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

Thermal Properties of Carbonic Acid at Low Temperatures. (Second Paper)

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XII. *Thermal Properties of Carbonic Acid at Low Temperatures.*

(*Second Paper.*)

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[Plate 6.]

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Introduction.

In a former paper (1) the authors described a series of measurements on the thermal properties of CO_2 and the construction of a $\theta\phi$ chart embodying those results. It was pointed out that the superheated area of the chart was incomplete, the constant pressure lines being only approximately accurate and the total heat (I) lines omitted. It was also pointed out that throttling experiments on the superheated gas would form a valuable check on the accuracy of the chart, and the construction of an $I\phi$ chart was postponed till more accurate measurements should have been made on the superheated gas and the whole had been checked by throttling experiments.

The present paper describes the additional experiments required to complete and check the $\theta\phi$ chart, including a re-measurement of the total heat of the liquid for which some extrapolated values had been used before, and finally the construction of the $I\phi$ chart. This chart has been constructed graphically, as the $\theta\phi$ chart was, directly from the observed data and its accuracy checked in various ways by thermodynamic equations. These equations apply quite generally to all $I\phi$ charts and are independent of the particular properties of carbonic acid.

The value of the $I\phi$ chart in all calculations connected with refrigeration was originally pointed out by Mollier, and has recently been emphasized in the Report of the Research Committee of the Institution of Mechanical Engineers (1914).

The authors hope that the new chart may be of practical use, as it extends and corrects the original one prepared by Mollier.

The experiments were made, as before, in the Engineering Laboratory at Oxford. The apparatus employed was generally similar to that used in the former experiments, but all the heat measurements were made in a new calorimeter, fig. 1, which eliminates radiation and conduction losses.

The measurements of the total heat of the gas for each pressure were made at several temperatures, so that the variation of specific heat with temperature was determined. The values of the specific heat found by these experiments were used to plot the new constant-pressure lines on the $\theta\phi$ chart. The method used for plotting these lines is explained in Appendix I. The re-measurement of the total heat of liquid CO_2 showed, as was expected, that the values previously used required correction; the liquid-limit curve of the $\theta\phi$ chart was corrected accordingly. The throttle experiments, which provide an independent check on both the gas-limit curve and constant-pressure curves, confirmed the accuracy of the pressure curves and of the limit curve above $-8°$ C., but showed that a small correction was required below that temperature. This correction having been made, the chart was completed by drawing the I lines in the superheated area. (See Appendix II., fig. 6.) The combined corrections of the two limit curves leave the values of the latent heat practically unaltered; the alteration at $-50°$ C. is only 0·3 per cent.

The Use of Throttling Experiments.

In a throttling experiment gas flows through a throttle valve while the pressures and temperatures are measured on each side of the valve. No other measurements are required. It is convenient to make a number of experiments starting from the same initial conditions, expanding the gas to a series of lower pressures. Such a group of experiments may be called a *line* of experiments, since it corresponds to expansion along one I line on the $\theta\phi$ chart. It is convenient to make a number of such lines of experiments all starting from the same initial pressure but from successively higher temperatures. The series of final pressures to which the gas expands must be the same in all the lines of experiments, if the method described below is to be used for plotting the results.

Throttling experiments cannot, without some other data, be used to plot any part of the $\theta\phi$ chart, but with a single constant-pressure curve they can be used to plot all the other pressure curves in the superheated area, and also the gas-limit curve. The resulting curves are not affected appreciably by errors in the total heat of the liquid (see Appendix III.), and are quite independent of errors in the latent heat, so that throttling experiments form an independent check on the accuracy of the gas-limit curve and all the constant-pressure curves.

A method of plotting the throttling experiments so as to check the constant-pressure curves is explained in Appendix IV. By this method a series of constant-pressure curves is drawn which are to be compared with the pressure curves already obtained from the specific heat measurements. If the curves coincide, the throttle experiments confirm the accuracy of the chart; if the curves are parallel but not coincident, the throttling experiments confirm the accuracy of the specific heat measurements, but indicate that there is an error in the position of the gas-limit curve, which may be shifted so as to make them coincide. If they are not parallel, there is a disagreement between the throttling experiments and the specific heat measurements and one or other must be wrong. Since shifting the gas-limit curve will make the curves, if parallel, coincide, a new gas-limit curve may be plotted derived directly from the throttle experiments—a method of doing this is described in Appendix V.; whether the new gas-limit curve is more reliable than the original depends on the reliability of the different experiments.

In order to use the methods we have adopted the throttling experiments must be arranged exactly in *lines*, and the series of lower pressures must be exactly the same in all the lines, as already stated. When actually making the experiment it is hardly possible to adjust the initial pressure and temperature and the final pressure exactly to the standard values, so that the observed results have to be reduced to standard conditions. A method of making this reduction is explained in Appendix VI.

Description of the Experiments.

Measurement of the Total Heat of CO_2 *Gas.*

The method employed in these experiments was the same as that used in the former series (Series III., p. 73), but the apparatus was modified in several details. The gas used was, as before, supplied by Messrs. Barrett and Elers, Limited; the same instruments were used for weighing the gas, measuring its pressure and temperature, and the electric heat given to it. The instruments were re-calibrated from time to time as a check, in the same manner as before.

The weighing flasks, condenser and drying flasks were the same as before, but calcium chloride was used in the drying flask instead of phosphorus pentoxide, which occasionally gave trouble. The single-stage pump was replaced by a larger two-stage pump lent for the purpose by Messrs. J. and E. Hall, of Dartford. With this pump the rate of working could be more easily controlled, and the attainment of low pressures was facilitated. The large calorimeter (No. I.) was discarded, and the evaporation and warming of the gas was done in calorimeter No. II. with the addition of a simple heating vessel made of a length of $2\frac{1}{2}$-inch steel pipe enclosing an electric heating resistance.

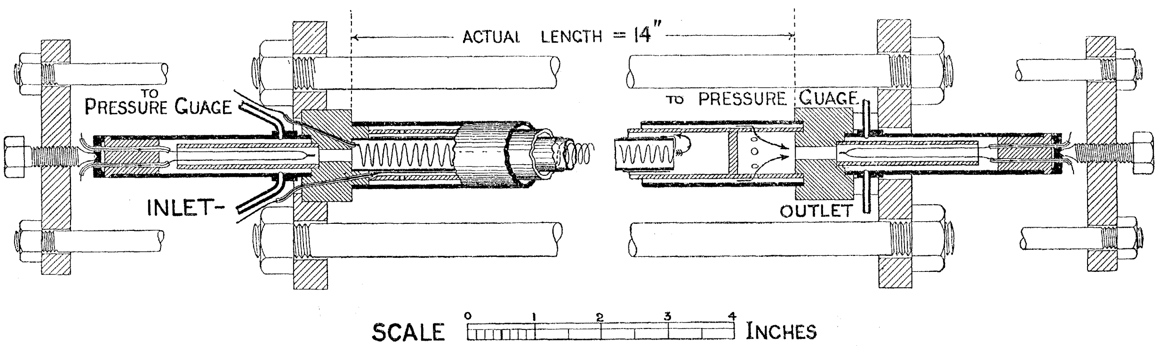

Fig. 1.

All measurements of heat were made in a new 1-inch tubular calorimeter, fig. 1. This calorimeter consists of a central body with a thermojunction fitting at each end. The central body is made up of three concentric pipes held between two vulcanite ends; the outer pipe is made of steel, the intermediate pipe of vulcanite, and the inner pipe of fused silica. Inside the inner pipe is a coil of nickel-chrome wire forming the heating resistance. Folded round the outside of the silica tube is a thin strip of copper which serves as the return lead for the current flowing through the heating coil. The whole is held together by two external bolts. The gas enters at one end, passes through the silica tube, and then returns outside the silica tube and inside the vulcanite one, and finally returns again outside the vulcanite and inside the steel tube. At each end are the two thermojunction fittings; they are the same fittings as were used with the throttle valve.

It will be seen that the temperature of the entering gas is measured just before it enters the body of the calorimeter, and the temperature of the issuing gas just after it leaves the body of the calorimeter; in neither case can the temperature of the gas in the calorimeter be affected by conduction along the pipes. Most of the experiments were made with the issuing gas at atmospheric temperature, so that the outer steel shell was at atmospheric temperature and could neither give out nor receive heat. To make this doubly sure the calorimeter was wrapped in cotton wool and placed inside a muff filled with water kept at approximately the same temperature as the shell of the calorimeter. The only remaining path by which heat can enter the calorimeter is through the left-hand vulcanite end; the amount flowing in by this path must be extremely small. There is a Hoskins alloy thermocouple clamped to the outside of the steel tube and connected to a very sensitive galvanometer which gives a deflection of 20 mm. per degree change of temperature of the junction. The electric power was regulated during an experiment so as to keep the temperature indicated by the galvanometer as steady as possible.

A few experiments were made with the issuing gas at +30° C. The muff was then heated to about the same temperature, but it is possible that a little heat leaks out at the ends of the muff, so that these experiments may be slightly wrong.

The passages through this calorimeter are rather small, so that there was an appreciable drop of pressure in the gas as it passed through it. The difference of pressure between the inlet and outlet was measured by means of a differential pressure gauge, the construction of which is shown in fig. 2. An inner glass tube dips into mercury contained in the outer steel tube. The difference of level of the mercury inside and outside the glass tube, which is proportional to the difference of pressure is measured by the change of resistance of a wire stretched down the centre of the glass tube. Several sorts of wire were tried; some made uncertain contact with the mercury, but a bright hard steel banjo wire answered very well. The resistance of the wire was measured with a simple Callendar and Griffith bridge. The gauge was calibrated by direct comparison with a glass U-gauge containing mercury. The arrangement of the valves enabled the pressure to be applied and released quickly, so that the zero and pressure readings could be repeated several times as a check on their accuracy.

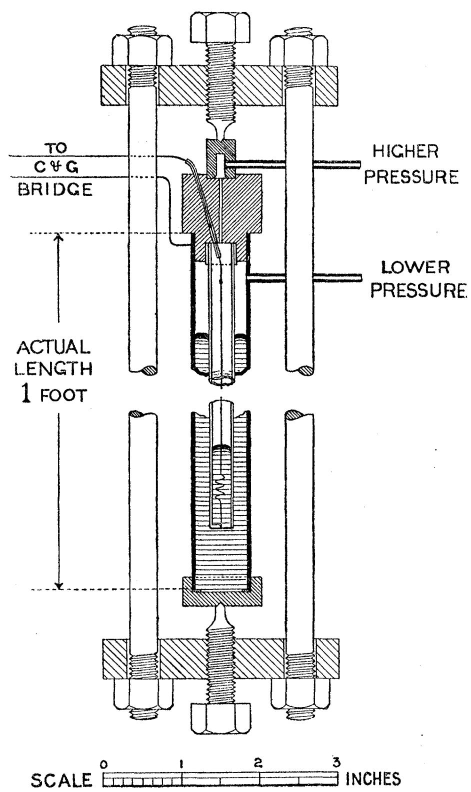

Fig. 2.

The general arrangement of the apparatus is shown in fig. 3. The liquid CO_2 from the weighing flask expands through the throttle valve V_1 and is evaporated in the $2\frac{1}{2}$-inch heater. From there it passes in the condition of nearly dry vapour into No. II. calorimeter where the evaporation is completed and the gas is warmed to the desired temperature. It then passes into the 1-inch calorimeter where its temperature is raised through an accurately measured range by the application of an accurately measured electric power. From this calorimeter it passes on through regulating valves and a drying flask to the pump, which compresses it into the condenser and so back to the weighing flasks.

The object of the $2\frac{1}{2}$-inch heater was to facilitate the regulation of the temperature of the gas. By adding most of the heat necessary for evaporation in the $2\frac{1}{2}$-inch

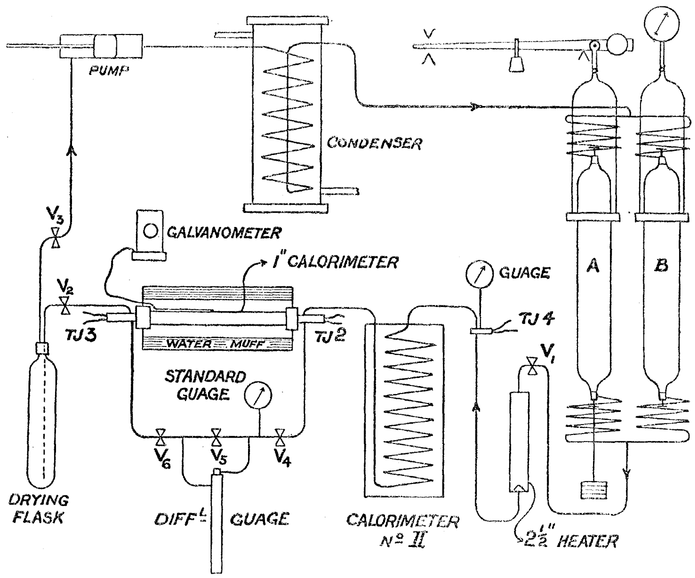

Fig. 3.

heater, the temperature of calorimeter No. II. could be kept only a few degrees above the required gas temperature, so it acted as a steadying reservoir of heat. Without the $2\frac{1}{2}$-inch heater the arrangement was unstable, for then the calorimeter No. II. had to be kept much warmer in order to transfer sufficient heat to the vapour. The point where the vapour became dry was then near the top of the coil, and the least variation in the rate of flow made this point move up or down and so left a varying amount of surface for superheating the gas, the temperature of which, therefore, varied widely. For experiments at low pressures, viz., 150, 200, 300 and 400 lbs. per square inch, the speed of flow was controlled by the valve V_1 while V_2 and V_3 were open. For the experiment at 500 lb. V_3 was also partially closed. For the experiments at 600 and 700 lb. V_3 was open and V_2 was partially closed. For the 700-lb. experiment the weighing flask had to be slightly warmed by a gas ring. During an experiment the valve V_5 was kept open and V_6 closed, so that the standard pressure gauge read the gas pressure p_1, and the differential pressure gauge was in equilibrium, which avoided any danger of blowing the mercury out of it. Just before the end of each experiment the valve V_5 was closed and V_4 and V_6 opened and readings taken on the differential gauge.

The quantities measured in an experiment were :—

The rate of flow of the gas.
Its initial pressure and the drop of pressure in the calorimeter.
The temperatures of the gas entering and leaving the calorimeter.
The electric power supplied to the calorimeter.

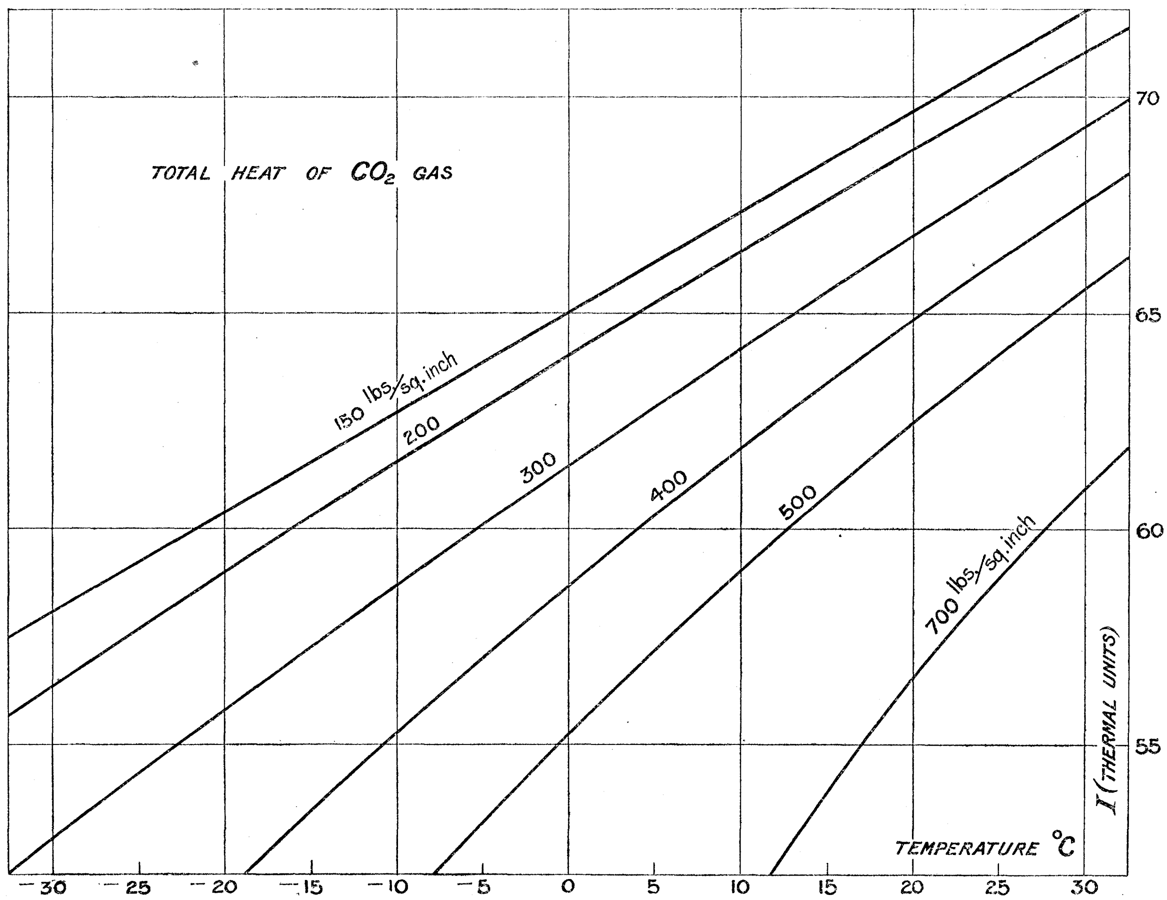

Fig. 4.

The following quantities were also noted :—

The temperature of the muff and of the atmosphere.
The galvanometer readings.

The results are given in Table A (p. 376), arranged in the same way as in Table IV. of the former paper. The correction for the small drops of pressure in the calorimeter is explained in Appendix VII. The results are plotted in fig. 4.

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The values of the mean specific heat of the gas for 10° C. intervals have been measured from the curves and are given in Table B. The pressure curves in the $\theta\phi$ chart were plotted with these values, by the method explained in Appendix I., after the limit curve had been corrected by the throttle experiments.

The values of the specific heat for each pressure at temperatures varying by 50° C. intervals from $-30°$ C. to $+30°$ C., as measured from the curves, are given in Table C.

Measurement of the Total Heat of Liquid CO_2.

The experiments described in the former paper on the total heat of the liquid CO_2 were not completely satisfactory for two reasons.

(i.) The lowest temperature reached was $-39{\cdot}1°$ C., so extrapolated values had to be used for drawing the $\theta\phi$ chart between $-40°$ C. and $-50°$ C.

(ii.) The measurements made from $-39{\cdot}1°$ C and $-35{\cdot}2°$ C. (the two lowest), both had considerable corrections for "fall of bath temperature" and "radiation," amounting together to $8\frac{1}{2}$ per cent. and $5\frac{1}{2}$ per cent. respectively of the measured heat. Subsequent experience has shown that the correction for the "fall of bath

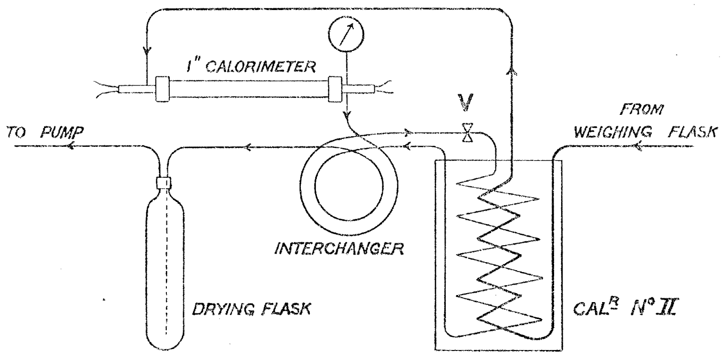

Fig. 5.

temperature" is liable to considerable error. It was assumed to be equal to the water-equivalent of the bath multiplied by the fall of temperature during the experiment. But the value of the water-equivalent of a composite body such as the calorimeter, consisting of a good heat conductor surrounded by an insulator, depends on the quantity of heat absorbed by the lagging, and this depends on the rate of change of temperature; as this may be very different in the actual experiment from what it was when the water-equivalent was measured, the value assumed for the water-equivalent may differ considerably from the effective value.

The effect of conduction along the pipes appears also to be somewhat uncertain; the correction for this was included in the radiation correction.

These considerations made it desirable to repeat the measurements of the total heat more accurately. The method employed for this purpose was the same as before (Series II., p. 72), but improved apparatus was used. By using the new 1-inch calorimeter described above, radiation and conduction losses and the correction for the change of temperature of the bath were eliminated, and the introduction of a heat interchanger enabled the temperature of the liquid to be carried down to −50·6° C., eleven degrees lower than before. The interchanger is made of two concentric copper pipes, 10 feet long, coiled into a ring 9-inch diameter. It is the same piece of apparatus which is described in the former paper on p. 92. By means of this

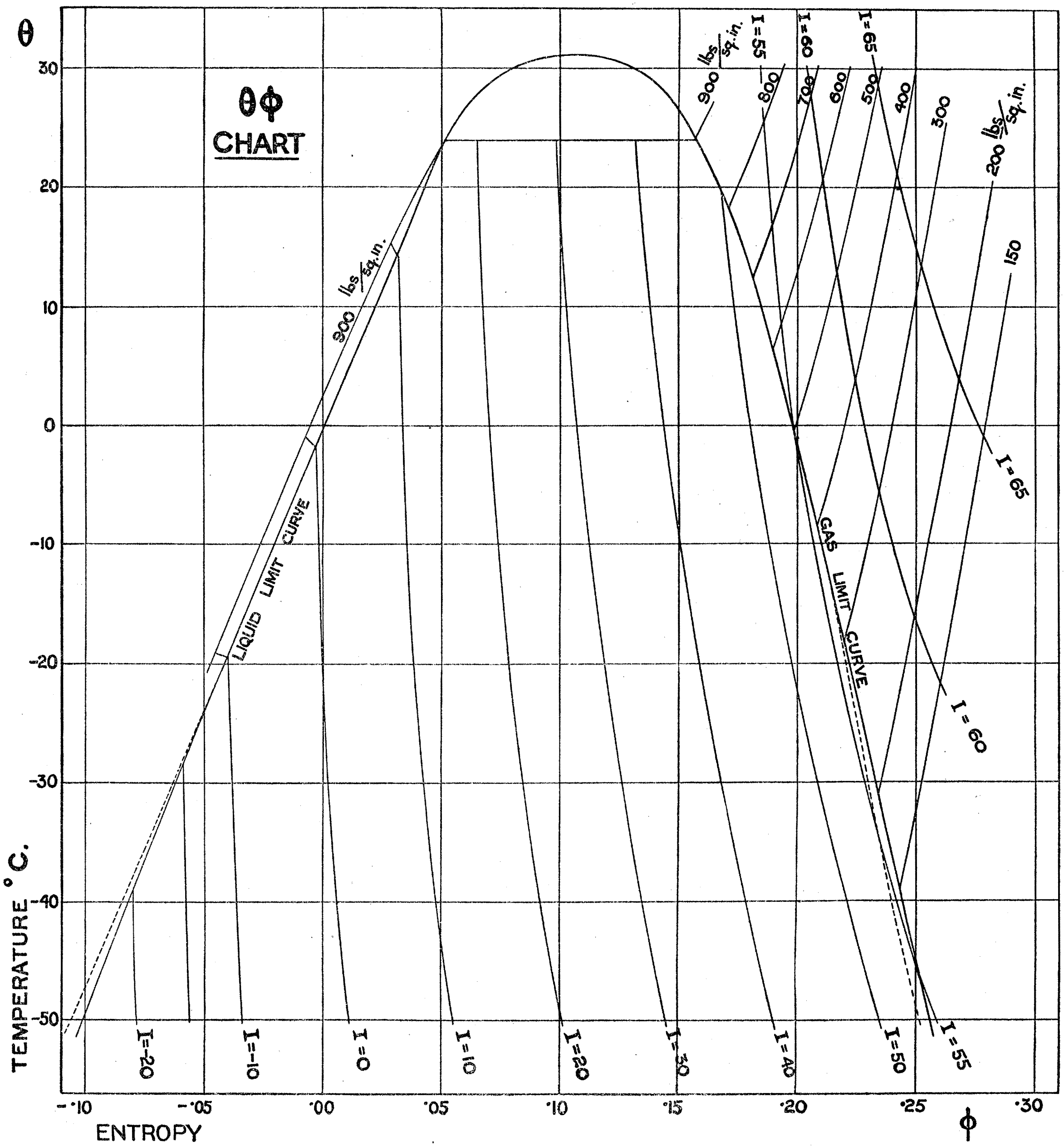

Fig. 6.

interchanger the liquid CO_2 was cooled before passing the throttle valve by the cold gas leaving calorimeter II., an arrangement which considerably increases the available refrigeration; it was only used for the last experiment at the lowest temperature.

The arrangement of the apparatus (including the interchanger) is shown in fig. 5.

The liquid from the weighing flask passes through one coil in calorimeter II. and then through the 1-inch calorimeter, then through the inner coil of the interchanger and expands through the valve V into the second coil in calorimeter II.; from there it passes through the outer coil of the interchanger, through the drying flask to the pump. The liquid is cooled to the desired starting temperature in calorimeter II. It is then warmed through an accurately measured range of temperature in the 1-inch calorimeter by the accurately measured electric power. The warm liquid is cooled in the interchanger and then, by expanding through the valve into the second coil, cools the calorimeter II., thus supplying the refrigeration required to cool the liquid in the first coil. The cold gas passing out of calorimeter II. serves finally to cool the liquid in the interchanger and then passes to the pump.

The quantities measured were :—

The rate of flow of the liquid CO_2.
The rise of temperature of the liquid in the 1-inch calorimeter.
The electric power supplied to the 1-inch calorimeter.

The results of the experiments are given in Table D, arranged in the same way as in Table III., of the former paper. The new results have been used to correct the liquid-limit curve on the $\theta\phi$ chart (see fig. 6), where the full line is the new and the dotted line the old curve. The maximum correction, at $-50°$ C., amounts to 0·0054 carnots and decreases to zero at $-20°$ C.

A correction of the limit curve produces a very small correction on the I lines, as is explained in Appendix III. The I lines have been shifted 0·0005 to the right at $-50°$ C.—too small a distance to be shown in the figure.

Throttling Experiments on Superheated Gas.

Throttling experiments are simple and quickly made. The only four quantities to be measured are the pressures and temperatures before and after the throttle valve. The rate of flow is immaterial; it is only necessary to adjust the apparatus till the conditions are steady and then to take the four readings. The throttle valve used in the new experiments was the same one that was used for the experiments on throttling the liquid CO_2 described in the former paper (Series IV., p. 91).

The arrangement of the apparatus is shown in fig. 7. The liquid CO_2 coming from the weighing flasks expands through the valve V_1 into the $2\frac{1}{2}$-inch heater where it is evaporated and then passed into calorimeter II., where it is warmed to the required initial temperature. It then passes through the special throttle valve where the pressure falls to the required lower pressure, and so through the drying flask to the pump. The valve V_2 serves to regulate the lower pressure when necessary.

The results are given in Table E where each line of experiment is denoted by a letter (column 1).

Columns 2 and 3 give the *standard* initial and final pressures.

Columns 4, 5, 6 and 7 the *observed* gauge pressures and corresponding absolute pressures.

Column 8 gives the *observed* initial temperature.

Column 9 gives the same temperature $+dt_1$ (see Appendix VI.).

Column 10 gives the *standard* initial temperature.

Column 11 gives the *observed* final temperature.

Column 12 gives the same temperature $+dt_2$ (Appendix VI.).

Column 13 gives θ_2 which is the observed final temperature $+dt_2+dT_2$ (Appendix VI.).

The lines of throttle experiments do not all extend over the same range of pressures.

Lines H, J, K, L, Q and R extend from 600 to 200 lb. (J misses two lines.)

M extends from 500–200.

N ,, ,, 400–200.

O ,, ,, 300–200.

M, N and O were limited at their upper ends by the maximum temperature to which the experiments could be carried. Lines S, T, U and V start at 600 but

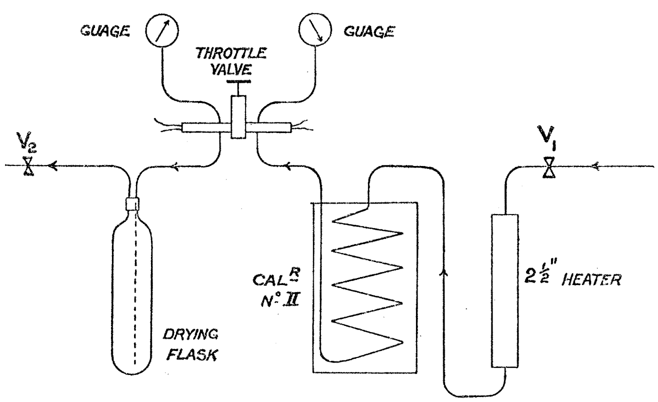

Fig. 7.

observations were only taken on the 200 and 150 curves. They were made to link on the 150 curve, which had been omitted from the earlier experiments. Line P extended from 700 to 600 and 500. This was the only line taken up to 700-lb. pressure.

These results were plotted on the $\theta\phi$ chart in the way explained in Appendix IV. The results for the 700, 600, 500 and 400 pressure curves were found to coincide with the curves already plotted, and the results for the 300, 200 and 150 pressure curves were parallel to the curves already plotted, thus confirming the values of the specific heats used to plot these curves, but indicating that the limit curve required a small shift at pressures below 400; the limit curve was accordingly redrawn below the 400 curve in the way explained in Appendix V. (see fig. 6), in which the full line represents the new curve and the dotted line the old curve. The maximum shift, at −50° C. is 0·0042 carnots. The three pressure curves, 300, 200 and 150 were then redrawn to start on the new limit curve, and the throttle experiments for these curves replotted. The calculations, made as explained in Appendix IV., for this second plotting are set out in Table F, which gives the co-ordinates θ and ϕ for the points on each line. The co-ordinates are arranged in columns; each column contains the results for one curve, the value of the pressure being stated at the top of the column. The second line in each column gives the value of I on the limit curve for that pressure.

The 400-pressure curve was assumed to be correct in plotting the results of all lines which had readings on that curve, *i.e.*, H, J, K, L, M, N, Q and R. The O line was plotted from the 300-pressure curve and S, T, U, V, from the 200 curve. P was plotted from the 500 curve. The results, with the three bottom curves replotted in this way, should all fall on the pressure lines: the agreement is remarkably good, the errors being too small to show in fig. 6. The alteration in the two limit curves which are shown to be necessary by the new experiments leave the width of the diagram between the limit curves practically unaltered, so that the values previously obtained for the latent heat are hardly changed.

The reasons for accepting the modification of the bottom of the gas-limit curve are as follows: the extreme simplicity of the throttling experiments make errors improbable. The close agreement between all the specific heat experiments and all the throttle experiments over wide ranges of temperature makes any systematic error in the throttle experiments improbable. The close confirmation of the accuracy of the upper part of the limit curve also supports the accuracy of the throttle experiment. The temperatures reached in the throttle experiments were *lower* than those given by the uncorrected chart. Had there been errors in the throttle experiments due to conduction or radiation the difference would have been in the other direction.

Construction of the Iϕ *Chart.*

The chart (Plate 6) is plotted on skew co-ordinates, the angle between the axes being arc-tan (−0·3 degrees). The vertical I scale is 1 inch = 5 Th.U.; the horizontal ϕ scale is 1 inch = 0·005 carnots. The whole chart is divided into a skew graticule, the distance between horizontal lines being 1 Th.U. ($\frac{1}{5}$ inch), and the horizontal distance between the sloping lines being 0·01 carnots (2 inch).

The part of the chart from − 50° C. to + 23° C. (and the super-heated area up to + 30° C. for pressures below 800) represents the results of the authors' experiments. The rest of the chart has been completed by using Mollier's (2) limit curve (approximately) and Amagat's (3) results for the relation between pressure, volume and temperature. These data alone are not sufficient—some data on heat quantities are necessary; we have therefore used Joly's (4) experiments on the specific heat at constant volume, which cover a considerable range (between the lines J_1 and J_4 on the chart), and for the rest of the area we have assumed a value for the specific heat at constant volume, viz., $C_V = 0{\cdot}214$. This assumption is probably close to the truth, since this value, found by JOLY for the line J_4 is exactly equal to the value deduced from our own experiments for the line A. MOLLIER assumed that C_V was constant and equal to 0·182 for the whole of the area outside the limit curve.

It would appear at first sight that most of the $I\phi$ chart might be constructed by simply replotting the $\theta\phi$ chart on the new co-ordinates, and our first chart was plotted in this way, but when it was checked it was found to be inaccurate. Investigation showed that the errors were due to three causes; the difficulty of reading the I values accurately enough from the $\theta\phi$ chart; the insufficient accuracy of MOLLIER's (5) table of AMAGAT's results which we had used; and lastly a small error in the limit curve which was greatly magnified when transferred to the new co-ordinates, where the ϕ scale is about five times as large as in the $\theta\phi$ chart. MOLLIER's table gives AMAGAT's results in a very convenient form; it is accurate enough for most purposes, but not for plotting the volume lines of the $I\phi$ chart, particularly near the critical point. We found it necessary to plot AMAGAT's results and interpolate graphically to obtain the required data with sufficient accuracy. The errors in the first chart led us to devise a number of ways of checking it, many of which turned out to be most useful in reconstructing it. For this purpose the following equations connecting the total heat I with the other variables, p, v, θ and ϕ are useful.

(1) The slope of any constant-pressure curve in an $I\phi$ chart is equal to the temperature, or

$$\left(\frac{dI}{d\phi}\right)_p = \theta. \qquad \text{(i)}$$

(2) The slope of any constant-temperature curve in an $I\phi$ chart is equal to the absolute temperature minus $\dfrac{1}{\text{the dilatation}}$, or

$$\left(\frac{dI}{d\phi}\right)_\theta = \theta - v\left(\frac{d\theta}{dv}\right)_p. \qquad \text{(ii)}$$

Cor. 1. At the critical point the limit curve, the constant-temperature curve, and the constant-pressure curve are mutually tangent to one another, and their slope is equal to the critical temperature. There is a point of inflexion in the constant-temperature curve, and the curvature of the constant-pressure curve is zero at this point.

Cor. 2. Constant-pressure curves do not change their direction on crossing either limit curve.

Cor. 3. There is no point of inflexion in any constant-pressure curve; curves of the shape shown by MOLLIER (7) for the 80 and 90 kg. curves in the CO_2 chart are therefore impossible.

Cor. 4. The slopes of all the constant-pressure curves are the same at the points where they are cut by any one temperature curve. Thus every constant-pressure curve on the CO_2 chart has the same slope at the point where it is cut by the 35° C. temperature curve, viz., 308.

Cor. 5. The slope of the constant-temperature curves is a convenient measure of the "imperfectness" of the gas, for the slope is equal to the difference between the reciprocals of the dilatation of a perfect gas and of the gas represented, *i.e.*,

$$\text{slope} = \frac{1}{\text{dilatation of perfect gas}} - \frac{1}{\text{dilatation of actual gas}}.$$

(3)
$$\left(\frac{dI}{dv}\right)_p = \frac{\theta}{J}\left(\frac{dp}{d\theta}\right)_\phi \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(iii)}$$

(4) The slope of any I curve in a $\theta\phi$ chart may be expressed in any of the following forms :—

$$\left(\frac{d\theta}{d\phi}\right)_I = \frac{\theta}{C_p}\left[1-\frac{\theta}{v}\left(\frac{dv}{d\theta}\right)_p\right] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (\text{iv}a)$$

$$= \frac{\theta}{C_p} - \frac{\theta^2}{v}\left(\frac{dv}{dI}\right)_p \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (\text{iv}b)$$

$$= \frac{\theta}{C_p} - \frac{J\,.\,\theta}{v}\,.\left(\frac{d\theta}{dp}\right)_\phi \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (\text{iv}c)$$

Equations (iv$b$) and (iv$c$) are particularly useful in the saturated area, where they reduce to :—

$$\left(\frac{d\theta}{d\phi}\right)_I = \frac{\theta^2}{v}\,.\,\frac{V_2-V_1}{I_2-I_1} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (\text{iv}d)$$

and

$$\left(\frac{d\theta}{d\phi}\right)_I = \frac{J\theta}{v}\,.\,\frac{d\theta}{dp} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (\text{iv}e)$$

of which the first is the more convenient.

Cor. 1. Equation (iv$d$) may be written :—

$$\left(\frac{d\theta}{d\phi}\right)_I = \frac{\theta^2}{V_1+x\,(V_2-V_1)} \times \frac{V_2-V_1}{I_2-I_1}$$

where x is the dryness fraction. Thus the slope of I lines varies with x across the $\theta\phi$ chart from one limit curve to the other.

Cor. 2. The forms (iv$a$), (iv$b$) and (iv$c$) become indeterminate at the critical point, but (iv$d$) or (iv$e$) may be used. For CO_2 the slope of the I line at the critical point is about 3730.

Cor. 3. The horizontal distance $\delta\phi$ between two constant-temperature lines in the saturated area of the Iϕ chart which differ in temperature by $\delta\theta$ is

$$\delta\phi = \frac{V}{\theta^2} \cdot \frac{I_2 - I_1}{V_2 - V_1} \, \delta\theta.$$

The distance may be found for any value of ϕ by using the corresponding value of V (depending on the dryness).

This expression was used in plotting the Iϕ chart to find the distance of the 30° C. line from the 23·2° C. line (900 lb.) and the distance of the critical point from the 30° C. line.

Using the above equations as checks a second Iϕ chart was drawn, plotting from the original data as far as possible instead of copying from the $\theta\phi$ chart. During construction it was constantly checked by the above formulæ and small corrections made; in this way we finally arrived at a result which represents all the experimental data and also complies with the above general theorems. The only part of the diagram which does not fit in quite satisfactorily is the short piece of the liquid-limit curve between +10° C. and +23° C.

In order to make sure of the remarkable form of the temperature curves on the left of the diagram, these curves were extended some distance further than they are shown. There was no difficulty in doing this, since AMAGAT'S results go to much higher pressures, but as the pressures increased we found it impossible to make the slopes of the pressure curves comply with equation (i). This discrepancy appears to point to some variation in the specific heat at constant volume in this region. As there are no data available we have omitted the curves beyond 1800 lb., up to which pressure the discrepancy is very slight.

If the chart be examined it will be seen that JOLY'S experiments and ours overlap and may therefore be compared. JOLY measured C_v and we measured C_p; to compare the results it is necessary to obtain an equation connecting the two. The most convenient equation is

$$C_p - C_v = A\theta \left(\frac{dp}{d\theta}\right)_v \left(\frac{dv}{d\theta}\right)_p \quad \ldots \ldots \ldots \quad \text{(i)}$$

a form which may be derived directly from the fundamental thermodynamic relations, and is quite general.

The familiar relation for a perfect gas—

$$C_p - C_v = Ap \left(\frac{dv}{d\theta}\right)_p$$

does not give even approximate results. Comparing JOLY'S results with ours by equation (i) and using AMAGAT'S figures to obtain the differential coefficients, we found that they agreed within the limits of accuracy of JOLY'S experiments.

The first lines drawn on the Iϕ chart were the 700-lb. line from zero down to

$-50°$ C. and the 900 line from zero up to $+23·2°$ C. where it meets the limit curve. The starting points for these curves are the points

$$I = +0·64, \qquad \phi = -0·0024 \text{ for 700-lb. line.}$$
$$I = +0·44, \qquad \phi = -0·0049 \text{ ,, 900-lb. ,,}$$

The limit curve from $-50°$ C. to $+23·2°$ C. was then set off from these curves; it passes through the zero temperature point where $\phi = 0$, $I = +0·9$. The sloping straight lines corresponding to pressures in the saturated area from 900 lb. to 150 lb. were then drawn from the limit curve at slopes equal to their temperatures. The gas-limit curve was then determined by marking points on each of these pressure lines at values of ϕ taken from the $\theta\phi$ chart. The apex of the limit curve was then plotted by means of equation (iv) Cor. (3).

The gas-pressure and temperature curves up to $+20°$ C. were then plotted from the throttle experiments; and starting from the 20° C. line JOLY'S four constant-volume lines J_1, J_2, J_3 and J_4 were plotted, ten degrees at a time, by means of the expressions $\delta I = C_v\delta\theta + Av\delta p$ and $\delta\phi = C_v \log_e \frac{\theta_2}{\theta_1}$ using JOLY'S values for C_v. Several more constant-volume lines were then drawn between J_4 and 0° C. in the liquid area, assuming that $C_v = 0·214$. The values of δp were in all cases calculated from AMAGAT'S data. The points on all these volume lines were then marked where they are cut by the constant-pressure curves—again using AMAGAT'S data. The constant-temperature curves for 10° C. intervals were then drawn through the points already marked on the volume lines. The constant-pressure curves were then drawn by drawing an envelope of tangents passing through the points already marked on the volume lines. Any error in the chart was shown up to this stage by the envelope of tangents missing the marked points on some of the volume lines. This check is a very rigorous one. An error of $\frac{1}{10}$ thermal unit in the position of the liquid-limit curve will throw a pressure curve $\frac{1}{5}$ inch away from the point it has to pass through.

AMAGAT'S data do not go below zero, so a different procedure was necessary for the liquid area below zero. Constant-temperature lines were drawn at $-25°$ C. and $-50°$ C.; the first is horizontal because $\left(\frac{d\theta}{dp}\right)_I = 0$ at $-25°$ C. as is shown in fig. 9 of the former paper; the second slopes upwards at an angle which can be calculated from the formula

$$\left(\frac{dI}{dp}\right)_\theta = -\left(\frac{dI}{d\theta}\right)_p \cdot \left(\frac{d\theta}{dp}\right)_I$$
$$= C_p \times \text{throttle drop* per 100 lb.}$$

using the data given in Table VIII. of the former paper, extrapolated to $-50°$ C.

* The throttle drop per 100 lb. is given in fig. 9 of the former paper, where it is called the Joule-Thomson effect.

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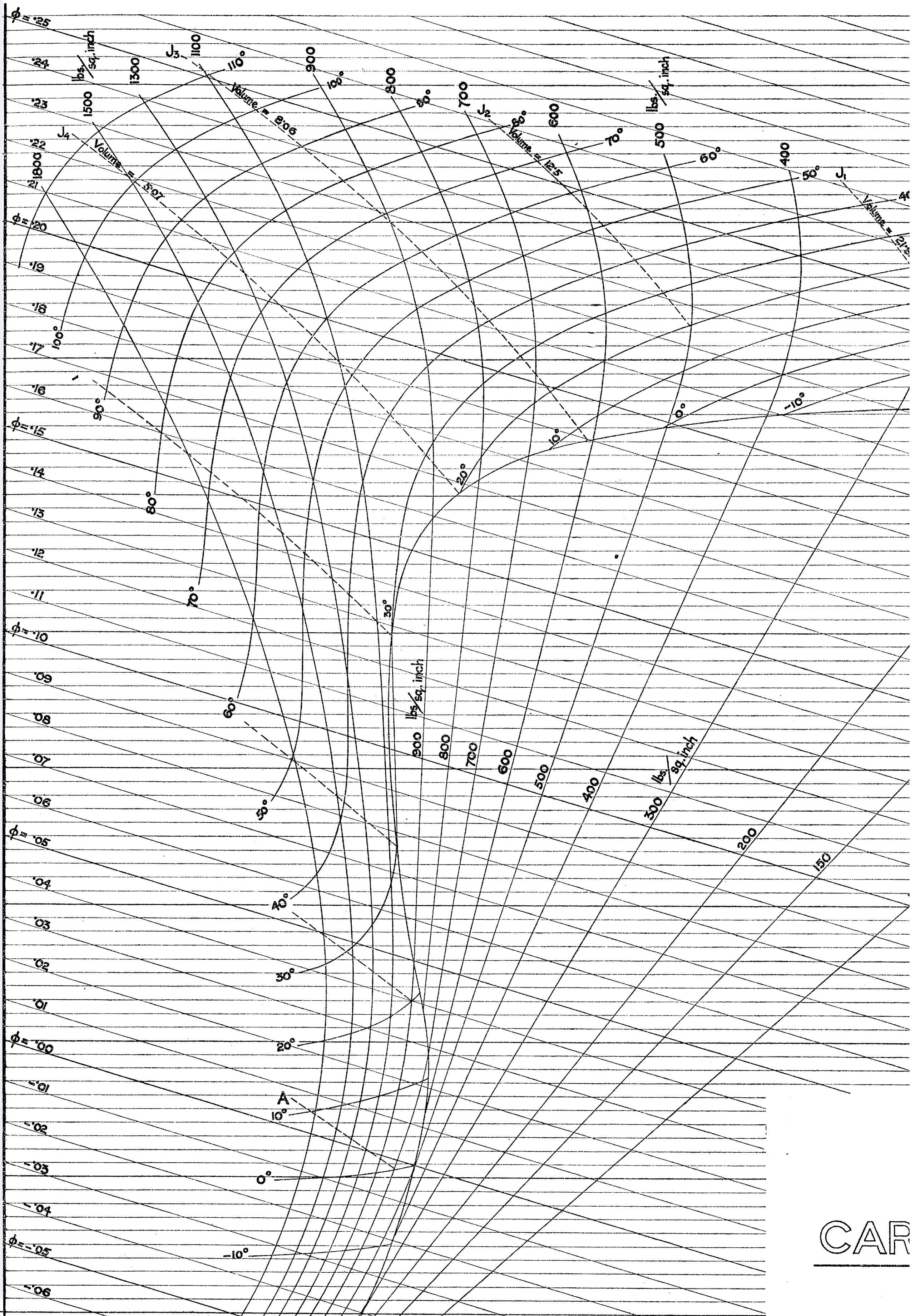
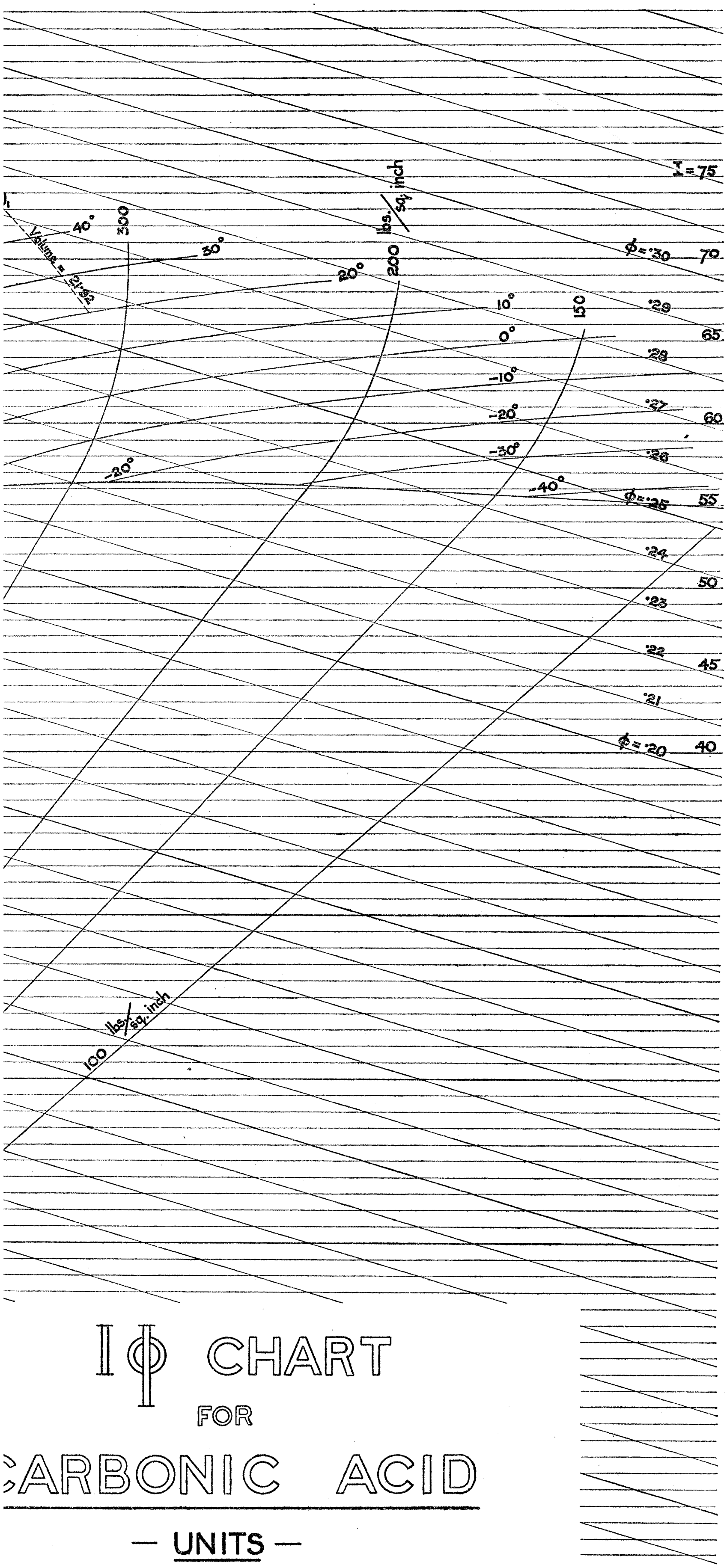


ϕ = ·25
·24
·23
·22
·21
ϕ = ·20
·19
·18
·17
·16
ϕ = ·15
·14
·13
·12
·11
ϕ = ·10
·09
·08
·07
·06
ϕ = ·05
·04
·03
·02
·01
ϕ = ·00
-·01
-·02
-·03
-·04
ϕ = -·05
-·06
-10
lbs/sq. inch
1800
1500
1300
1100
900
800
700
600
500
400
lbs/sq. inch
J₁
J₂
J₃
J₄
Volume = 2·06
Volume = 5·07
Volume = 12·5
Volume = 21·5
110°
100°
90°
80°
70°
60°
50°
40°
30°
20°
10°
0°
-10°
A
lbs/sq. inch
900
800
700
600
500
400
300
200
150
lbs/sq. inch
CAR



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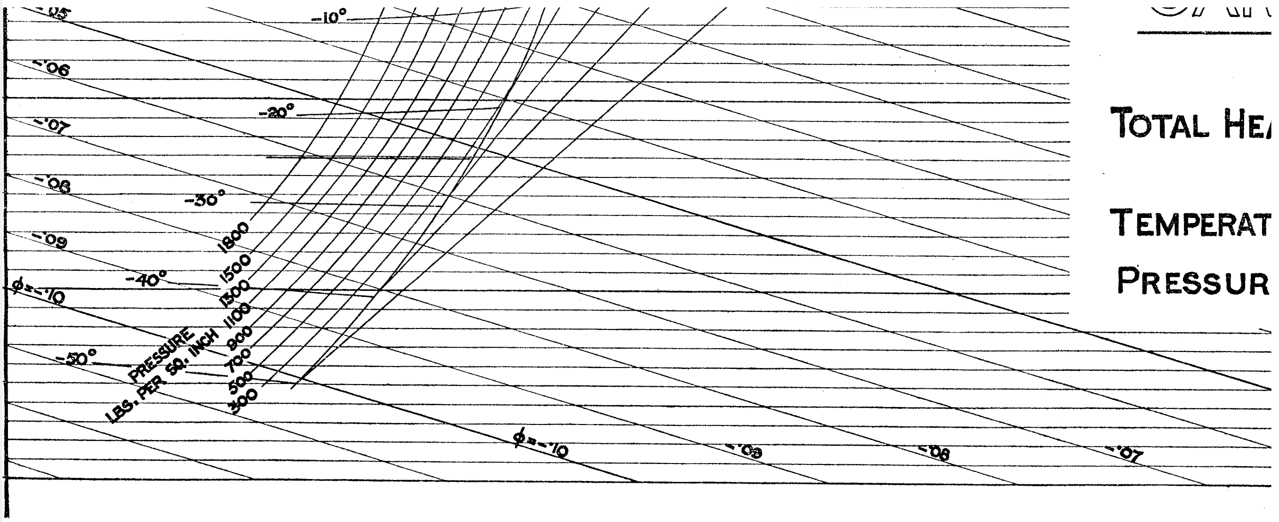
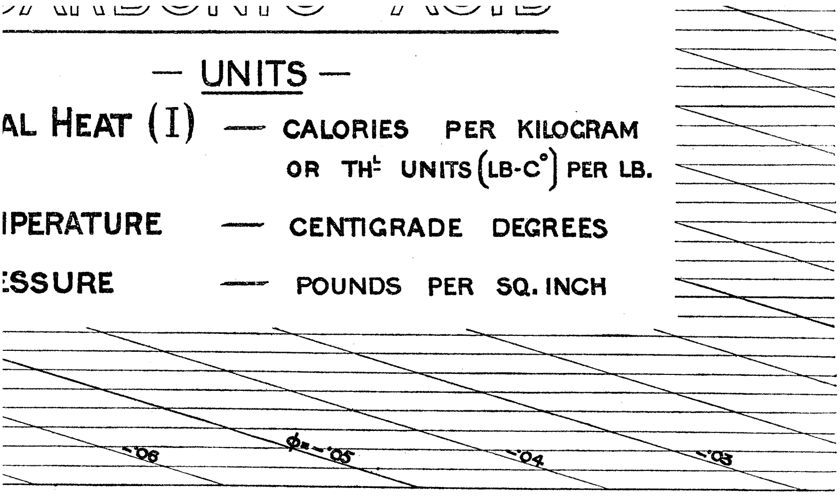


To face p. 368.

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


— UNITS —
AL HEAT (I) — CALORIES PER KILOGRAM
OR THL UNITS (LB-C°) PER LB.
IPERATURE — CENTIGRADE DEGREES
SSURE — POUNDS PER SQ. INCH
-·06
φ=-·05
-·04
-·03

The spacing of the pressure curves on the horizontal -25° C. temperature line is given by the expression

$$\delta\phi = \mathrm{A}\left(\frac{dv}{d\theta}\right)_p \delta p,$$

the values of $\left(\frac{dv}{d\theta}\right)_p$ were calculated from fig. 11 of the former paper.

The spacing of the pressure lines on the -50° C. temperature line was assumed to be uniform, which must be close to the truth as may be seen from fig. 11 of the former paper.

The pressure curves were then extended from the 0° C. volume line through the points marked at -25° C. and -50° C., keeping them similar in form to the 700-lb. line which was drawn from experimental data. The lower ends of the high-pressure curves have, however, been omitted from the final chart, because the data for plotting them were considered to be hardly sufficiently accurate.

Additional constant-temperature curves were interpolated using the above formula to give the initial slope, those above -25° C. being slightly curved to match those at higher temperatures whose form was known. These complete the $\mathrm{I}\phi$ chart.

APPENDIX I.

A Method of Plotting Constant-pressure Curves in the Superheated Area of the $\theta\phi$ Chart.

Each pressure curve starts from a point on the gas-limit curve whose temperature is given by the pressure-temperature curve for saturated vapour. Above this point it is plotted in 10° C. steps. For each vertical step of 10° C. the horizontal step, $d\phi$, is given by the equation :—

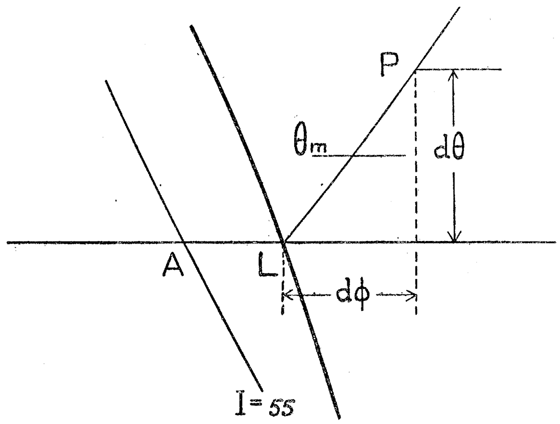
$$\theta d\phi = \sigma d\theta,$$

in which θ is the mean temperature of the step, $d\theta = 10^\circ$ C., and σ is the mean specific heat of the gas for the step (see Table B).

APPENDIX II.

A Method of Plotting I *Lines in the Superheated Area of $\theta\phi$ Chart.*

The I lines have already been drawn in the saturated area for values differing by 5 Th.U., *i.e.*, for I = 0, 5, 10, 15, &c. The last of these is I = 55. It is required to plot the lines I = 60, 65, &c., which fall in the superheated area. The line is plotted by finding the points where it crosses the pressure curves. Let ALP be any pressure curve, cutting the I = 55 line in A, and the limit curve in L. We have to find the point P on this curve where I = 60.



With the notation in the figure

$$I_L = I_A + (\phi_L - \phi_A)\,\theta_L.$$

Again

$$\theta_m d\phi = I_P - I_L$$

and also

$$\theta_m d\phi = \sigma d\theta.$$

Therefore

$$d\theta = \frac{I_P - I_L}{\sigma}.$$

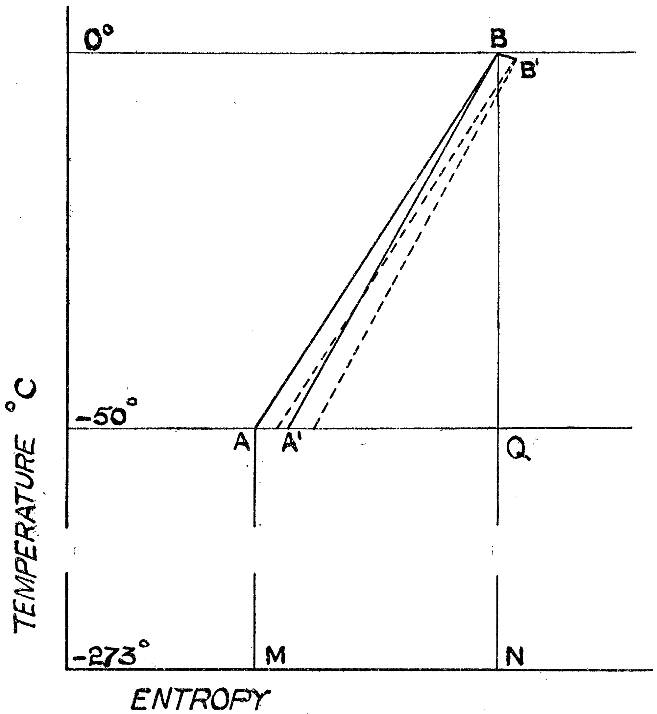
Having found $d\theta$, the point P on the pressure curve is marked off. Similar points are found on the other pressure lines and joined up, thus forming the required I curve. Points on all the curves after the first are plotted, each from the one before, by means of the equation

$$d\theta = \frac{5 \text{ Th.U.}}{\sigma}.$$

APPENDIX III.

Modifications Produced in the $\theta\phi$ Diagram by a Correction in the Values Accepted for the Total Heat of the Liquid CO_2.

If the line AB represents the constant-pressure curve, $p = 700$ lb. per sq. inch, then the area MABN under this curve down to absolute zero represents the heat required to raise the temperature of 1-lb. of CO_2 at 700-lb. pressure from θ_A to θ_B, *i.e.*, the total heat from θ_A to θ_B. If the total heat were assumed to be 5 per cent. less, then A would have to be shifted to A′, where AA′ is 5 per cent. of AQ, *i.e.*, about 0·005 carnots at −50° C. The limit curve, which is set off from the constant-pressure curve, would be shifted almost exactly the same distance to the right, pivoting round the point B′ which has the same I as B on the pressure curve.



The constant I lines would hardly be shifted. They are set out from points on the limit curve in the way explained on p. 80 of the former paper, and calculation shows that they would only be shifted about one-tenth as far as the limit curve is shifted. Thus on the $-50°$ C. line they would only be moved about 0·0005 carnots to the right.

APPENDIX IV.

A Method of Plotting the Results of Throttling Experiments.

In the following method the results of the throttling experiments are used to draw all the constant-pressure curves but one; the position of that one is assumed to be known. The pressure curves drawn in this way should coincide, if the chart is correct, with the curves drawn by means of the observed specific heat of the gas.

Let CHAA′ A″ be the pressure curve p_1, assumed to be correctly drawn, on which A, A′ ... represent the starting points of a number of experiments throttling down to a second pressure p_2. Let A be the starting point of the experiment beginning at the lowest temperature, and let the observed final temperature, when throttling down to p_2, be θ_B. Draw a horizontal line at this temperature. It is required to find the point B on this line representing the final condition.

We have

$$I_B = I_A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

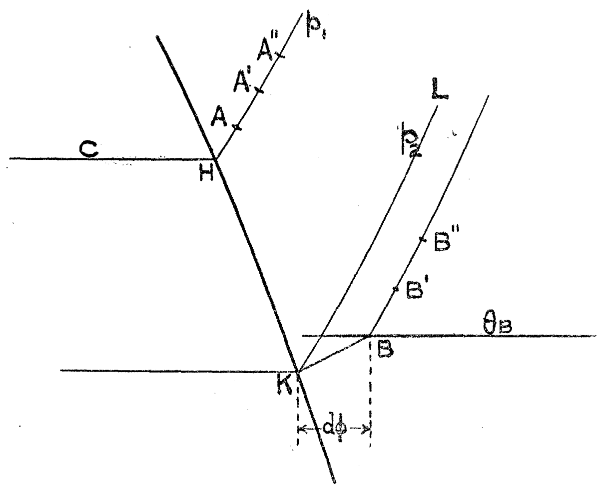
and $I_A = I_H + \sigma_1(\theta_A - \theta_C)$, where σ_1 is the specific heat of the gas at A, and I_H, on the limit curve, is known. Let K be the point on the limit curve corresponding to p_2 and let $d\phi$ be the horizontal distance between K and B.

Then

$$I_B = I_K + \frac{\theta_B + \theta_K}{2} d\phi = I_A,$$

an equation giving $d\phi$ and thus fixing B.

Choosing the next experiment, starting at A′, we find the point B′ by equating $I_{A'} - I_A = I_{B'} - I_{B'}$ and so on.



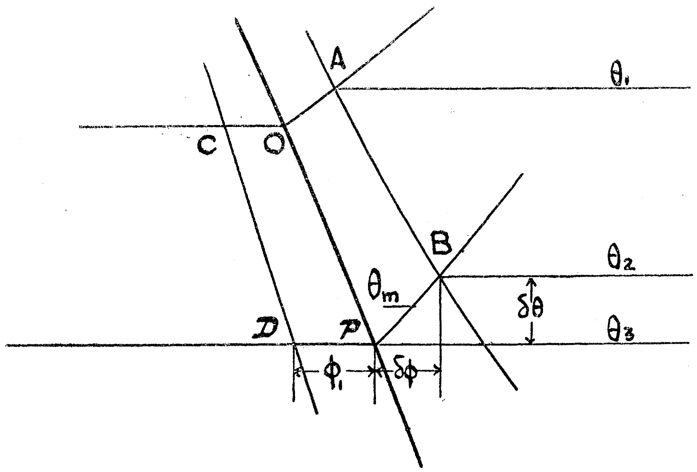
Joining up the points B, B′, &c., we have the constant-pressure curve corresponding to the pressure p_2 derived from the throttling experiments. A similar construction is used to plot the throttling results corresponding to all the other pressures. If the chart is correct the curve B, B′, B″ will coincide with KL, the constant-pressure curve plotted through K by means of the observed specific heat of the gas.

APPENDIX V.

A Method of Plotting the Gas-Limit Curve from the Results of a Line of Throttling Experiments.

The limit curve is plotted by finding the points where it cuts successive pressure curves. Let A $(\theta_1 p_1)$ and B $(\theta_2 p_2)$ represent the initial and final conditions of the gas in one of the lines of throttle experiments. COA and DPB are the pressure curves p_1 and p_2 through A and B, OP is the limit curve, and CD the last I curve in the saturation area.

We assume that the points O and A are known and we require to find P where the limit curve cuts p_2. Draw a horizontal line DP at θ_3. Then P will be fixed when $\phi_1 = \phi_P - \phi_D$ is found.



Let $\frac{\theta_2+\theta_3}{2} = \theta_m$ and δI be the difference of total heat between D and B.

Then

$$\delta I = (\phi_o - \phi_c)\theta_c + \sigma_1 \left(\frac{\theta_A+\theta_o}{2}\right) \quad \ldots \ldots \ldots \quad \text{(i)}$$

But

$$\delta I = \theta_3\phi_1 + \sigma_2\delta\theta,$$

therefore

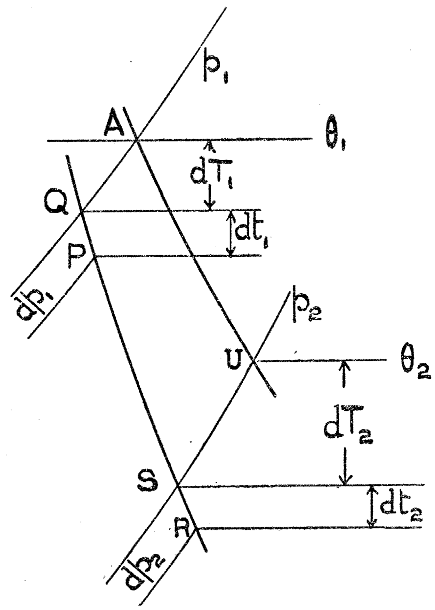
$$\phi_1 = \frac{\delta I - \sigma_2\delta\theta.}{\theta_3} \quad \ldots \ldots \ldots \ldots \quad \text{(ii)}$$

Similarly, selecting other pressure lines, we find a series of points P which all lie on the limit curve. The same method is applicable for finding points P on pressure curves above O, if O is not on the highest pressure curve. For checking our $\theta\phi$ chart the point O was chosen on the 400-lb. pressure curve.

APPENDIX VI.

A Method of Correcting the Results of a Throttling Experiment for a Small Departure from Standard Conditions.

Let A $(p_1\theta_1)$ be the standard starting point and p_2 the standard final pressure. P and R are the actual starting point and finishing point. P and R lie on an I line which cuts p_1 in Q and p_2 in S. The I line through A cuts the p_2 line in U. We have to find the temperature of U, *i.e.*, the temperature which would have been observed if the conditions had been standard.



With the notation in the figure

$$dt_1 = \left(\frac{d\theta}{dp}\right)_{\text{I}} . \, dp_1$$

$$d\text{T}_1 = \theta_1 - \theta_p - dt_1.$$

Similarly,

$$dt_2 = \left(\frac{d\theta}{dp}\right)_{\text{I}} dp_2$$

and

$$d\text{T}_2 = \frac{\sigma_1}{\sigma_2} \, d\text{T}_1.$$

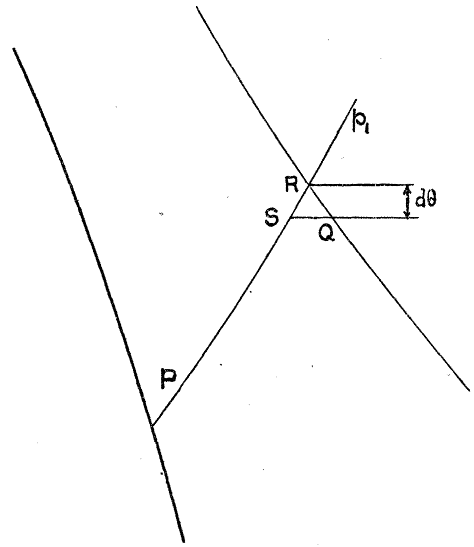
The required temperature of U, $\theta_2 = \theta_{\text{R}} + dt_2 + d\text{T}_2$.

The values of $\left(\frac{d\theta}{dp}\right)_{\text{I}}$ were measured from the $\theta\phi$ chart and plotted against temperatures, and it was found that for the range covered by the experiments the values were roughly constant for any one temperature (*i.e.*, independent of pressure). They may, therefore, be given with sufficient accuracy as follows :—

Mean temperature	° C.	30	20	10	0	– 10	– 20	– 30
$\left(\frac{d\theta}{dp}\right)_{\text{I}}$	° C./lb.	0·074	0·079	0·085	0·093	0·103	0·116	0·135

APPENDIX VII.

Allowance for the Small Drop of Pressure in the 1-inch Calorimeter when used to Measure the Total Heat of the Gas.



Let P be the point representing the condition of the gas entering the calorimeter, and Q the point representing the gas leaving the calorimeter. PR is the constant-pressure curve meeting the I curve through Q in R. Through Q draw a horizontal cutting the pressure line in S. Let the drop of pressure in the calorimeter be dp.

$$\text{The amount of heat given to the gas} = I_Q - I_P = I_R - I_P.$$

If there had been no drop of pressure in the calorimeter, this amount of heat would have raised the gas to θ_R instead of θ_Q. The actual heat given is $I_R - I_P$, but to raise the temperature to θ_Q (or θ_S), if there were no throttling, we should have needed only $I_S - I_P$. The heat may therefore be corrected by subtracting $I_R - I_S = \sigma d\theta = \sigma \left(\frac{d\theta}{dp}\right)_I \delta p$. The "throttle correction" (Table A) is calculated in this way; it is in all cases very small.

Papers, &c., Referred to.

Reference.

(1) "Thermal properties of carbonic acid at low temperatures" by Jenkin and Pye, 'Phil. Trans., Roy. Soc.,' Series A, vol. 213, p. 67 (1914).

(2) Mollier, 'Zeit. für die gesamte Kälte-Industrie,' Heft 4 and 5, pp. 65 and 85, 1895.

(3) Amagat, 'Annales de Chemie,' tome 29, 6th Series, 1893.

(4) Joly, 'Phil. Trans.' A, 1894, p. 943.

(5) Mollier, 'Zeit. für die gesamte Kälte-Industrie,' Heft 4, p. 65 (1896).

(6) Ewing, "The Mech. Production of Cold," 1908. The reference is to p. 195.

(7) Mollier, 'Zeit. des Vereins Deutsch. Ingenieure,' 1904.

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

TABLE A.—Observations on the Total Heat of CO_2 Gas.

Pressure	lb./sq. in.	150					200			
Weight of CO_2	lb.	7	6	5	6	6	10	9	9	8
Duration	min.	31·57	28·18	21·57	26·03	25·72	22·08	19·78	19·62	18·2
Initial temperature	° C.	+15·6	+11·2	−29·0	−14·6	+0·2	−23·2	−15·0	−0·5	+11
Final temperature	,,	+30·2	+29·6	+14·0	13·0	14·6	14·2	15·6	15·6	+30·7
Atmospheric temperature	,,	13·8	15·8	14·6	14·1	12·2	12·2	13·6	13·8	13·5
Muff temperature	—	29·2	29·7	11·0	12·0	15·3	14·4	15·1	14·9	29·7
Drop of pressure	lb./sq. in.	0·22	0·32	0·26	0·31	0·36	0·65	0·68	0·69	0·71
Electric heat	Th.U.	24·0	25·64	49·7	38·4	19·73	92·3	67·7	34·75	36·2
Heat per lb.	Th.U./lb.	3·43	4·28	9·95	6·41	3·29	9·23	7·52	3·86	4·53
Throttle correction	,,	0·004	0·005	0·005	0·006	0·007	0·01	0·01	0·01	0·01
Corrected total heat I	,,	3·43	4·27	9·94	6·40	3·28	9·22	7·51	3·85	4·52

Pressure	lb./sq. in.	300					400			500			700	
Weight of CO_2	lb.	11	12	12	11	10	14	14	15	16	12	10	13	8
Duration	min.	14·74	15·83	21·22	19·3	16·4	14·32	14·27	16·35	14·58	14·8	11·23	15·8	9·92
Initial temperature	° C.	−14·7	−6·2	−12·5	− 0·4	+13·4	− 2·9	+5·0	+15	+3·9	+10·05	+15·7	+15·9	15·75
Final temperature	,,	13·9	12·35	+16·1	+15·1	28·8	+15·1	15·5	29·1	13·0	19·6	30·2	21·3	28·9
Atmospheric temperature	,,	14·4	14·6	16·6	16·7	14·1	14·4	13·0	14·5	15·1	14·4	14·5	20·2	14·4
Muff temperature	—	12·4	12·0	15·0	15·0	29·8	14·9	?	29·8	12·1	20·1	29·6	15·8	29·7
Drop of pressure	lb./sq. in.	1·5	?	0·69	0·62	0·8	1·2	1·1	1·1	1·33	0·62	0·8	0·4	0·4
Electric heat	Th.U.	86·4	60·0	94·2	45·7	39·9	79·7	44·2	60·5	54·3	38·8	45·9	35·35	48·6
Heat per lb.	Th.U./lb.	7·85	5·00	7·85	4·16	3·99	5·69	3·16	4·03	3·395	3·235	4·59	2·72	6·08
Throttle correction	,,	0·03	?	0·01	0·01	0·01	0·03	0·03	0·02	0·038	0·015	0·02	0·02	0·02
Corrected total heat I	,,	7·82	5·00	7·84	4·15	3·98	5·66	3·13	4·01	3·357	3·22	4·57	2·70	6·06

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TABLE B.—Mean Specific Heats of CO_2 Gas for 10° C. Intervals.
(Measured from the curves, fig. 4.)

Note.—This table is used for plotting constant-pressure curves, see Appendix I.

Pressure.	Range.	Mean specific heat at constant pressure.
lbs. per sq. inch.		
700	12·5 to 20	0·535
	20 ,, 30	0·430
600	0 to 10	0·46
	10 ,, 20	0·415
	20 ,, 30	0·365
500	0 to 10	0·38
	10 ,, 20	0·345
	20 ,, 30	0·313
400	−10 to 0	0·34
	0 ,, 10	0·32
	10 ,, 20	0·29
	20 ,, 30	0·28
300	−20 to −10	0·291
	−10 ,, 0	0·282
	0 ,, 10	0·272
	10 ,, 20	0·262
	20 ,, 30	0·253
200	−30 to −20	0·262
	−20 ,, −10	0·255
	−10 ,, 0	0·248
	0 ,, 10	0·241
	10 ,, 20	0·235
	20 ,, 30	0·228
150	Constant	0·2315

TABLE C.—Specific Heats of CO_2 Gas at Constant Pressure.

(Measured from the curves, fig. 4.)

Temperature.	Pressure, lbs. per sq. inch.						
	150.	200.	300.	400.	500.	600.	700.
° C.							
−30	0·2315	0·270	—	—	—	—	—
−25	0·2315	0·266	—	—	—		—
−20	0·2315	0·262	—	—	—	Interpolated	—
−15	0·2315	0·258	0·292	—	—		—
−10	0·2315	0·253	0·287	—	—		—
−5	0·2315	0·250	0·282	0·342	—		—
0	0·2315	0·246	0·277	0·330	0·396		—
+5	0·2315	0·242	0·272	0·319	0·380		—
10	0·2315	0·238	0·267	0·308	0·364	0·450	—
15	0·2315	0·234	0·261	0·296	0·347	0·421	0·547
20	0·2315	0·230	0·256	0·285	0·330	0·392	0·490
25	0·2315	0·226	0·251	0·274	0·314	0·363	0·434
30	0·2315	0·221	0·246	0·263	0·298	0·334	0·378

TABLE D.—Observations on the Total Heat of Liquid CO_2.

Weight of CO_2	lbs.	13	6	8	10
Duration of experiment . .	minutes	27·87	34·4	26·33	20·65
Initial temperature	° C.	−50·6	−40·5	−38·0	−33·0
Final temperature	,,	+4·6	+5·8	+4·0	+3·4
Atmospheric temperature .	,,	8·2	11·8	13·1	14·1
Electric heat (total heat) . .	Th.U.	365	145·1	177·5	194·7
Heat per lb.	Th.U./lb.	28·04	24·2	22·19	19·47

TABLE E.—Throttle Experiments.

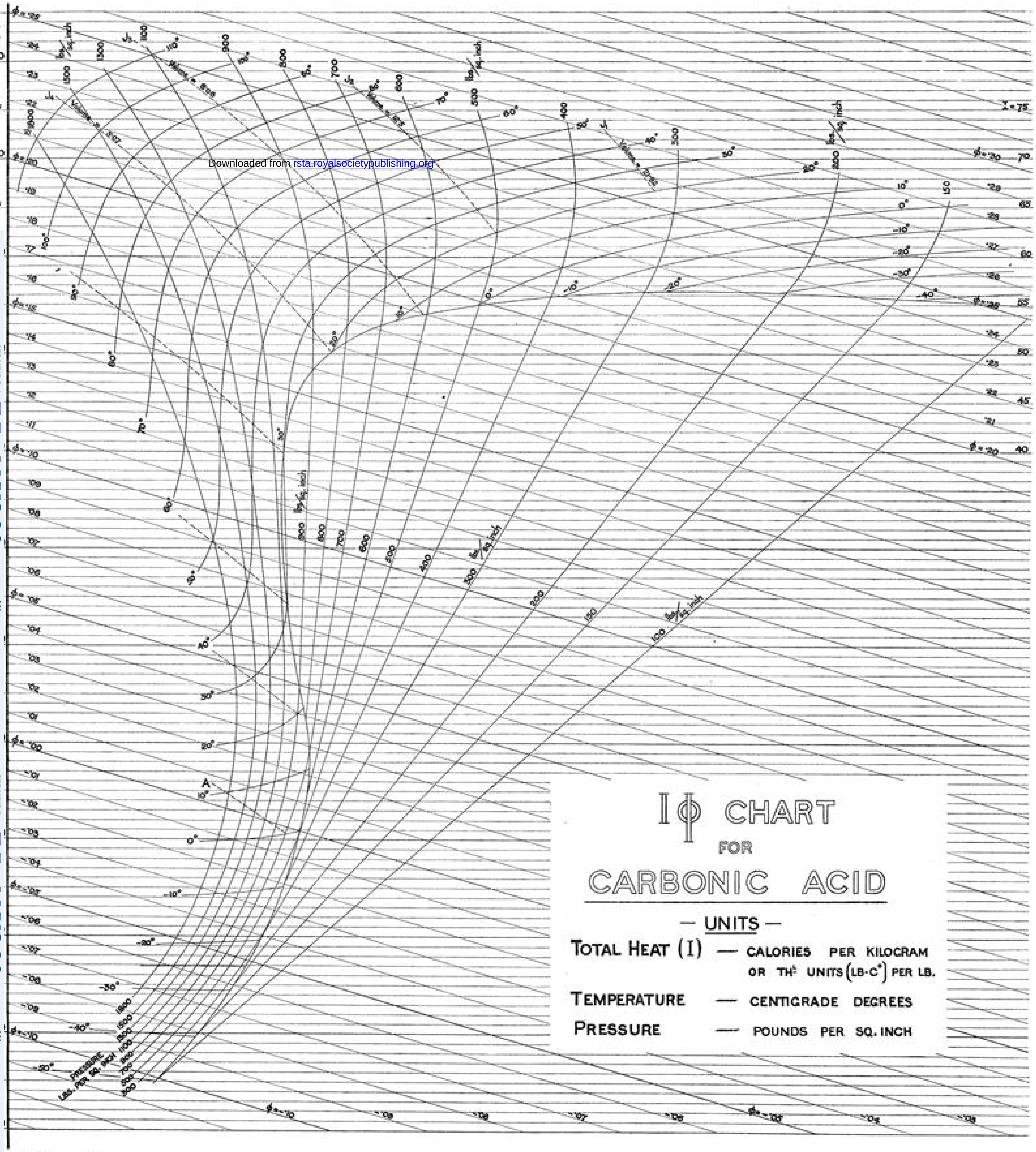
Line.	Standard pressures.		Initial pressure.		Final pressure.		Initial temperature.			Final temperature.		
	p_1.	p_2.	Observed.	Absolute.	Observed.	Absolute.	Observed.	$+dt_1$.	Standard. θ_1.	Observed.	$+dt_2$.	$+dT_2$. θ_2.
	lbs. per sq. inch.	lbs. per sq. inch.	lbs. per sq. inch.	lbs. per sq. inch.	lbs. per sq. inch.	lbs. per sq. inch.	° C.	° C.	° C.	° C.	° C.	° C.
H	600	500	594	602	483	501	29·6	29·44	29·5	+21·9	21·82	21·9
		400	593	601	383	401	29·5	29·46	—	+13·9	13·82	13·9
		300	591	599	282	299	29·6	29·68	—	+ 5·4	5·49	5·2
		200	594	602	183	201	29·6	29·44	—	− 3·7	− 3·81	− 3·7
J	600	400	593	601	382	400	12·2	12·12	12·2	− 6·7	− 6·7	− 6·6
		300	593	601	282	299	12·4	12·32	—	−17·2	−17·12	−17·3
K	600	500	592	600	481·5	500	12·9	12·9	12·4	+ 3·8	+ 3·8	+ 3·2
		400	591·5	599·5	382·5	400	12·6	12·64	—	− 6·0	− 6·0	− 6·33
		300	592	600	283·5	300	12·4	12·4	—	−16·9	−16·9	−16·9
		200	591	599	182·5	201	12·4	12·48	—	−28·8	−28·91	−29·05
L	600	500	591·5	599·5	483	501	14·1	14·14	14·2	+ 5·3	+ 5·22	+ 5·3
		400	591	599	380·5	399	14·2	14·28	—	− 4·3	− 4·22	− 4·3
		300	591·5	599·5	283	300	14·2	14·24	—	−14·3	−14·3	−14·4
		200	591	599	181	199	14·2	14·28	—	−26·0	−25·89	−26·0
M	500	400	491	500	384	402	29·3	29·3	29·3	+22·0	21·84	21·8
		300	492·5	501·5	283	300	29·1	28·97	—	+13·75	13·75	14·2
		200	491	500	182·5	200·5	29·3	29·3	—	+ 5·7	5·66	5·7
N	400	300	391	400·5	282·5	300	29·1	29·06	29·1	21·6	21·6	21·6
		200	390	399·5	181	199	29·1	29·16	—	13·7	13·79	13·75
O	300	200	290·5	300	182	200	29·1	29·1	29·1	21·7	21·7	21·7

TABLE E.—Throttle Experiments (continued).

Line.	Standard pressures.		Initial pressure.		Final pressure.		Initial temperature.			Final temperature.		
	p_1.	p_2.	Observed.	Absolute.	Observed.	Absolute.	Observed.	$+dt_1$.	Standard. θ_1.	Observed.	$+dt_2$.	$+dT_2$. θ_2.
	lbs. per sq. inch.	lbs. per sq. inch.	lbs. per sq. inch.	lbs. per sq. inch.	lbs. per sq. inch.	lbs. per sq. inch.	° C.	° C.	° C.	° C.	° C.	° C.
P	700	600 500	693 693	700 700	584·5 483	600 501	29·3 29·1	29·3 29·1	29·2 —	22·0 13·8	22·0 13·72	21·9 13·85
Q	600	500 400 300 200	592 592·5 592·5 592	600 600·5 600·5 600	484 381 282 182	502 399 299 200	24·5 24·4 24·4 24·5	24·5 24·36 24·36 24·5	24·5 — — —	16·7 7·9 − 1·0 − 10·6	16·53 7·98 − 0·92 − 10·6	16·5 8·2 − 0·7 − 10·6
R	600	500 400 300 200	592 592·5 592·5 592	600 600·5 600·5 600	485 381·5 282 182	503 399·5 299 200	20·1 20·1 20·1 20·1	20·1 20·06 20·06 20·1	20·1 — — —	11·8 2·8 − 6·7 − 17·3	11·55 2·84 − 6·66 − 17·3	11·6 2·9 − 6·6 − 17·3
S	600	200 150	592·5 592	600·5 600	182 131	200 150	13·6 13·6	13·56 13·6	13·5 —	− 27·1 − 33·8	− 27·1 − 33·8	− 27·2 − 34·0
T	500	200 150	491 491·5	500 500·5	180·5 131	199·5 150	13·5 13·6	13·5 13·56	13·5 —	− 15·1 − 20·6	− 15·05 − 20·6	− 15·05 − 20·7
U	300	200 150	292 291	301 300	182 131·5	200 150·5	13·2 13·2	13·12 13·2	13·2 —	+ 4·6 0·0	+ 4·6 − 0·05	+ 4·7 − 0·05
V	200	150	190	200	130·5	149·5	12·8	12·8	12·8	+ 8·4	8·45	8·4

TABLE F.—For Plotting Throttle Experiments.

Pressure.		150		200		300		400		500		600		700	
I on limit curve.		55·70		56·2		56·3		55·9		54·96		53·88		52·54	
Line on limit curve.	I.	θ.	ϕ.	θ.	ϕ.	θ.	ϕ.	θ.	ϕ.	θ.	ϕ.	θ.	ϕ.	θ.	ϕ.
		−38·9.	0·2430.	−30·8.	0·2339.	−18·3.	0·2200.	−8·6.	0·2089.	−0·6.	0·1990.	+6·3.	0·1900.	+12·5.	0·1813.
H	63·2	—	—	− 3·7	—	5·2	0·2459	13·9	0·2353	21·9	0·2276	29·5	0·2214	—	—
J	56·6	—	—	—	—	−17·3	0·2212	− 6·6	0·2114	—	—	12·2	0·1989	—	—
K	56·7	—	—	−29·05	0·2357	−16·9	0·2216	− 6·3	0·2118	+ 3·2	0·2048	12·4	0·1992	—	—
L	57·4	—	—	−26·0	0·2386	−14·14	0·2243	− 4·3	0·2144	+ 5·3	0·2073	14·2	0·2017	—	—
M	65·47	—	—	+ 5·7	0·2693	+14·2	0·2539	21·8	0·2431	29·3	0·2352	—	—	—	—
N	67·5	—	—	+13·75	0·2764	21·6	0·2609	29·1	0·2499	—	—	—	—	—	—
O	69·23	—	—	+21·7	0·2822	29·1	0·2667	—	—	—	—	—	—	—	—
P	60·57	—	—	—	—	—	—	—	—	13·85	0·2183	21·9	0·2126	29·2	0·2083
Q	61·47	—	—	−10·6	0·2542	− 0·7	0·2396	+ 8·2	0·2292	16·5	0·2216	24·5	0·2156	—	—
R	59·8	—	—	−17·3	0·2480	− 6·6	0·2334	+ 2·9	0·2232	11·6	0·2158	20·1	0·2099	—	—
S	57·2	−34·0	0·2492	−27·2	0·2376	—	—	—	—	—	—	Not	used	—	—
T	60·4	−20·7	0·2620	−15·1	0·2503	—	—	—	—	—	—	,,	,,	—	—
U	65·37	− 0·05	0·2807	+ 4·7	0·2689	—	—	—	—	—	—	,,	,,	—	—
V	67·3	+ 8·4	0·2876	+12·8	0·2758	—	—	—	—	—	—	,,	,,	—	—



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FOR
CARBONIC ACID
— UNITS —
TOTAL HEAT (I) — CALORIES PER KILOGRAM OR TH. UNITS (LB-C°) PER LB.
TEMPERATURE — CENTIGRADE DEGREES
PRESSURE — POUNDS PER SQ. INCH
PRESSURE LBS. PER SQ. INCH
I
A