does not appear to have been determined below 0° C., so the experiments called Series V. were undertaken to measure it. AMAGAT'S (5) results give a few values above 0° C.

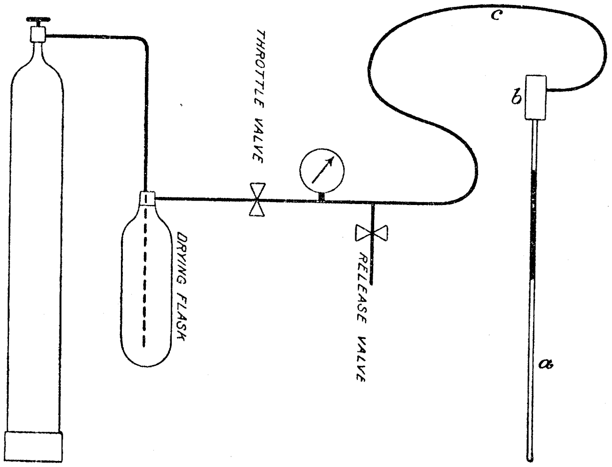

Fig. 10.

Series V.—The general arrangement of the apparatus is shown in fig. 10. A capillary glass tube, closed at the bottom, was partly filled with liquid CO_2; on the top rested a mercury indicator. The upper end of the tube was connected through a valve to a flask of CO_2 gas at high pressure. A release valve was also connected. By adjusting these two valves any desired pressure could be obtained in the glass tube. The glass tube was placed upright in the calorimeter, so that it could be kept at any desired temperature, while the volume of the liquid CO_2 was read directly by noting its length in the glass tube as shown by the position of the mercury indicator.

A series of measurements of volume were made at different temperatures and pressures. The results are plotted in fig. 11, with pressure and volume as co-ordinates. The slope of the curves is the elasticity $(dv/dp)_\theta$, and the distance between the curves divided by the temperature difference is the dilatation $(dv/d\theta)_p$.

To calculate $\delta\phi$, however, it is not necessary to evaluate these functions, for the area between any two adjacent curves at temperatures θ_1 and θ_2 is

$$(\theta_1-\theta_2)\int\left(\frac{dv}{d\theta}\right)_p dp.$$

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* The specific volume of the liquid at low temperatures for points on the limit curve is known. This enables the rate of change of volume with temperature, along the limit curve, to be calculated, but what is required is $(dv/d\theta)_p$, which is equal to

$$dv/d\theta + (dv/dp)_\theta\, dp/d\theta,$$

where $dv/d\theta$ and $dp/d\theta$ are taken along the limit curve.

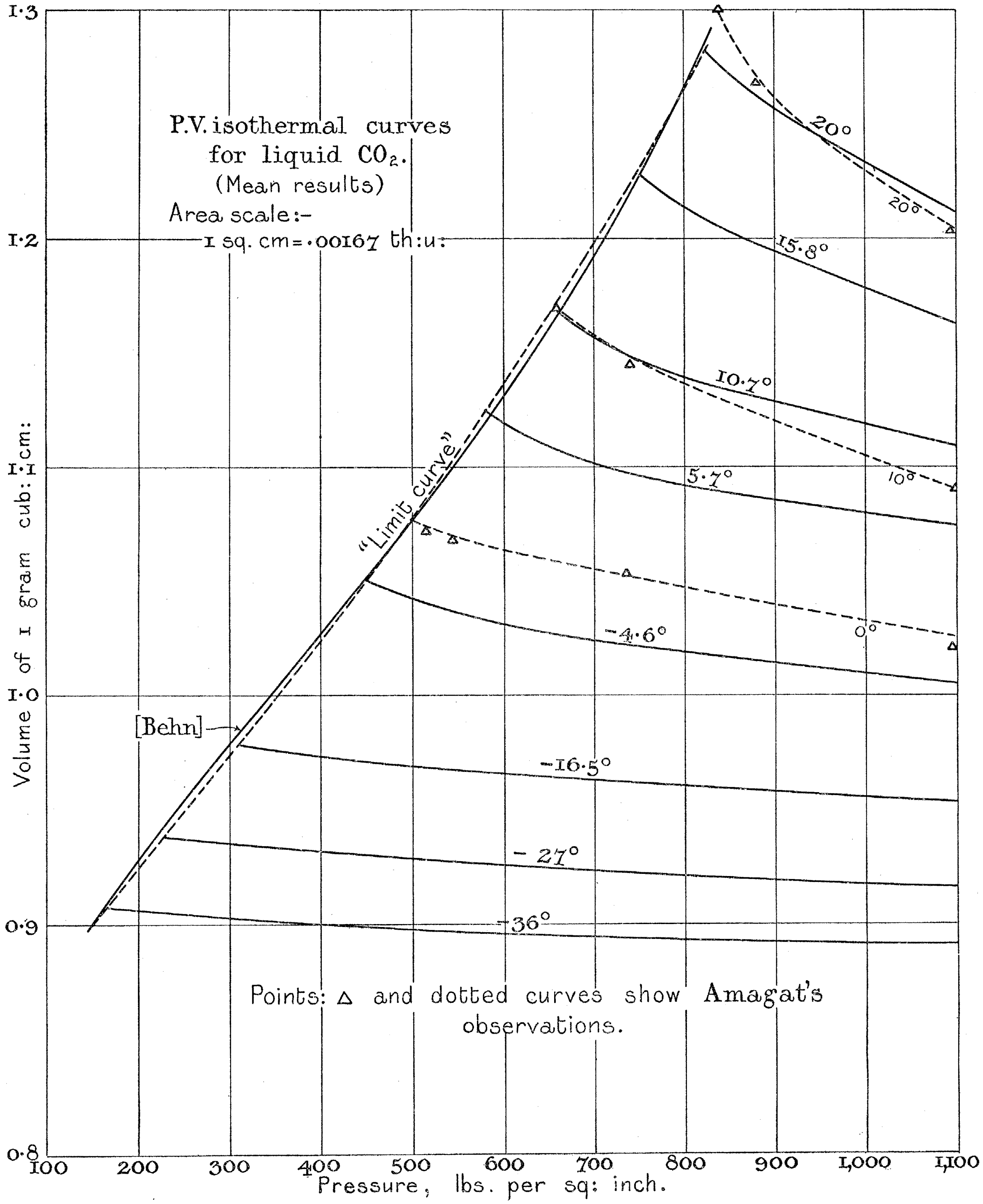

Fig. 11.

If the area between the θ_1 and θ_2 curves is bounded at the side by the ordinates at pressures p_1 and p_2, then the area is

$$(\theta_1 - \theta_2) \int_{p_1}^{p_2} \left(\frac{dv}{d\theta}\right)_p dp,$$

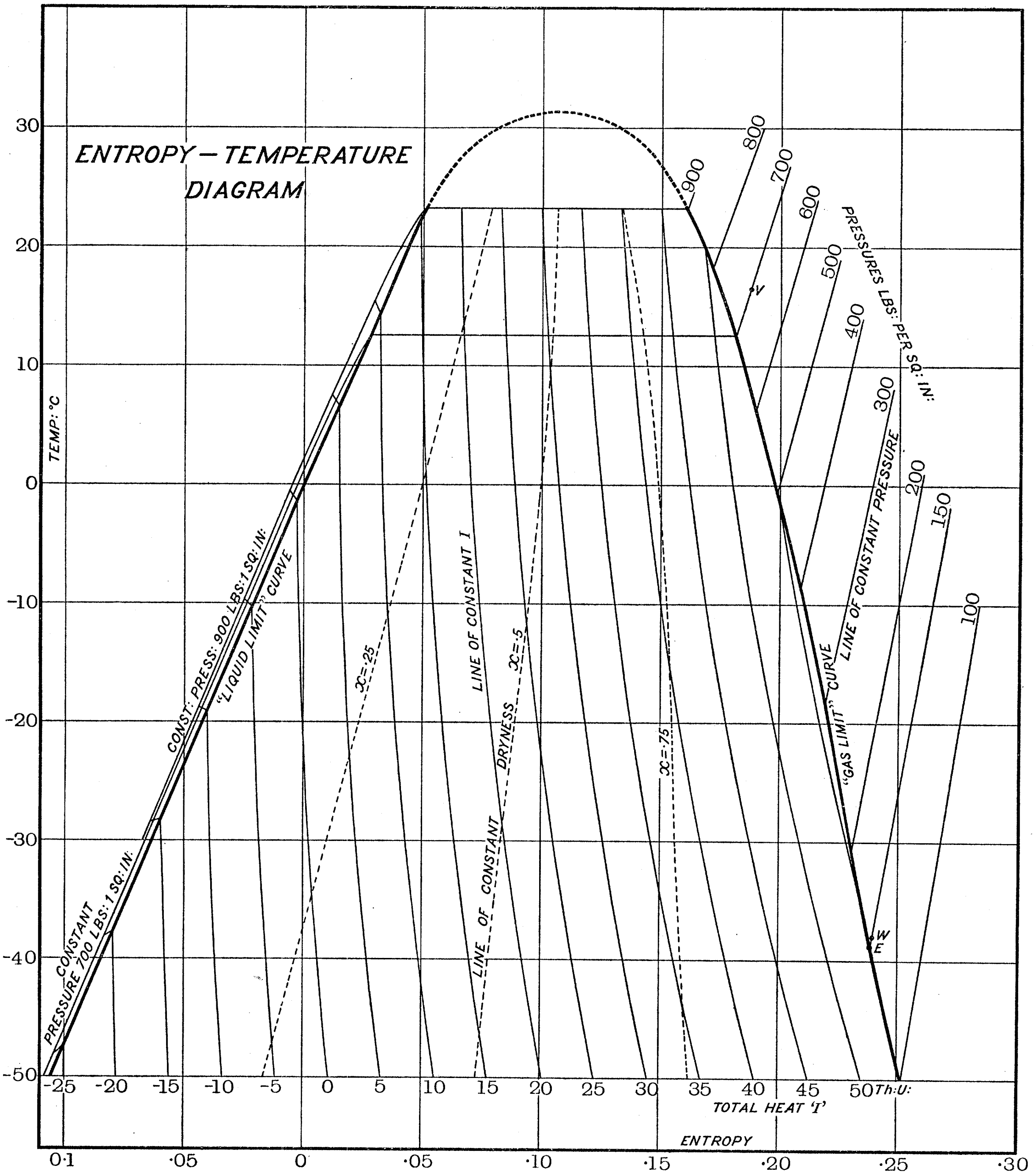

Fig. 12.

and therefore

$$\frac{\text{area}}{\theta_1-\theta_2} = \int_{p_1}^{p_2}\left(\frac{dv}{d\theta}\right)_p dp = \delta\phi \text{ between pressure curves } p_1 \text{ and } p_2.$$

Similarly, if the area is bounded by the limit curve and the ordinate at p_1, then

$$\frac{\text{area}}{\theta_1-\theta_2} = \delta\phi \text{ between limit curve and pressure curve } p_1.$$

$\delta\phi$ corresponds in each case with the mean temperature $\frac{1}{2}(\theta_1+\theta_2)$.

Values of $\delta\phi$ between the 700-lb. and 900-lb. pressure curves and the limit curve were calculated in this way and are given in Table VIII. From this table we see that the 700-lb. and 900-lb. pressure curves cut the 0° C. temperature line at $\phi = -{\cdot}0024$ and $\phi = -{\cdot}0049$ respectively. These two points serve as the *starting points* for plotting the two constant-pressure curves (700-lb. and 900-lb.) on the $\theta\phi$ diagram.

The corrected $\theta\phi$ diagram may now be constructed. The result is shown in fig. 12. This diagram was drawn as follows:—Starting at the points just found, the 700-lb. and 900-lb. pressure curves were drawn as before, remembering that the area under each curve on the $\theta\phi$ diagram between any two temperatures equals the difference of I for the same temperature range. The liquid-limit curve was then set off on the right of the pressure curves by plotting the small values of $\delta\phi$ given in Table VIII.

The gas-limit curve was then plotted by measuring off the values of L/θ, taken from Table VI., to the right of the liquid-limit curve.

To plot the constant I lines it is first necessary to find a starting point. At the origin ($\theta = 273$, $\phi = 0$) the value of I_0 is given by the equation $I_0 = Apv$, where

p is the saturation pressure at 0° C. = 508 lbs. per sq. in. = 73,200 lbs. per sq. ft.,
v is the volume of 1 lb. of liquid = ·0173 cub. ft.,*
$A = \frac{1}{1400}$; therefore $I_0 = {\cdot}905$ thermal unit.

The point on the 700-lb. curve having the same I was then calculated as follows:—The change of temperature at 0° C. is taken from the curve, fig. 9, p. 76, viz., ·24° C. per 100 lbs. difference of pressure. The difference of pressure is $700-508 = 192$. Therefore the temperature of the required point is $\cdot 24 \times 1\cdot 92 = \cdot 46°$ C. In other words, $I = {\cdot}905$ at a point + ·46° C. on the 700-lb. pressure curve. Similarly, $I = {\cdot}905$ at a point + ·94° C. on the 900-lb. pressure curve.

Having found in this way the true value of I for one point on each of the pressure lines, we can mark the true zero on the scale of the I curves, so that they shall give absolute values of I instead of only differences (see p. 72). Using the new scales, the points on the 700-lb. curve corresponding to $I = 0, -5, -10, -15, -20$, and -25 were marked off on the $\theta\phi$ diagram; also the points on the 900-lb. curve corresponding to $I = +5, +10$, and $+15$. The corresponding points on the limit curve were then calculated from the difference of pressure multiplied by the rise or fall of temperature, given in fig. 9. Having found these points, the rest of the I curves within the saturated area are easily constructed. Draw a horizontal (constant temperature) line through one of the points, say, where $I = 0$, on the limit curve. This is at temperature −1° C. = 272° abs. Along this line, starting at the limit curve, mark off a series of points, equally spaced, at distances $\delta\phi = \frac{5}{272}$ apart. These will be points on the +5, +10, &c., I lines.

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* BEHN'S (6) value of the density of liquid CO_2 at 0° C. is ·925.

Five horizontal lines were divided in this way and the I lines drawn through them. The values of I for the liquid, given in Table IX., were found by interpolation. The values of I given for the gas were obtained by adding the corresponding values of L to the values of I for the liquid.

Approximate constant-pressure lines in the dry area may be drawn, if the specific heat is assumed to be constant. They are logarithmic curves given by the equation

$$\frac{d\phi}{d\theta} = \frac{\sigma}{\theta}.$$

where σ is the specific heat of the gas at constant pressure.

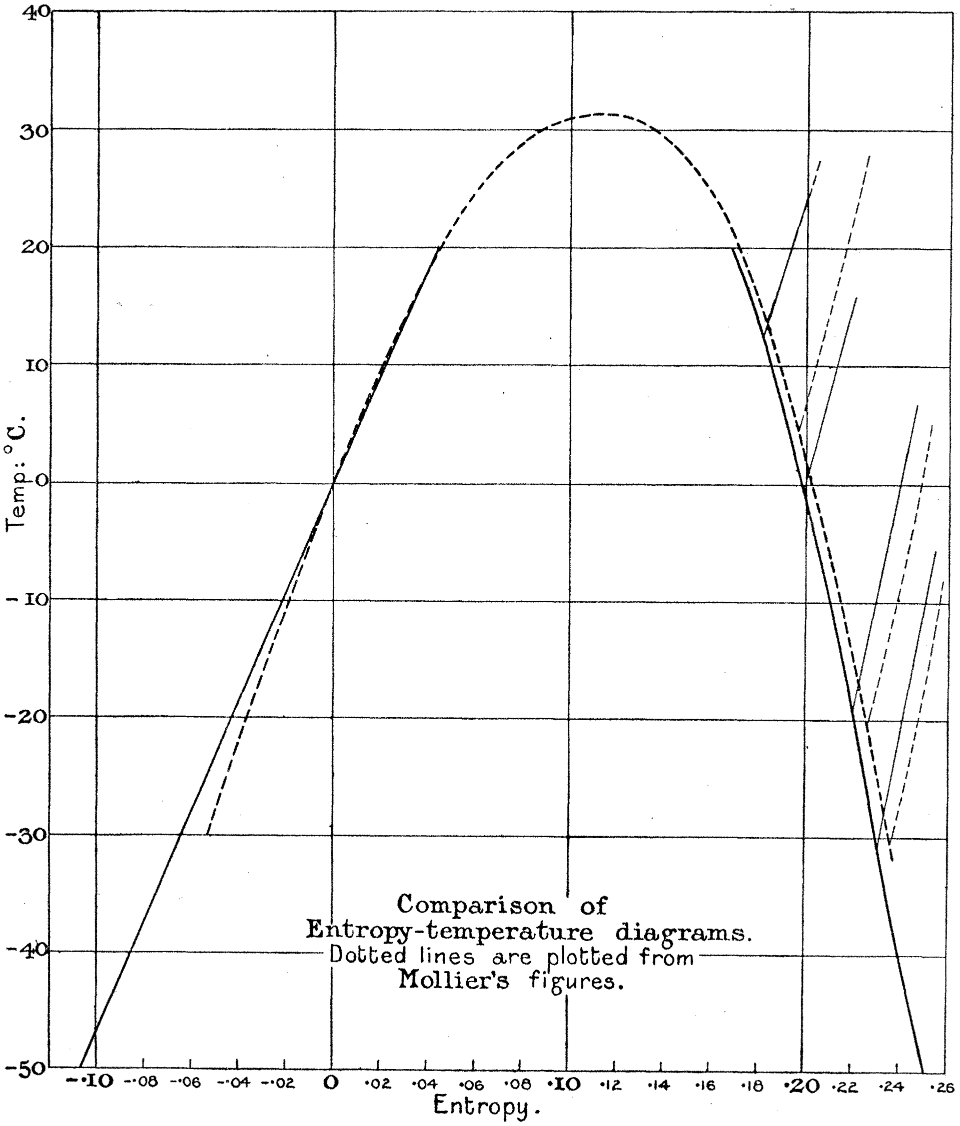

Fig. 13.

These curves are drawn in the diagram as straight lines, since for the short length shown the curvature is imperceptible. The values of σ are taken from the curve, fig. 6, p. 73. They agree closely with MOLLIER'S curves, as may be seen in fig. 13 (p. 81), where a few of each (at different pressures) are drawn for comparison.

The four dryness curves on the diagram were drawn by dividing the distances between the limit curves into quarters. This completes the construction of the diagram.

PART II.—DETAILED DESCRIPTION OF THE APPARATUS AND METHOD OF CARRYING OUT THE EXPERIMENTS SERIES I., II., AND III.

The compressor is a single acting pump made by Messrs. J. and E. Hall, of Dartford. It is driven by a variable speed electric motor. The piston-rod gland is formed of a pair of cup-leathers, between which oil is forced by an auxiliary piston, thus no leakage of CO_2 takes place, but a little oil enters the cylinder, and is pumped over with the CO_2; it is mostly caught in an oil separator, but a trace of oil is carried round the whole circuit with the CO_2. Under ordinary conditions the pump runs cold, but when working under the abnormal conditions of some of the tests it ran hot and gave trouble till a water-jacket was fitted round the cylinder.

The condenser is a coil of pipe in a tank through which cooling water flows.

The drying flask is a steel flask containing a little phosphorus pentoxide. The gas is led in by a pipe leading nearly to the bottom of the flask and leaves by a pipe from the top. A few ounces of P_2O_5 were put in the bottom of the flask and renewed from time to time. When the apparatus was first tried great trouble was experienced with moisture which collected and plugged the throttle valve with ice. The whole apparatus had to be thoroughly dried out and all the gas dried by passing it through calcium chloride in the drying flask before the difficulty was got over. After this all fresh charges of gas were passed through a small flask filled with calcium chloride before they entered the apparatus, and the above described drying flask was kept in circuit to eliminate any traces there might be left. Some of the oil carried round by the CO_2 collected in this flask.

The weighing apparatus (see fig. 1, p. 70) consists of two steel flasks, each capable of holding 40 lbs. of liquid CO_2; both were originally hung on spring balances. Each flask has valves at the top and bottom so that they may be alternately filled and emptied. The connections to the flasks are made of coils of copper pipe, flexible enough to allow of a small vertical motion. The spring balances were calibrated to allow for the stiffness of these coils. This arrangement had certain defects and was subsequently modified. In order to be sure that no CO_2 passed unweighed, it was necessary to stop the supply of CO_2 from one flask before starting it from the other; this inevitably caused a momentary variation in the rate of flow. There was also some doubt as to the effect of the weight of CO_2 in the coils of pipe connected to the flasks, which might be full or empty at the moment of weighing. The spring-balances were divided in pounds, and tenths of a pound could be roughly estimated.

The readings, however, had to be made in haste, and the probable error in the weight of CO_2 might amount to nearly 1 per cent. The balances had to be frequently recalibrated, as the stiffness of the pipes was found to change gradually. Only three of the 17 observations in Table VI., viz., those at $-26{\cdot}1$, $-14{\cdot}9$, and $-8{\cdot}6$, were made while working in this way.

To get over these defects the following modification was made:—One flask was hung on a steelyard, the arm of which was allowed only a very minute movement. When the arm fell it made an electric contact and rang a bell. This arrangement was found to be so sensitive that it would turn with ·01 lb. When the arm fell it was raised again by hanging a weight (usually 1 lb.) on the flask. When another pound of CO_2 had passed out of the flask the bell rang again and another weight was hung on, and so on. The increased sensitiveness of this arrangement made it possible to record the rate of flow of CO_2 accurately at short intervals and to complete the whole test with one flask full or less of CO_2, for as small a quantity as 10 lbs. could be weighed to $\frac{1}{10}$ per cent. No calibration or allowance for the copper pipes is necessary. A simple dash-pot made of a disc of tin in a vessel of oil got over all difficulties due to vibration without reducing the sensitiveness.

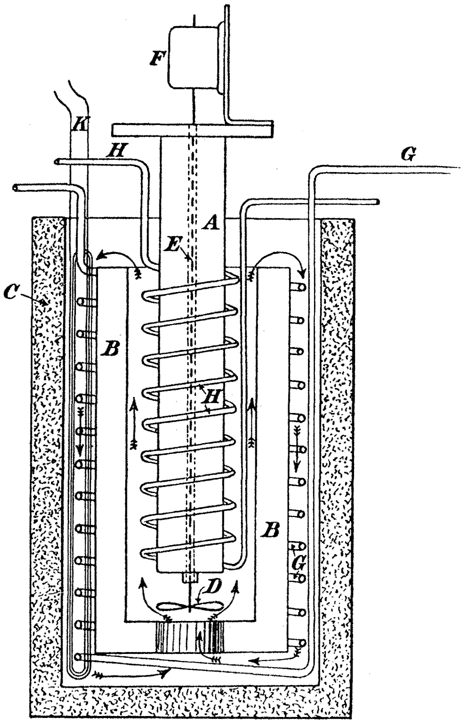

Fig. 14.

The *calorimeters* are tin-plate tanks containing coils of copper pipe and electric heaters; the tanks are lagged on the outside to prevent the inflow of heat. The larger calorimeter, fig. 14, contains two copper coils and the smaller one a single coil. The coils can be connected in different ways for the different series of tests. Calcium chloride brine was used to fill the tanks for the first experiments, but was replaced later by methylated spirits, which answered much better. Special care was taken in the design of the calorimeters to provide a definite path for the circulation of the liquid, which was maintained by a screw propeller driven by an electric motor. The large calorimeter was originally lagged with 2 inches of slag wool; this was found to be insufficient and 2 inches of felt were added, covered by varnished calico to keep out the moisture. A wooden top was fitted, covered by felt and calico. The small calorimeter, which was completed after experience had been gained with the larger one, was wrapped in $2\frac{1}{2}$ inches cotton wool surrounded by about 2 inches slag wool, all contained in a wooden box. The cover was formed of 3 inches of wood. Several sorts of heater were tried and failed;

finally coils of No. 16 S.W.G. Eureka wire, insulated with vulcanized indiarubber and wound directly on to the coils of the evaporating pipe, were tried; these answered perfectly. Each coil was about 50 yards long, had a resistance of about 10 ohms, and would absorb 1000 watts, taking 10 amperes from the 100-volt power mains. There are three such coils in the larger and two in the smaller calorimeter.

Measurement of the Electrical Heat.—The electrical power entering the calorimeters was calculated from the measured resistances of the heating coils and the observed E.M.F. across their terminals. The E.M.F. was measured by means of a Siemens millivoltmeter with fine pointer and mirror, which was calibrated against a cadmium cell with N.P.L. certificate. The scale is divided in single volts and $\frac{1}{10}$ volts can be accurately estimated. Two of the coils in the large calorimeter were always connected, when in use, on the full supply voltage (100), and the third was used in series with an adjustable resistance. The voltmeter has a two-way switch so that the two E.M.Fs. could be read successively. Readings were taken every minute throughout the tests. At the full voltage of 100 an error of ·1 volt means an error of ·2 per cent. in the power. At the lowest readings, 30 volts, an error of ·1 volt means an error of ·6 per cent. in the power. The resistance of each heating coil was measured before the tests were begun by a bridge which was checked against a standard ohm with N.P.L. certificate. The resistances were measured again after the tests were completed and had not altered appreciably. No temperature correction was made as the coils were made of Eureka, but corrections were made for the resistance of the leads.

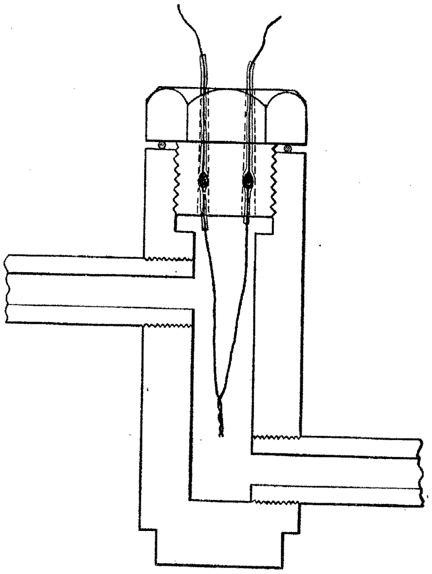
Fig. 15.

The temperature measurements were all made with Eureka-copper thermo-couples. The couples were made of No. 22 gauge double cotton and indiarubber-covered Eureka and copper wire, all cut from the same coils, soldered together at the ends. The couples used in the baths for measuring the temperature of the circulating liquid were put into rubber tubes, the bare ends projecting about $\frac{1}{2}$ inch. The couples used for measuring the temperature of the CO_2 were held in the special fittings shown in fig. 15, so that the bare wires projected into the CO_2 about $1\frac{1}{2}$ inches. The wires were carried through the gunmetal plugs in fine rubber tubing (bicycle valve tubing). The holes in the gunmetal were tapered and small brass beads were soldered on the wires, so that when the wires were drawn back the beads jammed in the holes. This simple device made an insulated joint which was gas-tight under the highest pressures used (1100 lbs. per sq. inch).

Preliminary calibrations showed that the relation between the E.M.F. of the thermo-junctions and temperature could not be satisfactorily represented by the empirical formula often used, viz., $\log E = n \log t + m$. A calibration curve was therefore drawn, points on it being obtained as follows. For temperatures between +100° C. and 0° C. the junction was compared with a standard mercury thermometer with N.P.L. certificate.

At −20° C. it was compared with a mercury thermometer which had been verified at that temperature by the N.P.L. The melting-point of mercury was then observed. The mercury was purified by dropping it through nitric acid, washing it in water, drying it at 120° C., and finally distilling it *in vacuo*. About $1\frac{1}{2}$ lbs. of the purified mercury was put in a glass vessel and frozen by packing it with CO_2 snow. The mercury was then gradually melted and the temperature of the melting-point observed. There was no difficulty in keeping the mercury half-melted and half-frozen for any length of time desired. The melting-point was assumed to be −38°·80 C.* A calibration curve was drawn through these points and extrapolated to −50° C. As this extrapolation was open to doubt a further point at −50° C. was afterwards obtained by comparison with a platinum-resistance thermometer which had been carefully calibrated against the standard thermometer. The new point obtained in this way fell within $\frac{1}{20}$° C. of the curve, thus confirming it satisfactorily. The curve is believed to be correct to $\frac{1}{10}$° C.

To maintain the other junctions of the wires at a steady known temperature they were immersed in a large tin of paraffin oil, well jacketed with slag wool, fitted with a calibrated thermometer and lens so that the temperature of the "cold junction" (in our case usually the warmer of the two) could be read to $\frac{1}{100}$° C. The oil was stirred by blowing air into it. An incandescent lamp was placed in the oil, so that the oil could be warmed to approximately atmospheric temperature. The temperature of the oil was read several times during each test and rarely varied more than $\frac{1}{10}$° C.

The E.M.F. produced by the thermo-couples was measured against the standard cadmium cell by a potentiometer with twenty 1-ohm coils and a gilt manganin slide-wire, 1 m. long, and of just over 1-ohm resistance. Special precautions were taken to avoid thermo-electric effects. The various thermo-junctions could be switched on in turn to the potentiometer by a two-pole six-way selector switch, designed to avoid thermo-electric effects. The potentiometer was sensitive enough to measure temperature differences of $\frac{1}{70}$° C. Such accuracy was of use when measuring the small rise or fall of the temperature of the bath during the run; also in Series IV. experiments, which depend on small differences of temperature, and in measuring the slow temperature rise during radiation tests.

The pressure of the gas was measured by steel tube Bourdon gauges made by Messrs. Schaeffer and Budenberg with specially fine needles and fine scale-divisions. They were calibrated by means of a dead-weight testing machine, in which a dead-

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* Chappuis, 1900, quoted Kaye and Laby, p. 48. Dr. J. A. Harker, of the N.P.L., has informed the authors that 38°·86 C. is probably a more accurate figure.

weight rests on a plunger in an oil cylinder. There was some doubt as to the effective area of the piston, since it was not exactly uniform in diameter, and there was a small clearance between it and the cylinder. In order to clear up this point the testing machine was checked against a mercury column about 1 m. high. The value of the effective area of the plunger was found in this way; it only differed by $\frac{1}{500}$ from the maximum measured area. The testing machine only gave pressures up to 400 lbs. per sq. inch. Up to this pressure the gauges showed a practically constant error, and it was assumed that the error remained the same at the higher pressures.

The gauge used for the pressure-temperature curve, and for experiments where accurate high-pressure readings were needed, was subsequently calibrated for its whole range by the N.P.L.; the results agreed closely with those obtained by the authors. In a few of the experiments, where accurate low pressures were needed, a low-pressure gauge was used, which was calibrated over its whole range. The pressures are believed to be correct to about 1 lb. per sq. in.

Adjustments.—Before beginning any test the apparatus was run for a considerable time while the conditions were adjusted to what was required; the test was not begun until a steady *régime* had been attained and all the parts had reached steady temperatures; moreover, unless a test was completed without anything more than trifling changes of any of the conditions, the results were discarded. The conditions were adjusted by regulating the speed of the pump, opening or closing the throttle valve, and switching on more or less electrical power to the calorimeters. While the adjustments were being made the flask B was emptied and the flask A filled, so that before the actual test began the CO_2 was circulating through A, which was full. The potentiometer and the temperature of the cold junction were also adjusted.

As soon as everything was ready, the valve on the top of flask A was closed and that on B opened, and the regular readings of all the instruments was commenced. In most tests these readings were made every minute. Each time the weighing bell rang the time was entered to the nearest second—the first ring marking the time of start of the test, which usually continued till the flask was almost empty.

In Series I. the apparatus was connected as shown in fig. 3, p. 71, the object being to measure the heat represented by the area NBCQ (fig. 7, p. 74) for a series of temperatures θ_2, ranging from the highest to the lowest attainable. To keep the rate of flow of CO_2 within convenient limits the pump was run as slowly as possible for the higher values of θ_2 and as fast as possible for the lower values of θ_2. The temperature θ_2 was not directly measured, but was deduced by the pressure-temperature curve from the pressure shown by the gauge connected to the pipe leaving the calorimeter; the throttle valve was adjusted so as to keep this pressure steady at the figure selected for each test.* The electrical power was adjusted so as to keep the temperature of

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* If the percentage of air present was not always approximately constant, this method of estimating θ_2 is liable to error.

the bath a few degrees above θ_2, so as to make sure that the gas leaving the calorimeter was slightly superheated. This was checked by the direct measurement of the final gas temperature θ_3 by a thermo-junction in the pipe.

During the test the following observations were made :—

Times when the weighing bell rang ;
E.M.F. on each heating coil, observed every minute ;
Pressure of gas leaving coil, ,, ,, ,, ;
Temperature θ_1 of liquid CO_2 before the throttle valve, every three minutes ;
,, of gas θ_3 leaving calorimeter, every three minutes ;
,, ,, bath, every three minutes ;
,, ,, cold junction, several times during test ;
,, ,, atmosphere, ,, ,, ,, ,, .

During the test small adjustments of the throttle valve and of the electric power were made so as to keep the pressure and bath temperature as constant as possible. As an example, the complete records for one experiment are given in Tables XI. and XII. The times when the weighing bell rang were plotted as a check on the uniformity of the rate of flow of CO_2 during the experiment. The initial temperatures of the liquid CO_2 were plotted to obtain the true mean.

In Series II. the apparatus was connected as shown in fig. 4, p. 72, the object being to measure the total heat I of the liquid, *i.e.*, the heat represented by the area SKAM, fig. 7, p. 74, for a series of ranges of temperature. The speed of the pump was settled as in Series I. The electrical power entering the large calorimeter was adjusted so as to keep its temperature a few degrees below θ_4, so that the liquid CO_2 might be cooled to the desired temperature θ_4. The electrical power put into the small calorimeter was adjusted so as to keep it at the selected temperature θ_1. The throttle valve was adjusted so as to keep the evaporation temperature a little below the temperature of the large calorimeter, but this temperature was of no importance in this series.

During the test the following observations were made :—

Times when the weighing bell rang ;
E.M.F. on each heating coil in calorimeter II., observed every minute ;
Temperature θ_4 of liquid CO_2 entering calorimeter II., every three minutes ;
,, θ_1 ,, ,, leaving ,, ,, ,, ,, ,, ;
,, of bath, calorimeter II., observed every three minutes ;
,, ,, cold junction, several times during test ;
,, ,, atmosphere, ,, ,, ,, ,, .

No observations were entered for the large calorimeter, which was only used as a cooler for the liquid, but the power was adjusted as required to keep its temperature constant.

As an example, the complete records for one experiment are given in Tables XIII. and XIV.

In Series III. the apparatus was connected as shown in fig. 5, p. 73, the object being to measure the specific heat of the gas at various temperatures near the saturation points. The adjustments of the pump, throttle valve, and electrical power for the large calorimeter were made exactly as in Series I. The electrical power put into the small calorimeter was adjusted so as to keep it at a steady temperature, a moderate amount above θ_3. It was not possible to start heating the gas exactly at θ_2, but θ_3 was kept as close to θ_2 as possible, so that the range through which the gas was heated began only a few degrees above the saturation temperature. The actual ranges are shown in lines 4 and 5, Table IV. The last line gives the mean specific heat for this range of temperature.

During the test the following observations were made :—

Times when weighing bell rang ;
E.M.F. on each heating coil in calorimeter II., observed every minute ;
Temperature θ_3 of gas entering calorimeter II., every three minutes ;
,, ,, ,, leaving ,, ,, ,, ,, ,, ;
,, ,, bath, calorimeter II., every three minutes ;
,, ,, cold junction, several times during test ;
,, ,, atmosphere, ,, ,, ,, ,, .

As an example, the complete records for one experiment are given in Tables XV. and XVI. The times when the weighing bell rang were plotted as a check on the uniformity of the rate of flow of CO_2 during the experiment.

Corrections.

Before making use of the data obtained in the tests, it is necessary to consider the effects of differences between the actual and theoretical cycles and also the corrections for radiation, conduction, and change of temperature of the calorimeter during the test.

Differences between the Actual and the Ideal Cycle.

(i.) Friction in the evaporation coil produces a small difference of pressure between the two ends. The evaporation, therefore, should not be represented by the constant-pressure line BE (fig. 7), but by a curved line starting a little above B and falling to E. It is easy to show that this has no effect on the heat absorbed, which is always $I_E - I_A$, and is accurately represented by the rectangle NBEP.

(ii.) The vapour is moving in the pipe with some velocity and consequently possesses kinetic energy. A simple calculation shows that the kinetic energy is always small enough to be neglected.

(iii.) The compression in the pump is not adiabatic and there are other deviations in the condenser, but as this part of the cycle is not included in the measurements they have no effect.

(iv.) *Change of Temperature of the Bath during a Test.*—The temperatures of the bath at the beginning and end of a test were accurately determined by taking several observations of temperature at short intervals before and after the actual moment of the start or finish and plotting them. The temperature at the actual moment of start or finish was then read from the graph. Any change of temperature of the bath showed that the electric heat supplied had been slightly too much or too little. The balance of heat (excess or shortage) is simply the temperature rise or fall multiplied by the water equivalent of the calorimeter. The water equivalent was determined by a simple heating experiment when the bath was at approximately the atmospheric temperature so that radiation could be neglected. The results obtained in this way are not quite accurate since the heat capacity of the lagging varies with the rate of heating.

Radiation.

A number of experiments were made to determine the rate at which heat entered the calorimeters from the surrounding air before concordant results were obtained. In the end good results were arrived at and the radiation was found to be proportional to the difference of temperature between the calorimeter and the atmosphere. The rate for the large calorimeter was ·83° C. per hour with a temperature difference of 40° C. The water equivalent being 97·5 this radiation corresponds to $\cdot 83 \times 97\cdot 5 = 81$ thermal units per hour for 40° C. difference of temperature. The small calorimeter rate was 1°·92 C. per hour or $1\cdot 92 \times 15 = 28\cdot 8$ thermal units per hour for 40° C. difference of temperature. These figures include the mechanical work put in by the stirrer motors, which in the small calorimeter was measured and found to be about 2·2 thermal units per hour.

Conduction along the Pipes.

The calorimeter coils, and most of the connecting pipes, were made of copper, $\frac{1}{2}$ inch external diameter, $\frac{1}{4}$ inch internal diameter. Such a pipe would conduct about 11 thermal units per hour with a temperature gradient of 40° C. per foot. To minimise conduction, the small calorimeter had a piece of thin-walled steel pipe inserted in both the ingoing and outgoing connections which would conduct heat at about one-sixth of the above rate. All the pipes were well lagged. When the apparatus is working it can easily be shown that there can be only a very small temperature gradient beyond the thermo-junctions so that no appreciable conduction can take place. Temperature measurements along the pipes confirmed this. When the vapour is not circulating the conditions are not quite the same and a small amount of conduction takes place. This conduction makes the apparent radiation rather too large, so that the corrections applied for radiation are a little too large. An approximate estimate shows that the error introduced is not greater than ·3 thermal units in the value of L at the lowest temperature and that it will not be appreciable above $-30°$ C.

PART III.—DETAILED DESCRIPTION OF THE APPARATUS AND METHOD OF CARRYING OUT THE EXPERIMENTS SERIES IV. AND V.

In Series IV. the apparatus was arranged as shown in fig. 8, p. 75, the object being to measure the Joule-Thomson effect, *i.e.*, the change of temperature $\theta_2-\theta_4$ (fig. 7), corresponding to a change of pressure from p_1 to the pressure on the limit curve p_2. In the actual tests the pressure could not be allowed to fall quite down to the limit curve for fear of introducing errors due to the commencement of evaporation. To get the total $\theta_2-\theta_4$, the observed difference of temperature was increased in the proportion of the observed drop to the total drop of pressure. In fig. 8 the pressure drop is measured by the gauges *a* and *b* and the temperature change by the thermo-junctions A and B. The liquid CO_2 from the weighing flask first passes through the inner coil of the calorimeter and is there cooled to any desired temperature. It then flows in order past :—

Gauge *a* and thermo-junction A.
Throttle valve V_1.
Thermo-junction B and gauge *b*.
Throttle valve V_2.
Outer coil in the calorimeter and gauge *c*.

The CO_2 is liquid up to the second valve, V_2.

The pressure of the liquid up to the valve V_1 is p_1. The valve V_1 is adjusted so as to allow it to drop to a pressure p_x a few pounds above p_2.

The valve V_2 is adjusted so as to allow it to drop from p_x to p_2, which is the saturation pressure corresponding to the temperature of the liquid. The difference of temperature $\theta_A-\theta_B$ between A and B is the Joule-Thomson effect corresponding to the drop of pressure p_1-p_x. Therefore

$$\theta_4-\theta_2=\frac{p_2-p_1}{p_x-p_1}(\theta_A-\theta_B).$$

In the first series of experiments the valve V_1 was a large bronze hydraulic valve, and the thermo-junctions were inserted in the gunmetal fittings shown in fig. 15, which were connected to the valve by pipes about 6 inches long. The whole apparatus was well lagged, but the amount of heat which leaked in when the temperature was low was sufficient to raise the temperature of the CO_2 to an extent which was large compared with the small temperature change which had to be determined; this leakage was allowed for by observing the temperature change due to the leakage only, when the valve V_1 was full open, and subtracting this from the temperature change when V_1 was throttled, the rate of flow being kept the same in the two experiments. Conduction along the pipe between A and B has no effect. Each observation was repeated a number of times and the means taken. It was not found possible to make observations at temperatures below −30° C., and even at this temperature the results were open to criticism as being small differences between large measurements, see Table V. (first part).

To get reliable results it was therefore necessary to design a special apparatus, combining two thermo-junctions and a throttle, which should not allow of appreciable radiation. Experience with the original apparatus showed that the throttle had to be adjustable to enable the required pressure ranges to be obtained. After one or two experiments the apparatus shown in fig. 16 was made and answered perfectly.

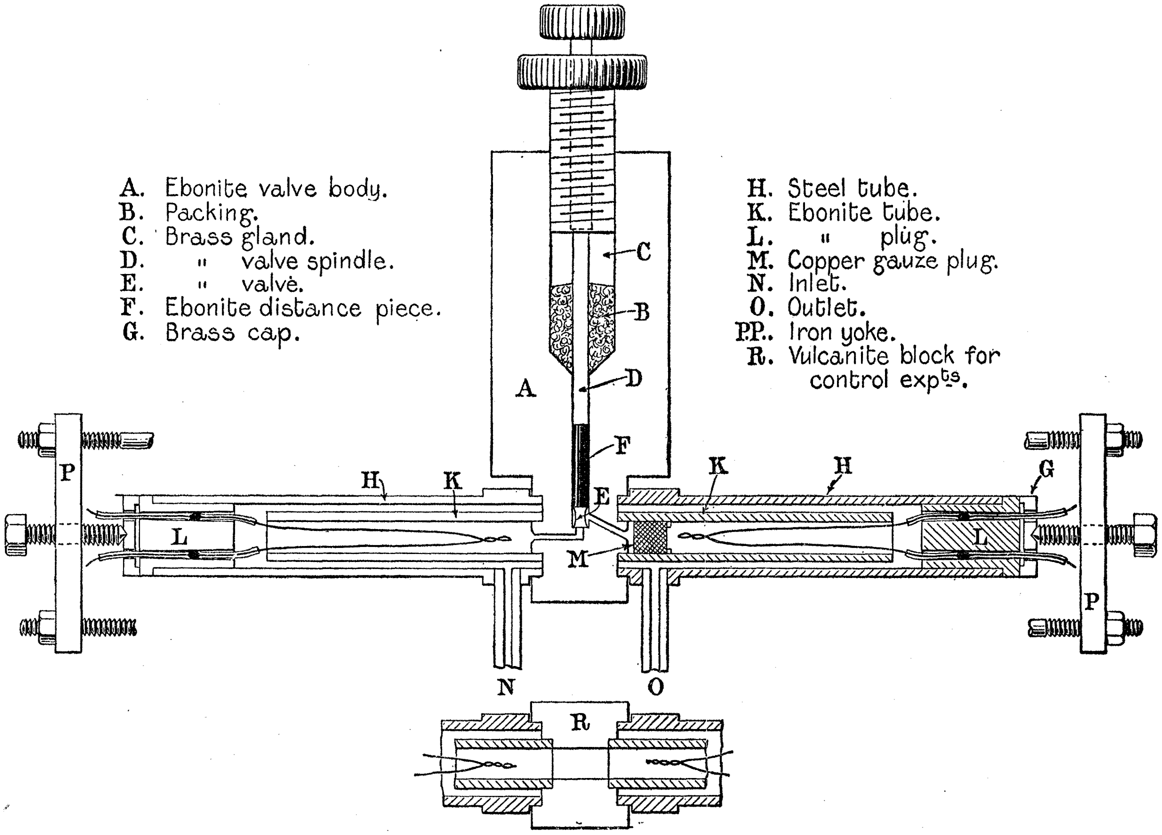

Fig. 16.

The body of the valve is vulcanite, the gland and screw are brass, but the screw is insulated from the passage through the valve by an extension rod of vulcanite. A minute brass valve is inserted under the extension rod, and is the only metal encountered by the CO_2 in passing through the valve. The two thermo-junctions are held in vulcanite plugs inserted in the steel tubes on either side of the valve. They project inside the inner vulcanite tubes, shown in the figure. The outer space forms a jacket of CO_2 at approximately the same temperature as the inner space—which is entirely protected by the vulcanite tubes from any external influence. Vulcanite is one of the best thermal insulators—the specific conductivity is given by Kaye and Laby as ·00042. The whole apparatus is held together by an iron yoke, and can be taken to pieces in a moment by slackening one of the set screws at the end. The four joints between the steel tubes and the vulcanite pieces were perfectly tight under the maximum pressure used, 900 lbs. per sq. in. The bore of the valve is $\frac{1}{16}$ inch diameter and the passages are bell-mouthed on both sides. A plug formed of rolled copper gauze serves to dissipate the kinetic energy of the jet issuing from the valve. The time occupied in the passage from one thermo-junction to the other, at the slowest rate of flow, was only a fraction of a second.

The thermo-junctions were connected to the selector switch (p. 85) in such a way that the temperature of either junction, or the difference between the two, could be measured. The latter arrangement was convenient, since it was the difference of temperature which was being investigated.

Before using the new apparatus tests were made to ascertain whether the heat insulation was in fact perfect, and also what difference, if any, there was between the readings of temperature given by the two thermo-junctions. The construction of the apparatus makes these tests very simple.

To avoid the slightest drop of pressure between the thermo-junctions, a simple full-bore block of vulcanite (also shown in fig. 16) was substituted for the adjustable valve, then liquid CO_2 was passed through the apparatus, first with the thermo-junctions in their normal positions, and again when the thermo-junctions had been interchanged, end for end. The apparent difference of temperature between the thermo-junctions in the first case represents the sum, and in the second case, the difference, of the two quantities to be determined, viz., the actual change of temperature of the liquid and the difference of the thermo-junctions.

Experiments were made with liquid CO_2 at temperatures ranging from +20° C. to −50° C. They showed that there was no change in the temperature of the liquid, but that there was a very slight difference between the thermo-junctions. This was allowed for in subsequent measurements.* As a further check, similar tests were made with wet CO_2 vapour instead of liquid CO_2. The difference between the readings of the thermo-junctions was confirmed. There could be no difference of temperature of the vapour in this case, since the pressure was the same at the two junctions.

As the calorimeter could not be cooled much below −40° C., and readings were wanted at −50° C., an "infra-cooler" was inserted in the pipe between the calorimeter and the throttle valve, by which the liquid could be cooled to any extent desired. By this means readings were obtained down to −55° C. The "infra-cooler" consisted of two concentric copper pipes 10 feet long, the inner one $\frac{1}{4}$ inch external diameter, the outer one $\frac{3}{8}$ inch internal diameter. The liquid CO_2 passed through the inner tube, while a separate supply of liquid CO_2 was admitted to the outer tube and evaporated at a pressure of about 80 lbs. per sq. in., escaping through a throttle valve into the atmosphere. The concentric pipes were bent into a coil about 9 inches diameter and well lagged with cotton wool. The arrangement worked well, though

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* See note on Table V.

it was not possible to keep the temperature of the liquid CO_2 absolutely constant during an observation. Slight variations of temperature account for the irregularities of the observations below −30° C.; above that temperature the "infra-cooler" was not used. The results of the tests with the original and with the new apparatus are summarised in Table V., and both are plotted in fig. 9, p. 76. The two sets of results are in good agreement, considering the smallness of the quantities being measured.

Series V.—The apparatus used for measuring the elasticity and dilatation of liquid CO_2 is shown in figs. 10 and 17 :—

a is a capillary glass tube, the lower end of which is closed and the upper end thickened and blown into a thistle funnel. A centimetre scale was etched along its whole length, and it was carefully calibrated by measuring the variation in the length of a thread of mercury in different positions.

b is a gunmetal socket, shown in detail in fig. 17, turned to hold the glass tube, the joint being made by a thin rubber sleeve. The top of the socket is closed by a screw plug.

c is a fine copper pipe, $\frac{1}{8}$-inch bore, 12 feet long, connecting the socket to the regulating valves, pressure gauge, and, through a drying flask, to the CO_2 flask. This pipe is sufficiently flexible to allow the glass tube to be moved about as required while under pressure.

The glass tube was charged as follows :—The tube was laid in a nearly horizontal position and a small quantity of mercury poured into the thistle funnel, where it lay without obstructing the entrance to the tube. The plug was then inserted in the gunmetal head. The air was removed by means of an air pump, successive charges of CO_2 gas being admitted and exhausted. The lower half of the glass tube was then surrounded with ice, and CO_2 gas was admitted up to a pressure slightly above the saturation pressure at 0° C. The gas then condensed in the glass tube, and the meniscus could be seen travelling up the tube. The rate of condensation could be regulated with ease by modifying the pressure. When sufficient liquid was condensed, the tube was raised into a vertical position so that the mercury in the funnel flowed into it, on to the top of the liquid CO_2. The tube, kept vertical, was then lowered into the calorimeter, the temperature of which had been adjusted to a few degrees below 0° C. The amount of liquid used and the length of the mercury column were chosen so that the whole of the liquid CO_2 was below the level of the bath in the calorimeter, and therefore at a uniform temperature, and the top of the mercury showed above the lid of the calorimeter, so that its position could be observed with a cathetometer.

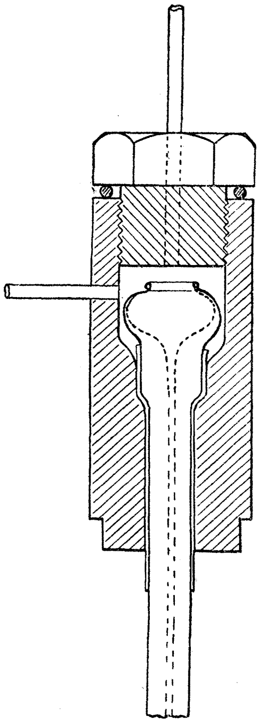

Fig. 17.

When making an experiment, the bath was first cooled to the desired temperature. Then readings were taken with the cathetometer as the pressure was varied step by step from the maximum available to a pressure just above the saturation pressure corresponding to the temperature of the bath. These readings give a constant-temperature curve on the p.v. diagram. A series of experiments was made with different temperatures, so that a number of constant-temperature curves were obtained, as shown in fig. 11, p. 78.

The apparatus appeared to work satisfactorily, but the results obtained are not in perfect agreement amongst themselves; the cause of this has not yet been ascertained. The curves shown in fig. 11 have been arbitrarily constructed to represent the mean results of several sets of observations and to agree amongst themselves; they must be taken as only approximate, but they are sufficiently accurate to determine the small correction δ, Table VI., for which they are required. AMAGAT'S (5) curves have been added to fig. 11 for comparison.

By extrapolation the curves may be extended to the left to the saturation pressure, which is only just below the lowest pressure observed. This has been done in fig. 11. By joining up the ends of all the curves, the new curve (named "limit curve" in the figure) is obtained which shows the change of volume along the limit curve. A curve giving BEHN'S (6) observations is also drawn for comparison. The agreement is fairly good.

It is not necessary to describe the lengthy and rather complex calculations required to reduce the data obtained in these experiments. Allowance was made for the changes of volume of the glass and of the mercury indicator at different temperatures, and corrections applied to allow for the variation in the bore of the tube. All these corrections are small compared with the changes of volume of the CO_2 due to temperature. Since the actual weight of the column of liquid CO_2 was not measured, the density at some one temperature had to be assumed; BEHN'S value, viz., 0·925 at 0° C., was used.

The elasticity and dilatation may be derived from the curves directly. The elasticity $(dv/dp)_t$ is the slope of the constant temperature lines. The dilatation $(dv/dt)_p$ is the distance apart of the constant temperature lines divided by the difference of temperature.

These quantities have not been worked out because of the known inaccuracy of the observations. The authors intend to repeat the experiments and hope to obtain accurate results.

PART IV.—DISCUSSION OF RESULTS.

Pressure-Temperature Curve. (Fig. 18. Tables I. and X.)

The relation between the pressure and temperature of saturated CO_2 vapour has been observed by REGNAULT (7), CAILLETET (8), AMAGAT (5), KUENEN and ROBSON (9), Zeleny and Smith (10), and others. The observations are tabulated in parallel columns in Table X. and all plotted in fig. 18 besides the authors' curve.

The most accurate determinations are probably Kuenen and Robson's below zero and Amagat's above zero. Our curve agrees closely with Kuenen and Robson's, only differing by 3 lbs. at 510 lbs. pressure. It also agrees fairly closely with Amagat's, differing by 6 lbs. at 830 lbs. Both these differences are almost exactly equal to the calculated effects of the presence of the observed ·11 per cent. of air (by volume) under the special conditions of our test.

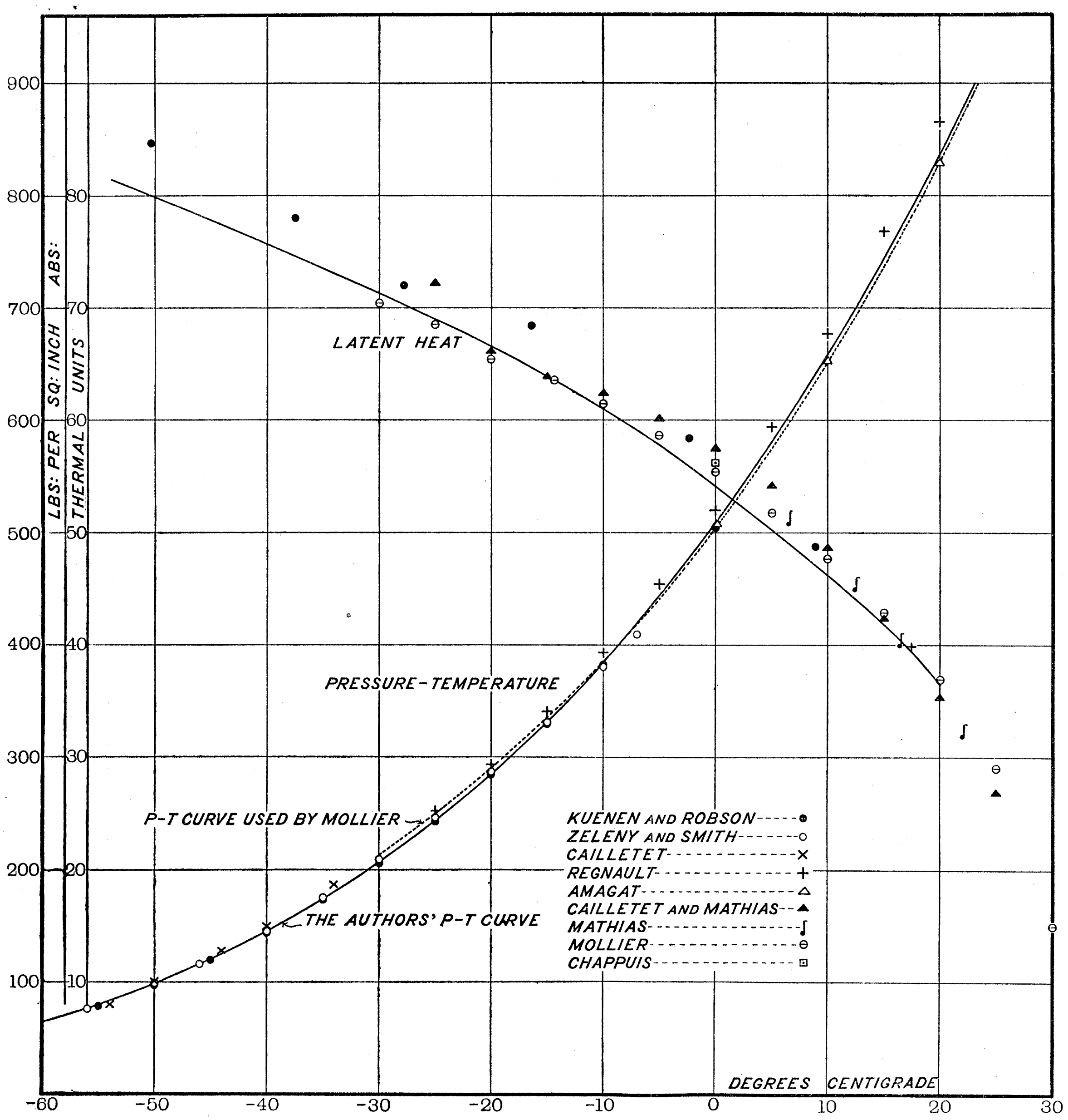

Fig. 18.

ZELENY and SMITH's points lie close to our curve, but a curve through their points would be definitely flatter than ours. There is a difference of 10 lbs. at their highest pressure, 410 lbs.

CAILLETET's figures only go up to −34° C. They do not agree very closely in position or slope.

REGNAULT's figures lie well above the others. He states that his experiments did not satisfy him.

MOLLIER adopted a composite curve, using AMAGAT's figures above zero and REGNAULT's below zero, modified so as to make them fit together. His curve is shown dotted in fig. 18.

An accurate determination of the pressure-temperature curve is important because its gradient, $dp/d\theta$, is one of the factors in CLAPEYRON's equation, which may be used to calculate the latent heat or the vapour density.

The gradient of MOLLIER's curve is clearly too small, particularly at low temperatures. It is remarkable how large a difference in the gradient results from a very small divergence between the curves. The values of $dp/d\theta$, used by CAILLETET and MATHIAS (11), MOLLIER, and KUENEN and ROBSON for calculating L, and by the authors who only used it for calculating the specific volume of the gas, are given below:—

VALUES of $dp/d\theta$.

T.	C. and M. (11).	MOLLIER (1).	K. and R. (9).	Authors.
° C.	lbs./in.^{2} ° C.	lbs./in.^{2} ° C.	lbs./in.^{2} ° C.	lbs./in.^{2} ° C.
+20	20·4	19·4	—	19·6
+10	17·18	16·6	—	16·3
0	14·12	13·18	13·46	13·6
−10	11·32	10·69	11·01	11·1
−20	8·84	8·55	8·73	8·9
−30	—	6·79	6·87	7·0
−40	—	—	5·37	5·3
−50	—	—	4·06	4·0

The Total Heat I *and Specific Heat* C_p *of the Liquid.*

Our observations were plotted and values read from the smooth curve are given in Table VII. No experimental determinations of these quantities appear to have been published. Figures for comparison might be deduced from MOLLIER's (3) Iϕ diagram, but this is beyond the range of this paper.

The probable errors in the values of I do not exceed about $\frac{1}{3}$ per cent., from +20° C. to −30° C., but rise to 1 per cent. at −50° C. The presence of ·073 per cent. of air has no appreciable effect on the results.

Experiments have been made by DIETERICI (15) and by MARGULES (16) on the differences between the total heats at 0° C. and at a few other temperatures. These quantities refer to heating along the limit curve and not to heating at constant pressure.

Specific Heat of the Gas. (Fig. 6.)

No experimental determinations of this quantity appear to have been made at temperatures below 0° C., though much work has been done at high temperatures.

The specific heat is believed to vary considerably near the limit curve. Our measurements give a mean value for a moderate range of temperature, starting in each case a few degrees above the limit curve; they are probably not correct for higher temperatures than those at which they were measured. They are only used for the small correction given in column γ, Table VI., and for plotting the pressure lines in the superheated area.

Latent Heat of Liquid CO_2.

Our observations were plotted and values read off the smooth curve are given in Table VI. The figures are probably correct to about $\frac{1}{2}$ per cent. from +20° C. to −30° C. and to 1 per cent. at −50° C. One point, at −8°·6 C. lies 1 per cent. off the curve. This was the result of the first experiment made, when the spring balances were still used for weighing the CO_2. The trace of air present only produces a proportionate error in the value of L, *i.e.*, ·073 per cent., which is negligible.

No experimental determinations of L below zero have been published. REGNAULT* made a single determination at +17° C.; CHAPPUIS (13) a single determination at 0° C. and MATHIAS (12) made a series of measurements between +6° C. and +31° C. CAILLETET and MATHIAS (11) calculated L from their own determination of the liquid and vapour densities and REGNAULT'S pressure-temperature curve. KUENEN and ROBSON (9) calculated L from AMAGAT'S (5) vapour density (extrapolated) and BEHN'S (6) liquid densities and their own pressure-temperature curve. MOLLIER (1) calculated L from AMAGAT'S (5) vapour and liquid densities (extrapolated) and the compound pressure-temperature curve mentioned above, based on AMAGAT and REGNAULT'S results.

All these results are plotted in fig. 18 beside our curve. If the drawing is examined it will be seen that the mean of all the previous determinations lies above our curve. We have investigated the causes of this divergence in detail as it appeared to cast some doubt on the accuracy of our results. The investigation has shown, first why the previous results tend to agree amongst themselves, secondly why they differ from ours, and, finally, has resulted in an indirect confirmation of our results.

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* Recalculated by MATHIAS (12).

The cause of the rough agreement among the observations is that the same data have been repeatedly used. Thus Cailletet and Mathias' densities were used by—

$$\left.\begin{array}{l}\text{Mathias}\\ \text{Chappuis}\end{array}\right\}\text{ in working out their observations,}$$

$$\left.\begin{array}{l}\text{Cailletet}\\ \text{and Mathias}\end{array}\right\}\text{ in their calculations.}$$

Amagat's densities were used by—

$$\left.\begin{array}{l}\text{Kuenen and Robson}\\ \text{Mollier}\end{array}\right\}\text{ in their calculations.}$$

Regnault's pressure-temperature curve was used by—

$$\left.\begin{array}{l}\text{Cailletet and Mathias}\\ \text{Mollier (in part)}\end{array}\right\}\text{ in their calculations.}$$

The difference between the various results and ours may be traced to the inaccuracy of Regnault's (and consequently Mollier's) pressure-temperature curve and to the error in Cailletet and Mathias' gas densities below −20° C, and to the uncertainty of the extrapolated values of the densities used by Mollier and Kuenen and Robson.

All the calculated values of L were obtained by means of Clapeyron's equation

$$L = (V-v)\,\frac{\theta}{J}\,\frac{dp}{d\theta},$$

where

V = specific volume of saturated vapour,
v = " " liquid at saturation temperature.

Their accuracy therefore depends on the accuracy of the two factors $dp/d\theta$ and $(V-v)$.

The differences in the pressure-temperature curves and their gradients have already been discussed, so that it is only necessary to consider now the other factor $(V-v)$. The specific volume of the liquid v is much smaller than of the vapour, and the values obtained by different observers do not differ much; it is, therefore, not necessary to discuss it here. The specific volume of the saturated vapour, V, is much more doubtful. In fig. 19 are plotted—

(1) Amagat's (5) smooth curve from his observations of V.

(2) Cailletet and Mathias' (11) smooth curve from their observations of V.

(3) Kuenen and Robson's (9) extrapolation (by the Law of Corresponding states) of Amagat's curve.

(4) Mollier's (1) extrapolation of Amagat's curve.

(5) Our values, calculated from our observed values of L by Clapeyron's equation, using Behn's (6) liquid densities.

Values taken from our smooth curve are given in Table IX.

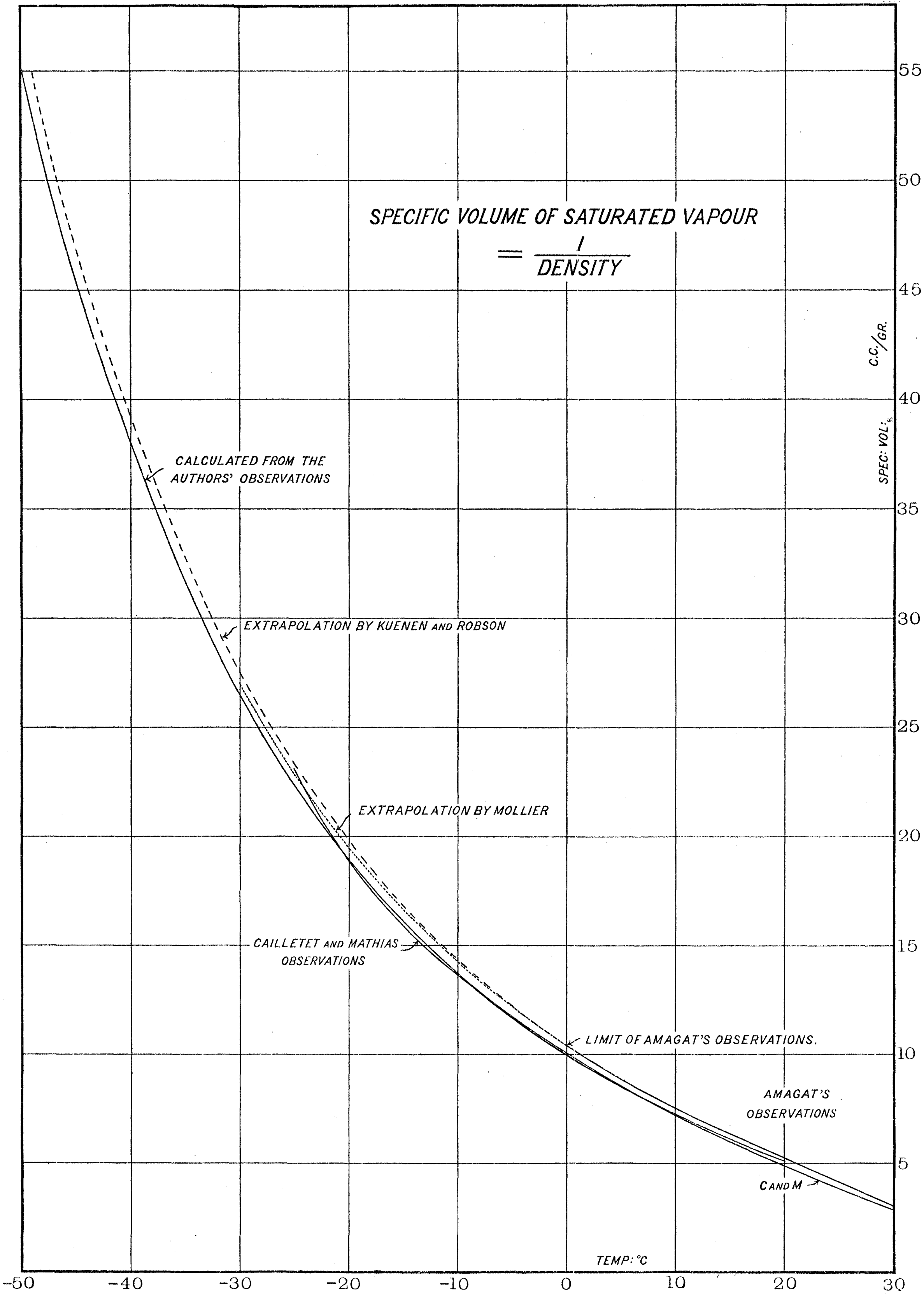
SPECIFIC VOLUME OF SATURATED VAPOUR
= 1/DENSITY
CALCULATED FROM THE AUTHORS' OBSERVATIONS
EXTRAPOLATION BY KUENEN AND ROBSON
EXTRAPOLATION BY MOLLIER
CAILLETET AND MATHIAS OBSERVATIONS
LIMIT OF AMAGAT'S OBSERVATIONS.
AMAGAT'S OBSERVATIONS
C AND M
SPEC: VOL: C.C./GR.
TEMP: °C
55
50
45
40
35
30
25
20
15
10
5
-50
-40
-30
-20
-10
0
10
20
30

Fig. 19.

The observations on which CAILLETET and MATHIAS' smooth curve is founded lie very erratically and at considerable distances from the curve. The curve is clearly erroneous below −20° C.

It will be noted that our values agree very closely with CAILLETET and MATHIAS' from −20° C. to +10° C. Our curve also lies almost exactly parallel with AMAGAT'S curve and KUENEN and ROBSON'S theoretical extension of it. The agreement between our curve, the observations, and the theoretical curve is a confirmation of the accuracy of the shape of our L curve.

The inaccuracy of our pressure-temperature curve, due to the presence of ·11 per cent. of air, referred to on p. 69, introduces an error into our values of $dp/d\theta$ which probably does not exceed 2 per cent. If this were allowed for, it would raise our specific-volume curve by 2 per cent., and bring it closer to KUENEN and ROBSON'S. The value of V does not enter into the construction of our $\theta\phi$ diagram.

Joule-Thomson Effect. (Fig. 9.)

No experiments on the Joule-Thomson effect for liquid CO_2 appear to have been published. Figures for comparison might be deduced from MOLLIER'S $I\phi$ diagram (3), but that would be beyond the range of this paper. It is not easy to say what effect the presence of the trace of air may have on these results.

Dilatation and Elasticity of Liquid CO_2.

As has been explained, the results of the Series V. experiments were not sufficiently concordant to warrant the publication of values of the dilatation and elasticity derived from them, though they are accurate enough to determine the values of $\delta\phi$ between the constant-pressure curves and the limit curve on the $\theta\phi$ diagram. The confirmation of BEHN'S densities, shown in fig. 11, must not have much weight attached to it for the same reason.

The only results previously published are a single curve at 13°·1 C., given by ANDREWS (14), and three curves given by AMAGAT (5) at 0° C. +10° C., and +20° C. We have failed to fit ANDREWS' curve on our figure, but AMAGAT'S curves are shown for comparison in fig. 11. ANDREWS suggests that the curvature of the lines near the saturation pressure may be due to the presence of air.

$\theta\phi$ *Diagram.* (Fig. 12.)

As stated at the beginning of this paper, the primary object, for which all the quantities already discussed were measured, was the construction of a $\theta\phi$ diagram for comparison with MOLLIER'S.

It may be useful to recapitulate here the steps in the construction of the two diagrams. Fig. 12 was drawn as follows :—

The starting points of the 700-lb. and 900-lb. constant-pressure curves ($\theta = 273°$ C., $\phi = -·0024$ and $-·0049$), found on p. 80, were first marked, and the two constant-pressure curves were then drawn in segments of 10 degrees each.

The liquid-limit curve was then set off from these pressure curves at the distances $\delta\phi$ given in Table VIII.

The gas-limit curve was then set off from the liquid-limit curve at the distances $\delta\phi = \mathrm{L}/\theta$ (Table VI).

A constant I line was then drawn through the origin, at a slope determined by the Joule-Thomson effect. Thus the value of I at the origin (calculated on p. 80) was transferred to the two constant-pressure curves. The points I = 0, +5, +10, +15, and −5, −10, −15, −20, −25 were then marked on these curves and transferred back to the limit curve by drawing I lines as before. Thus the starting points of the I lines on the limit curve were determined. Measuring from these, a number of points were then marked off at distances $\delta\phi = 5/\theta$, $10/\theta$, $15/\theta$, &c., and I lines drawn through these points. The space between the limit curves was then divided into quarters, thus determining a few dryness lines. The constant-pressure curves in the superheated area were then drawn, starting at the corresponding saturation temperatures at slopes

$$\frac{\delta\phi}{\theta_1 - \theta_2} = \frac{\sigma}{\frac{1}{2}(\theta_1 + \theta_2)},$$

where the values of $\theta_1 - \theta_2$ were the actual temperature ranges in the experiments, Series III., and σ was the corresponding specific heat of the gas at constant pressure, given in fig. 6.

The maximum probable error in the liquid limit curve is $\delta\phi = ·0008$ at −30° C. and ·0032 at −50° C. At higher temperatures the error is probably not more than ·0005.

MOLLIER'S $\theta\phi$ diagram was constructed in a very different manner. He assumed that the characteristic equation of the gas might be expressed in VAN DER WAAL'S form

$$p = \frac{\mathrm{R}\theta}{v - \alpha} - \frac{\mathrm{C} \,.\, f(\theta)}{(v + \beta)^2},$$

and determined the constants by means of AMAGAT'S observations. He also assumed that $f(\theta)$ was of the form $f(\theta) = e^{\left(1 - \frac{\theta}{\theta_\kappa}\right)}$, and by means of these equations obtained a general expression for the entropy of the gas, which would hold down to the limit curve. With this he plotted the gas limit curve on the $\theta\phi$ diagram.

He then found an empirical mathematical formula for the slope of the pressure-temperature curve, $dp/d\theta$, which, on integration, corresponded well with the pressure-temperature curve constructed from AMAGAT'S and REGNAULT'S observations. With this and AMAGAT'S values for the vapour and liquid densities (extrapolated) he calculated the values of L, and set off the liquid limit curve *to the left* of the gas limit curve at distances $\delta\phi = \mathrm{L}/\theta$.

To construct the constant-pressure lines in the superheated area he assumed (2) that the specific heat at constant volume, C_v, was constant, which he points out is not quite true. On this assumption the constant-volume lines on the $\theta\phi$ diagram are the same as those for a perfect gas (logarithmic curves). The constant-pressure curves were then determined from these constant-volume curves by the p.v. θ curves observed by AMAGAT. MOLLIER does not draw I lines on his $\theta\phi$ diagram. His values of I are given in his Iϕ diagram (3), which is outside the range of the present discussion.

The agreement between the two diagrams, constructed by such widely different methods, is remarkable, the more so because MOLLIER had no data to go on below 0° C., except REGNAULT'S very imperfect pressure-temperature curve. The following brief comparison between the two methods shows how widely they differ.

Our diagram is based in the most direct manner possible on experiments at the temperatures and pressures represented, whereas MOLLIER'S is based on a mathematical equation obtained from experiments at higher temperatures. Our diagram is constructed from the left, his from the right hand. Our diagram is based on measurements of heat, his on measurements of density and pressure.

The two diagrams are superposed in fig. 13, and values of ϕ and L are given in Table XVII. for comparison. In Table XVIII. our data are arranged for direct comparison with the tables given by MOLLIER (1) and EWING (4).

The differences between the diagrams are due to the differences in the various data, which have been already discussed. The authors take this opportunity of expressing their great admiration for the judgment and skill by which Dr. MOLLIER has selected the most reliable data and devised mathematical methods capable of giving results which direct experiments have confirmed so closely.

SUMMARY.

The authors have reconstructed the $\theta\phi$ diagram by a new method and, at the same time, extended it from −30° C. to −50° C. The reconstruction is based on direct heat measurements, and the results are believed to be more accurate than those arrived at indirectly by MOLLIER.

The observations include the direct measurement of the following quantities:—

The latent heat;
The total heat of the liquid;
The specific heat of the gas;
The dilatation and elasticity of the liquid;
The Joule-Thomson effect for the liquid.

From these direct measurements the following quantities have been calculated:—

The specific volume of the saturated vapour;
The specific heat of the liquid at constant pressure.

Most of these measurements are new; the details of what has been done before are given on p. 68 and in Part IV., p. 94.

In addition to the ordinary data given in $\theta\phi$ diagrams and tables, the authors have given the values of I, so that a complete $I\phi$ diagram might be constructed from the data supplied in the paper. The authors have made this diagram, but before publishing it they intend to make a series of throttling experiments on superheated gas to check the constant-pressure curves, which have so far only been approximately determined.

P.S.—Since this paper was completed the authors have commenced the gas-throttling experiments referred to above. These may be used as an independent check on the accuracy of the $\theta\phi$ diagram. Choosing an experiment as close to the gas-limit curve as possible—to avoid possible errors in the approximate constant-pressure lines—the confirmation obtained is remarkably good.

Starting at the point "V," fig. 12, on the 700-lbs. pressure line, the gas was throttled down to the 150-lbs. pressure line. The point reached is marked "W." Calculated from the $\theta\phi$ diagram, the point W should have fallen exactly on the limit curve, *i.e.*, at "E." If the limit curve be moved ·0001 to the left, W and E will coincide. A shift of ·0001 corresponds to an error of ·3 per cent. in the value of L. This is the accumulated error in the whole set of measurements for the complete cycle KAVWEGK shown in fig. 20.

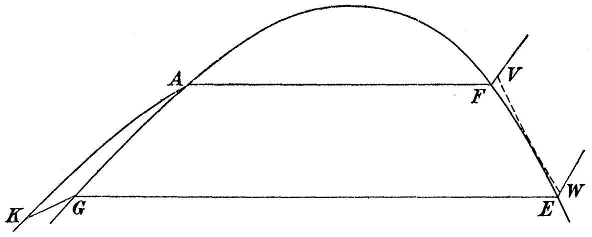

Fig. 20.

The authors desire to express their special gratitude to Brasenose College for the gift of the freezing machine with which the experiments were made. They also have to thank Mr. D. H. Nagel, of Trinity College, and Mr. H. B. Hartley, of Balliol College, for advice on chemical questions and for having generously placed the College Libraries at their disposal.

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Table I.—Pressure-Temperature Observations.

Pressure.	Temperature.	Pressure.	Temperature.
lbs./in.².	° C.	lbs./in.².	° C.
96	−51·0	354·5	−13·0
128	−43·2	387·5	− 9·8
167	−35·8	407	− 8·15
185	−33·3	429·5	− 6·2
206	−31·5	474·5	− 2·6
220·5	−28·0	511	+ 0·2
243	−25·0	514	+ 0·4
270	−21·6	612	+ 7·15
295	−18·8	711	+13·15
310	−17·1	812	+18·8
316	−16·6	898·5	+23·05
331	−14·9		

TABLE II.—Series I. Observations. (Refrigeration.)

Temperature evaporation, θ_2	° C.	−53 ·4	−51 ·6	−48 ·3	−43 ·2	−40 ·9	−35 ·6	−30 ·0	−26 ·1	−21 ·4	−14 ·9	−11 ·6	−8 ·6	−8 ·0	−1 ·7	+6 ·6	+13 ·4	+20·05
Pressure evaporation, p_2	,,	85	92	105	108 ·5	140	169 ·5	205 ·5	234	272	332 ·5	367	401 ·5	407 ·5	485	603 ·5	714	837
Weight of CO_2 . . .	lbs.	11 ·0	10 ·0	6 ·0	15 ·0	30	18	33 ·0	80 ·7	30	86 ·6	30	106 ·35	20	18	17	13	15
Duration	min.	36 ·5	80 ·6	51 ·5	53 ·2	82 ·4	31 ·3	41 ·3	85 ·5	25 ·2	89 ·85	20 ·97	98 ·0	30	31 ·8	37 ·17	21 ·73	23 ·6
Mean liquid temperature, θ_1	° C.	15 ·8	13 ·7	14 ·7	12 ·9	10 ·7	8 ·6	10 ·3	10 ·1	9 ·7	9 ·2	12 ·4	9 ·7	15 ·05	14 ·6	16 ·9	20 ·0	22 ·9
Exit gas temperature, θ_3	,,	−32 ·0	−34 ·6	−30 ·6	−26 ·2	−33 ·9	−29 ·2	−24 ·7	−18 ·7	−15 ·0	−9 ·0	−5 ·2	+1 ·1	+4 ·7	+4 ·7	+15 ·2	+24 ·2	+27 ·6
Mean bath temperature	,,	−37 ·1	−43 ·2	−39 ·2	−31 ·4	−37 ·8	−32 ·0	−26 ·3	−20 ·7	−16 ·1	−10 ·1	−6 ·0	−0 ·6	+4 ·7	+8 ·5	+15 ·1	+24 ·0	+28 ·1
Fall of bath	,,	−1 ·63	−0 ·69	0 ·02	0·175	− ·156	0 ·26	0 ·34	1 ·21	0 ·14	0 ·725	0 ·32	−0 ·94	−1 ·07	0 ·27	0 ·18	0 ·83	0 ·12
Atmospheric temperature	,,	16 ·5	14 ·7	16 ·0	14 ·0	12 ·4	11 ·7	13 ·8	15 ·7	13 ·5	12 ·4	14 ·0	13 ·5	16 ·0	16 ·0	19 ·2	19 ·2	18 ·9
Electric heat	Th.U.	518 ·2	427	257 ·0	646 ·8	1326	830	1560	3861	1484	4306	1453	5696	1022 ·6	853	780	568	591 ·5
Bath fall	,,	−22 ·8	−10 ·4	+0 ·3	+17 ·0	−15	+25 ·4	+33	+117 ·5	+13 ·6	+70 ·6	+31	−91	−15 ·0	+3 ·8	+2 ·5	+12 ·5	+1 ·7
Radiation	,,	21 ·7	60 ·9	31 ·9	79 ·8	143	46 ·2	56	106 ·3	25 ·2	69 ·8	15	32	3 ·8	2 ·7	1 ·6	−1 ·2	−2 ·5
Total heat	,,	517 ·1	477 ·5	289 ·2	743 ·6	1454	901 ·6	1649	4085	1523	4446	1499	5637	1011 ·4	859 ·5	784 ·1	579 ·3	590 ·7
Heat per lb	,,	47 ·0	47 ·75	48 ·2	49 ·5	48 ·5	50 ·1	50 ·0	50 ·7	50 ·8	51 ·3	50 ·0	53 ·0	50 ·57	47 ·75	46 ·1	44 ·5	39 ·35

TABLE III.—Series II. Observations. (Total Heat of Liquid.)

Weight of CO_2	lbs.	8	17	14	20	26	16	15	18	18	19	18
Duration	min.	33·0	32·3	27·0	29·2	24·9	16·4	16·6	12·15	19·05	20·0	17·9
Initial temperature	° C.	−39·1	−35·2	−30·3	−25·6	−15·3	−11·9	−11·8	−11·3	−11·4	− 6·8	− 1·4
Final temperature	”	8·3	6·5	7·7	8·3	8·0	19·25	12·2	7·1	3·9	7·8	7·7
Mean bath temperature	”	8·5	7·1	7·6	8·2	7·9	19·6	12·2	7·1	3·9	7·7	7·8
Fall of bath temperature	”	0·83	1·1	− 0·21	0·19	− 0·19	− 0·07	− 0·08	0·01	0·03	0·17	0·375
Atmospheric temperature	”	13·8	13·1	14·4	16·5	15·4	17·3	16·1	14·6	16·5	13·1	13·5
Electric heat	Th.U.	197·1	379·2	298	377·5	357·9	306·4	212·5	195·3	158·9	164·3	97·1
Bath fall	”	12·5	16·6	− 3·2	2·9	− 2·8	− 1·0	− 1·1	0·1	0·4	2·6	5·7
Radiation	”	4·3	4·2	3·5	3·4	2·9	0·0	0·7	1·4	2·7	0·5	0·4
Total heat	”	213·9	400·0	298·3	383·8	358·0	305·4	212·1	196·8	162·0	167·4	103·2
Heat per lb.	Th.U./lb.	26·75	23·5	21·3	19·19	13·8	19·1	14·15	10·93	9·0	8·81	5·73

TABLE IV.—Series III. Observations. (Specific Heat of Gas.)

Pressure	lbs./sq. in.	138	188	278	408	504	608	733	824
Weight of CO_2	lbs.	10	15	20	17	19	24	16	18
Duration	min.	30·5	23·9	18·6	14·6	14·45	18·07	16·45	21·52
Initial temperature	° C.	−30·4	−22·4	−13·0	− 1·9	8·3	14·9	20·4	24·6
Final temperature	”	7·8	8·6	11·2	9·1	19·5	25·6	30·5	35·4
Mean bath temperature	”	7·3	8·3	11·1	9·2	19·6	25·6	30·6	35·6
Fall of bath	”	+ 0·33	− 0·13	+ 0·04	− 0·47	− 0·33	− 0·85	+ 0·07	+ 0·04
Atmospheric temperature	”	15·0	15·3	15·3	14·8	14·8	14·8	14·8	14·4
Electric heat	Th.U.	78·87	112·3	131·9	67·0	93·1	125·2	81·5	111·5
Bath fall	”	+ 4·98	− 2·0	+ 0·6	− 7·1	− 4·7	−12·1	+ 1·0	+ 0·6
Radiation	”	1·12	0·8	0·45	0·36	− 0·3	− 1·5	− 2·4	− 4·4
Total heat	”	84·97	115·1	132·95	60·36	88·1	111·6	80·1	107·7
Heat per lb.	Th.U./lb.	8·5	7·68	6·65	3·55	4·63	4·65	5·01	5·99
Specific heat	—	0·22	0·25	0·275	0·32	0·41	0·435	0·495	0·55

TABLE V.—Series IV. Observations. (Joule-Thomson Effect.)

With Original Apparatus.

Initial temperature	° C.	10	5	−0·5	− 11	− 22	− 30	−30·3
Pressure before throttle valve	lbs./in.².	827	800	820	785	768	760	760
Pressure after throttle valve	,,	680	610	550	420	310	250	500
Drop of pressure at valve	,,	147	190	270	365	458	510	260
Change of temperature, throttling	° C.	−0·66	−0·575	−0·49	−0·10	0·62	1·47	1·38
Change of temperature, not throttling	,,	−0·00	−0·055	0·11	0·35	0·73	1·36	1·30
Change of temperature, due to throttling	,,	−0·66	−0·63	−0·60	−0·45	−0·11	0·11	0·08
Change of temperature per 100 lbs. drop of pressure	,,	−0·45	−0·33	−0·22	−0·12	−0·024	+0·02	+0·03

With Special Throttle Valve (fig. 16, p. 91).

Initial temperature, ° C.	+15·1	+10·6	+ 4·9	− 2·1	−11·3	−20·7	− 31	− 35	−37·9	−41·7	−43·2	−53·6	− 55
Initial pressure, p_1	857	799	802	788	668	664	651	651	648	649	650	646	647
Final pressure, p_2	745	688	630	562	433	360	312	295	268	265	273	245	243
Fall of pressure	112	111	172	226	235	304	339	356	380	384	377	401	404
Change of temperature*	−0·72	−0·53	−0·56	−0·44	−0·26	−0·135	+0·04	+0·18	+0·345	+0·595	+0·38	+0·81	+0·73
Change of temperature per 100 lbs.	−0·64	−0·48	−0·325	−0·195	−0·11	−0·04	+0·01	+0·05	+0·09	+0·15	+0·10	+0·20	+0·18

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* These figures include the correction for the difference between the thermo-junctions. This correction varies from zero at + 15° C. to 25 per cent. of the reading at − 55° C.

TABLE VI.—Calculation of Latent Heat.

Evaporation temperature, θ_2.	α.	β.	γ.	δ.	Latent heat. $L = \alpha+\beta-\gamma+\delta$, RGEP.*
	Refrigeration. Series I., NBCQ.*	$I_1 - I_2$. Series II., THAM.*	$\sigma(\theta_3 - \theta_2)$. Series III., PECQ.*	$I_2 - I_4$. Series IV., SKHT.*	
° C.	Th.U.	Th.U.	Th.U.	Th.U.	Th.U.
−53·4	47·0	37·9	4·4	+0·69	81·2
−51·6	47·75	35·7	3·5	+0·51	80·45
−48·3	48·2	34·8	3·72	+0·45	79·75
−43·2	49·5	31·2	3·7	+0·35	77·35
−40·9	48·5	28·6	1·5	+0·3	75·9
−35·6	50·1	24·7	1·49	+0·18	73·5
−30·0	50·0	22·8	1·3	+0·08	71·6
−26·1	50·7	20·6	1·87	0	69·4
−21·4	50·8	17·9	1·7	−0·07	66·9
−14·9	51·3	14·0	1·7	−0·1	63·5
−11·6	50·0	14·4	2·0	−0·21	62·2
− 8·6	53·0	11·0	3·1	−0·2	60·7
− 8·0	50·57	14·0	4·22	−0·25	60·1
− 1·7	47·75	10·0	2·27	−0·32	55·2
+ 6·6	46·1	6·7	3·61	−0·37	48·8
+13·4	44·5	4·5	5·2	−0·55	43·25
+20·05	39·35	1·7	4·2	−0·35	36·50

* These letters denote the areas shown in fig. 7, p. 74.

TABLE VII.—Total Heat I and Specific Heat C_p of Liquid CO_2 at Constant Pressure. Taken from Curves.

Temperature.	I, 700 lbs.	I, 900 lbs.	C_p.
° C.			
−50	−25·9	—	0·47
−40	−21·0	—	0·49
−30	−16·0	—	0·515
−20	−10·7	—	0·54
−10	− 5·2	− 5·5	0·57
0	+ 0·6	+ 0·3	0·60
+10	+ 6·8	+ 6·5	0·64
+20	—	+13·1	0·68

TABLE VIII.—$\delta\phi$ between Pressure Curves and Limit Curve.

Mean temperature.	$\delta\phi$ between limit curve and 700 lbs./sq. inch line.	$\delta\phi$ between 700 and 900 lbs./sq. inch lines.	$\delta\phi$ between limit curve and 900 lbs./sq. inch line.
° C.			
− 31·5	0·00289	0·00104	0·00393
− 21·7	0·0029	0·00122	0·0041
− 10·6	0·0031	0·00157	0·0047
+ 0·5	0·0024	0·0025	0·0049
+ 8·2	—	0·0033	0·0049
+ 13·2	—	—	0·00485
+ 17·9	—	—	0·0031

NOTE.—700 lbs. curve meets limit curve at + 12°·5 C.
900 lbs. " " " + 23°·2 C.

TABLE IX.—Collected Results.

Temperature.	Pressure,* Authors.	Liquid.		Latent heat.	Vapour.		Vapour density.	Pressure,* K. and R. and AMAGAT.	
		I.	ϕ.	L.	I.	ϕ.			
° C.	lbs./in.²						gr./c.c.	lbs./in.²	atmospheres.
− 50	98	− 26·4	− 0·1064	79·9	53·9	0·2515	0·0181	97	6·60
− 45	120	− 23·8	− 0·0958	77·8	54·2	0·2458	0·0220	119·5	8·12
− 40	145	− 21·2	− 0·0850	75·7	54·5	0·2403	0·0263	144·5	9·82
− 35	174	− 18·6	− 0·0742	73·6	55·0	0·2350	0·0316	173·5	11·8
− 30	206	− 15·95	− 0·0635	71·3	55·35	0·2300	0·0378	206	14·0
− 25	242½	− 13·3	− 0·0528	69·0	55·7	0·2253	0·0448	242·5	16·5
− 20	284	− 10·5	− 0·0422	66·5	56·0	0·2207	0·0528	284	19·3
− 15	331	− 7·7	− 0·0318	63·8	56·1	0·2154	0·0621	329·5	22·4
− 10	384	− 4·9	− 0·0211	60·9	56·0	0·2100	0·0730	382·5	26·0
− 5	443	− 2·05	− 0·0105	57·7	55·6	0·2042	0·0855	441	30·0
0	508	+ 0·91	0·0	54·1	55·0	0·1981	0·100	505	34·35
+ 5	580	+ 4·05	+ 0·0110	50·3	54·35	0·1919	0·117	—	—
+ 10	658	+ 7·25	+ 0·0223	46·2	53·45	0·1850	0·138	653	44·4
+ 15	743	+ 10·4	+ 0·0331	41·9	52·3	0·1775	0·163	—	—
+ 20	835	+ 13·45	+ 0·0435	36·55	50·0	0·1682	0·196	829	56·4

* The pressures given in the last column, taken from KUENEN and ROBSON'S figures from − 50° C. to 0° C. and from AMAGAT'S from 0° C. to + 20° C., are probably more accurate than the authors', for reasons explained on p. 95.

TABLE X.—Comparison of Pressure-Temperature Observations for Saturated CO_2 Vapour.

Pressure in Atmospheres (760 mm. Hg).

Temperature.	Authors.	REGNAULT.	CAILLETET.	AMAGAT.	K. and R.	Z. and S.
	1912.	1862.	1878.	1891.	1902.	1906.
° C.						
– 60	4·35	—	—	—	4·30	4·35
– 56	5·24	—	—	—	—	5·19
– 55	5·44	—	—	—	5·35	—
– 54	5·64	—	5·46	—	—	—
– 50	6·66	—	6·8	—	6·60	6·73
– 46	7·86	—	—	—	—	7·89
– 45	8·16	—	—	—	8·12	—
– 44	8·50	—	8·72	—	—	—
– 40	9·86	—	10·25	—	9·82	9·88
– 35	11·84	—	—	—	11·8	11·92
– 34	12·25	—	12·7	—	—	—
– 30	14·0	—	—	—	14·0	14·21
– 25	16·52	17·12	—	—	16·5	16·74
– 20	19·3	19·93	—	—	19·3	19·52
– 15	22·5	23·14	—	—	22·4	22·46
– 10	26·1	26·76	—	—	26·0	25·83
– 7	28·5	—	—	—	—	27·80
– 5	30·1	30·84	—	—	30·0	—
0	34·55	35·40	—	34·4	34·3	—
+ 5	38·43	40·47	—	—	—	—
+ 10	44·75	46·07	—	44·4	—	—
+ 15	50·5	52·2	—	—	—	—
+ 20	56·8	58·85	—	56·4	—	—
+ 25	—	66·1	—	—	—	—
+ 30	—	73·85	—	70·7	—	—

Table XI.—Series I. Test I. on March 25, 1912.

C.F.J. Record.

Time.	Gauge pressure.	Voltmeter.		Time of ring.	Weight on flask.	Cold junction temperature.	Atmospheric temperature.
		Coil A.	Coil C.				
h. m.	lbs./in.^{2}	volts	volts	m. s.	lbs.	° C.	° C.
12 18	266	98·2	99·3	18 21	5	—	*Start.*
19	3	8·3	9·4	—	7	12·47	13·4
20	3	99·4	100·3	20 2			
21	4	8·3	99·8	—	11		
22	2	8·0	9·4				
23	3	8·1	9·2	23 17			
24	4	8·1	9·3	—	15		
25	5	6·1	9·8	—	—	12·475	13·4
26	5	6·1	9·8	26 34			
27	4	6·2	9·7	—	19		
28	3	5·7	9·6				
29	3	90·0	100·1	29 57			
30	2	88·8	99·6	—	23		
31	3	89·1	99·3				
32	5	89·2	9·2				
33	5	89·3	9·3	33 18			
34	5	9·9	9·9	—	27		
35	3	9·5	9·5				
36	2	9·4	9·3	36 45			
37	2	9·7	9·8	—	31		
38	3	9·9	9·9				
39	3	95·6	9·9				
40	2	4·9	9·5	40 9			
41	1	5·0	9·5	41 50	33		
42	3	5·1	100·2		35		
43	3	5·8	0·2	43 34	—	12·51	13·50 *Stop.*
Mean pressure	263·3	Duration, 25·217 mins.					

Mean readings, Coil A . . $\left\{\begin{array}{lll} 97\cdot5 & \text{for} & 9\cdot65 \text{ mins.} \\ 89\cdot48 & ,, & 10\cdot0 \quad ,, \\ 95\cdot28 & ,, & 5\cdot57 \quad ,, \end{array}\right.$ 99·646 for 25·22 mins., Coil C.

Mean volts, Coil A . . . $\left\{\begin{array}{lll} 97\cdot14 & \text{for} & 9\cdot65 \text{ mins.} \\ 89\cdot06 & ,, & 10\cdot0 \quad ,, \\ 94\cdot80 & ,, & 5\cdot57 \quad ,, \end{array}\right.$ 99·106 for 25·22 mins., Coil C.

Mean absolute pressure, 272.

Mean θ_2, $-21\cdot4$.

Heat = 1484 Th.U.

TABLE XII.—Series I. Test I. on March 25, 1912.

D.R.P. Record.

T.J. No. 1.			T.J. No. 2.			T.J. No. 5.			
Bath temperature.			Exit gas temperature.			Liquid temperature.			
Time.	Potentiometer.		Time.	Potentiometer.		Time.	Potentiometer.		
h. m. s.	ohms	cm.	h. m. s.	ohms	cm.	h. m. s.	ohm	cm.	
12 10 0	−5	74½	12 12 0	−5	56½	12 14 30	+0	19½	
15		71½				16	+0	19½	
18 30		72½	19		53½	20	+0	15	*Start* 12h. 18m. 47s.
22		71½	23		52½	24	−0	5	
26		70½	27		51½	28	−0	29	
30		70	31		52	32	−0	52½	
34		71½	35		53	36	−0	78	
38		73½	39		54	40	−1	14	
41		75½							
42		75¾	43		55¾	44	−1	43¼	*Stop* 12h. 44m. 0s.
45		75¾							
46 30		76							*Note.*—D.R.P. watch was 26s. fast on C.F.J. watch.
48		75¼							
Means. . .	−5	73½		−5	53		Plotted.		
Temperature from calibration curve }		−16°·1 C.			−15°·0 C.			+ 9°·7 C.	

	ohms	cm.	
Bath temperature at start	−5	72·4	
,, ,, finish	−5	75·75	
,, fall		3·35 cm. =	0°·19 C.
Correction for change of cold junction temperature . . .		=	−0°·05 ,,
Therefore nett bath fall			0°·14 ,,

Table XIII.—Series II. Test III. on March 26, 1912.

C.F.J. Record.

Time.	Voltmeter, coil D.	Time of ring.	Weight on flask.	Cold junction temperature.	Atmospheric temperature.	
h. m.	volts.	m. s.	lbs.	° C.	° C.	
4 46	63·6	—	14	14·51*	16·3*	* At 4h. 42m.
47	4·2	46 32	—	—	—	*Start.*
48	4·4	—	16			
49	4·1	49 29				
50	5·9	—	18			
51	4·2					
52	5·2	52 25				
53	4·7	—	20			
54	4·1					
55	3·9	55 17				
56	4·3	—	22			
57	3·9					
58	3·9	58 9				
59	3·8	—	24			
5 00	4·0					
1	4·1	1 1				
2	3·9	—	26			
3	4·9	3 54				
4	4·6	—	28			
5	3·9					
6	4·0	6 48				
7	4·1	—	30			
8	3·2					
9	3·3	9 45				
10	2·5	—	32			
11	1·8					
12	3·2	12 43				
13	3·0	—	34			
14	3·8					
15	4·1	15 43	— 36	14·51	16·7	*Stop.*

Mean . . 63·96

Corrected volts } 63·70

Duration, 29·18 mins.

$$\text{Heat} = \frac{(63 \cdot 7)^2 \times 29 \cdot 18\text{m.} \times 3 \cdot 189}{10^3} = 377 \cdot 5 \text{ Th.U.}$$

TABLE XIV.—Series II. Test III. on March 26, 1912.

D.R.P. Record.

T.J. No. 1.					T.J. No. 3.					T.J. No. 4.					
Bath temperature.					Initial temperature.					Final temperature.					
Time.			Potentiometer.		Time.			Potentiometer.		Time.			Potentiometer.		
h.	m.	s.	ohm	cm.	h.	m.	s.	ohms	cm.	h.	m.	s.	ohm	cm.	
4	42	0	−1	$26\frac{3}{4}$	4	43	0	−8	$8\frac{1}{4}$	4	44	0	−1	24	*Start* 4h. 47m. 29s. *Stop* 5h. 16m. 39s. *Note.*—D.R.P. watch 56s. fast on C.F.J. watch.
	45			$26\frac{1}{2}$		46			8		47			24	
	48			$26\frac{1}{4}$		49			$6\frac{3}{4}$		50			$23\frac{3}{4}$	
	51			25		52			$6\frac{3}{4}$		53			$22\frac{1}{2}$	
	54			$24\frac{3}{4}$		55			6		56			$22\frac{3}{4}$	
	57			$25\frac{3}{4}$		58			5		59			$23\frac{1}{4}$	
5	0	0		$26\frac{1}{4}$	5	1	0		$4\frac{3}{4}$	5	2	0		$24\frac{3}{4}$	
	3			$27\frac{3}{4}$		4			5		5			25	
	6			$27\frac{1}{2}$		7			$6\frac{1}{4}$		8			$25\frac{1}{4}$	
	9			$27\frac{3}{4}$		10			7		11			$25\frac{1}{2}$	
	12			29		13			$8\frac{1}{4}$		14			$26\frac{1}{4}$	
	15			30		16			$8\frac{3}{4}$		17			$26\frac{1}{4}$	
	17	30		$29\frac{3}{4}$											
	18			30											
Means. . .			−1	27·5				−8	6·6				−1	24·3	
Temperature				+ 8°·5C.					− 25°·6C.					+ 8°·3C.	

	ohm	cm.	
Bath temperature at start	−1	26·3	
,, ,, finish	−1	29·85	
,, fall		3·55 cm. =	0°·195 C.
Correction for cold junction			0°·0 ,,
Nett fall			0°·195 ,,

TABLE XV.—Series III. Test IV. on March 28, 1912.

C.F.J. Record.

Time.	Voltmeter, coil D.	Time of ring.	Weight on flask.	Cold junction temperature.	Atmospheric temperature.	
h. m.	volts.	m. s.	lbs.	° C.	° C.	
5 19	—	—	12	14·32*	15·0†	* At 5h. 9m. † At 5h. 16m.
20	46·9	20 32	—	—	—	*Start.*
21	·9	—	14			
22	·9	22 23				
23	·8	—	18			
24	·9					
25	·7					
26	47·1	26 7	—	14·34		
27	·3	—	22			
28	·4					
29	·5	29 46				
30	·1	—	26			
31	·2	—	—	—	15·3	
32	·0					
33	46·9	33 31				
34	·9	—	30	14·36		
35	47·0					
36	·1					
37	·0	37 18				
38	·1	—	32			
39	·2	39 12	—	14·365	15·2	*Stop.*

Mean . . 47·15

Volts . . 46·96

Duration, 18·67 mins.

$$\text{Heat} = \frac{(46 \cdot 96)^2 \times 18 \cdot 67\text{m.} \times 3 \cdot 189}{10^3} = 131 \cdot 2 \text{ Th.U.}$$

TABLE XVI.—Series III. Test IV. on March 28, 1912.

D.R.P. Record.

T.J. No. 1.			T.J. No. 3.			T.J. No. 4.		
Bath temperature.			Initial temperature.			Final temperature.		
Time.	Potentiometer.		Time.	Potentiometer.		Time.	Potentiometer.	
h. m. s	ohm	cm.	h. m. s.	ohm	cm.	h. m. s.	ohm	cm.
5 17 0	−0	57	5 17 30	−5	49¾	5 18 0	−0	54¾
19		57¼	20		50¾	21		55¼
22		58	23		51	24		55¾
25		58¾	26		48½	27		55¾
28		58¾	29		47½	30		56
31		59	32		45¾	33		55¾
34		59½	35		47¼	36		55½
37		59	38		51¾	39		55½
40		59						
Means . .	−0	58·4		−5	49		−0	55·7
Temperature	+	11°·1 C.		−	13°·0 C.		+	11°·2 C.

	ohm	cm.
Bath temperature at start . . . . =	−0	57·75
" " " finish . . . . =	−0	59·0

" fall . . . . 1·25 cm. = 0°·07 C.

Correction for change of cold junction temperature . . . − 0°·03 "

Nett fall . . . . 0°·04 "

TABLE XVII.—Comparison of $\theta\phi$ Diagrams.

Temperature.	ϕ liquid.		Latent heat.		ϕ vapour.	
	Authors'.	MOLLIER'S.	Authors'.	MOLLIER'S.	Authors'.	MOLLIER'S.
° C.						
+20	+0·0435	+0·045	36·55	36·93	0·1682	0·171
+10	+0·0223	+0·021	46·2	47·74	0·1850	0·189
0	0	0	54·1	55·45	0·1981	0·203
−10	−0·0211	−0·019	60·9	61·47	0·2100	0·215
−20	−0·0422	−0·036	66·5	65·35	0·2207	0·226
−30	−0·0635	−0·053	71·3	70·4	0·2300	0·236
−40	−0·0850	—	75·7	—	0·2403	—
−50	−0·1064	—	79·9	—	0·2515	—

TABLE XVIII.—New Data arranged as in MOLLIER'S paper (1) and EWING'S 'Mechanical Production of Cold' (4).

Temperature.	Pressure.	BEHN'S volume liquid.	Volume of vapour.	q.	Latent heat, r.	ϕ.	
						Liquid.	Vapour.
° C.	kg./cm.^{2}	c.c./gr.	c.c./gr.				
−50	6·82	0·866	55·2	−26·6	79·9	−0·1064	0·2515
−45	8·41	0·881	45·4	−24·0	77·8	−0·0958	0·2458
−40	10·16	0·896	38·0	−21·45	75·7	−0·0850	0·2403
−35	12·20	0·912	31·65	−18·9	73·6	−0·0742	0·2350
−30	14·49	0·930	26·45	−16·3	71·3	−0·0635	0·2300
−25	17·05	0·958	22·30	−13·75	69·0	−0·0528	0·2253
−20	19·96	0·970	18·95	−11·0	66·5	−0·0422	0·2207
−15	23·16	0·993	16·10	− 8·3	63·8	−0·0318	0·2154
−10	26·9	1·02	13·70	− 5·6	60·9	−0·0211	0·2100
− 5	31·0	1·048	11·70	− 2·85	57·7	−0·0105	0·2042
0	35·5	1·08	10·00	0·0	54·1	0·0000	0·1981
+ 5	40·5	1·119	8·55	+ 3·00	50·3	+0·0100	0·1919
+10	45·9	1·163	7·25	+ 6·05	46·2	+0·0223	0·1850
+15	51·8	1·222	6·13	+ 9·10	41·9	+0·0331	0·1775
+20	58·3	1·295	5·10	+11·95	36·55	+0·0435	0·1682