

## EXPERIMENTAL STUDY OF THE JOULE-THOMSON EFFECT IN CARBON DIOXIDE

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### ABSTRACT

**Joule-Thomson effect in carbon dioxide.**—(1) *Experimental results for both vapor and liquid phases for 20 to 75 atm. and 0 to 120°C.* Dried CO<sub>2</sub>, after compression to a high pressure controlled by a special regulator, was brought to a definite temperature, then adiabatically expanded radially inward through the walls of a porous porcelain tubular plug, successively to each of several lower pressures controlled by a second regulator. Pressures were measured with a modified Amagat differential free-piston manometer; the temperatures before and after passage through the plug were measured by Pt resistance thermometers. Since the expansion was adiabatic, the enthalpy,  $g = (u + pv)$ , was constant, and the observations secured, properly reduced, yielded *isenthalpic throttling curves* the slopes of which determine  $\mu = (\partial t / \partial p)_g$ , the Joule-Thomson coefficient. For both liquid and vapor phases  $\mu$  is found to be a linear function of the isenthalpic temperatures and an exponential function of the isenthalpic pressures of such curves. In the liquid region  $\mu$  becomes zero at  $-24^\circ\text{C}$  for all pressures involved, and is negative at lower temperatures. The CO<sub>2</sub> used contained from 0.25 to 1.5 per cent air, but the author's results, obtained in 1910, are consistent with those of Jenkin and Pye (1914, 1915) which extended down to 10 atm. and to  $-55^\circ\text{C}$  and were obtained with purer CO<sub>2</sub>; also with those of Kester, and of Joule and Thomson, where comparable. (2) *Empirical formulas.* The entire experimental field for both phases, including the transition region in the vicinity of the critical point and along the saturation curve, has been represented by an empirical formulation, necessarily rather complicated. Isenthalps, isotherms and isobars of  $t$ ,  $p$ , and  $\mu$  computed from these formulas for the range 0 to 100 atm. from the solid-liquid phase-boundary at about  $-55^\circ\text{C}$  through the liquid field into the super-heated vapor field as far as  $+150^\circ\text{C}$  are presented in tabular and graphical form. More complete details will be given in a Bulletin of the University of Wisconsin.

**Vapor pressure of CO<sub>2</sub>,  $-20^\circ$  to  $+30^\circ$  C.**—Results obtained from the experimental isenthalpic curves are compared with those of others, and all show good agreement with Keyes' equation.

WHEN a fluid is caused to pass adiabatically through a restricted passage or a porous plug under such conditions that its kinetic energy of flow on either side of the plug is negligible, then

$$u_1 + p_1 v_1 = u_2 + p_2 v_2, \text{ or } u + pv = \text{a constant} \quad (1)$$

in which  $u_1$  and  $u_2$  are the specific intrinsic energies,  $v_1$  and  $v_2$  are the corresponding specific volumes at the respective pressures  $p_1$  and  $p_2$  before and after passing through the plug. The function  $(u + pv)$ , here designated by  $g$ , is known as the *enthalpy* of the fluid.

In a constant enthalpy porous plug expansion changes in both temperature and volume usually accompany the pressure drop across the plug; the limiting ratio of the temperature change  $\Delta t$  to the pressure change  $\Delta p$  as the latter approaches zero is variously known as the Joule-Thomson effect, the Joule-Kelvin effect, or simply the porous plug effect. This ratio, here designated by  $\mu$ , is analytically defined by the relation

$$\mu = (\partial t / \partial p)_h \quad (2)$$

The present paper contains an account of the experimental arrangements and procedure by which values of  $\mu$  for  $\text{CO}_2$  have been obtained over considerable ranges of pressure and temperature; a brief discussion of the writer's data, their subsequent treatment and combination with similar data from other sources for grouping into isenthalpic curves; a brief discussion of the considerations controlling the development of an algebraic formulation of  $\mu$  over the field covered by the data; and a comparison with the results of previous attempts by others to determine these relations.

#### EXPERIMENTAL APPARATUS

The writer's experimental results were obtained in 1910 by the use of the almost ideal conditions obtained with the "radial flow" porous plug then described by Burnett and Roebuck.<sup>1</sup> For a complete description of this apparatus and the experimental procedure the reader is referred to the detailed account of this work to be published soon as a Bulletin of the University of Wisconsin.

The carbon dioxide was circulated by a single-stage refrigerating machine compressor which limited the investigation to a pressure range extending from 20 or 25 atmospheres to 70 or 75 atmospheres. From the compressor the  $\text{CO}_2$  was passed through calcined calcium chloride for removing any water vapor that it might carry; then through a special and sensitive high pressure regulator that usually kept the initial pressure of the  $\text{CO}_2$  constant to within two or three tenths of an atmosphere at seventy atmospheres pressure. It was then delivered (see Fig. 1) to a heat interchanger wherein the high pressure fluid passed the return flow from the plug and was thereby brought to a temperature approximately that of the liquid bath surrounding the plug chamber at which it arrived after passing through about seventy feet of one-quarter inch copper tubing coiled within the bath. The kerosene oil of the bath was circulated by a propeller in the direction shown by the arrows. Variations of temperature of the air in the brass-walled air-

<sup>1</sup> Burnett and Roebuck, *Phys. Rev.* **30**, 529, 1910

chamber which also served to direct the flow of the bath liquid, resulted in pressure and volume variations of this confined air which were used to

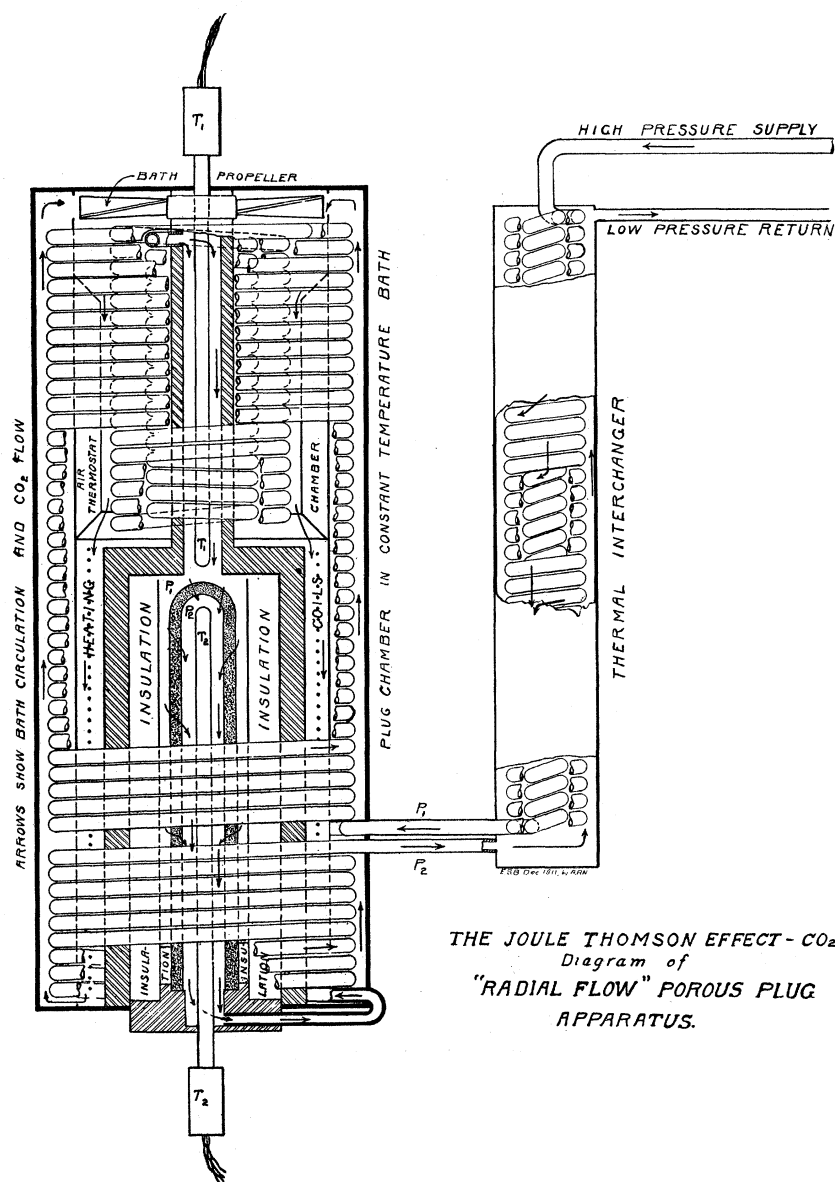


Fig. 1. Diagram of "radial flow" porous plug apparatus (approximately one-fourth size).

effect thermostatic control of the electric current applied to the heating coils located in the bath about the plug chamber.

The plug was of porous porcelain of the shape and proportions shown, copper plated at its open lower end and soldered to a steel block, details of which are not shown in the diagrammatic figure. The  $\text{CO}_2$  then passed down along the outer plug surface within a slightly larger glass tube that was surrounded by a roll of asbestos paper which insulated the plug and glass tube from the walls of the plug chamber and also effectually prevented meandering of the  $\text{CO}_2$  elsewhere than along the passage between the glass tube and the plug. It then diffused radially through the porous walls of the plug towards its inner surface, emerged at reduced pressure and temperature, and passed axially along the "low side" thermometer  $T_2$ ; at the open base of the plug it was delivered to a short copper coil located in the lower part of the bath chamber and thence to the interchanger wherein it exchanged heat with the incoming high pressure  $\text{CO}_2$ ; thence it proceeded through a low pressure regulator similar to the high pressure regulator above mentioned, and back to the compressor for re-compression and re-circulation.

Temperatures were measured, at the points shown, by two platinum resistance thermometers which could be used independently or differentially. The low side pressure was measured at the base of the plug, and the high side pressure was measured within the plug chamber outside of the plug. Pressures were measured with a modified form of the Amagat differential free-piston manometer<sup>2</sup> far more accurately than is possible with gauges of the Bourdon bent tube type.

#### CALIBRATION OF APPARATUS

*Resistance-bridge and platinum resistance thermometers.* Several calibrations of the binary scale resistances of the Callender and Griffiths' bridge by their method of substitution with the bridge wire were made during the course of these experiments. The fundamental intervals of the two platinum resistance thermometers were also checked several times during this period by comparison of their resistances at the ice and steam points; but because the range of temperature covered by these experiments was only from  $-20^\circ$  to  $+120^\circ$  C, no third point calibration was considered, since the makers (Cambridge Scientific Co.) had supplied the value 1.57 for the  $\delta$  coefficient of the platinum wire of these thermometers.

From these data a table was prepared based upon the nominal values of the bridge box coils arranged in ascending series by steps of one box unit from  $-28$  (bridge reversed) to  $+128$ , giving the corresponding

<sup>2</sup> E. H. Amagat, *Ann. de Chimie et de Phys.* (6), **29**, 1893; *Harpers Scientific Memoirs, The Laws of Gases*, p. 55.

centigrade temperatures for each thermometer after all box coil corrections, corrections for differences of fundamental intervals, and the  $\delta$  correction were applied. Some slight variations shown by these calibrations are of small moment compared to variations in experimental results that appeared from other causes.

*Differential free-piston manometer.* Careful measurements of the essential dimensions of the free-piston manometer and of the relative displacements of the levels of the mercury in the mercury well and mercury column connected therewith, upon which the pressure measurements depended, taking into proper account the density of mercury at the latitude and elevation of the laboratory and at the mean temperature prevailing during the course of these experiments, gave the relation: change of pressure on free-piston manometer (in atmospheres) = 0.6495 times the observed mercury column displacement.

#### EXPERIMENTAL PROCEDURE

Having set the bath stirrer into operation and established a circulation of fluid from the compressor throughout the apparatus, the control pressures in the regulator receivers were set to give the desired initial high pressure and lowest final pressure. The thermostat and heating circuits were then adjusted to maintain the required initial temperature with the least possible variation. As soon as constancy of conditions had become established, observations were recorded in numbers sufficient to insure proper averages, after which conditions were changed and a new steady state sought.

Observations were recorded of resistances  $R_1$ ,  $R_2$  and  $R_\Delta$ ; respectively, of the high side thermometer  $T_1$ , the low side thermometer  $T_2$ , and of these thermometers differentially connected so as to give their temperature difference  $T_\Delta$ ; also of the heights  $H_1$  and  $H_2$ , of the mercury column when the high side pressure  $p_1$  or the low side pressure  $p_2$ , respectively, was acting on the differential free-piston manometer. The time of each observation was noted; also the zero of the mercury column, its temperature and that of the bridge box, the number and nominal values of the bridge coils in use for each bridge setting, and other items as occasion demanded.

Thus series of observations were obtained corresponding to several different pressure drops across the plug from as nearly as possible the same initial high side condition. The next run would yield similar series from some different initial condition, preferably from the same high side pressure but with a different high side temperature. From these observations, when properly reduced and grouped, were obtained isenthalpic curves the slopes of which determine  $\mu$  (see Fig. 2).

*Sampling and analysis of the carbon dioxide.* Samples of the CO<sub>2</sub> were drawn from the delivery or low pressure side of the plug and were analyzed in an Orsat gas analysis apparatus. The results indicated about 0.025 per cent by volume of CO in the original samples of CO<sub>2</sub> and a trace of hydrogen. The general conclusion from the several

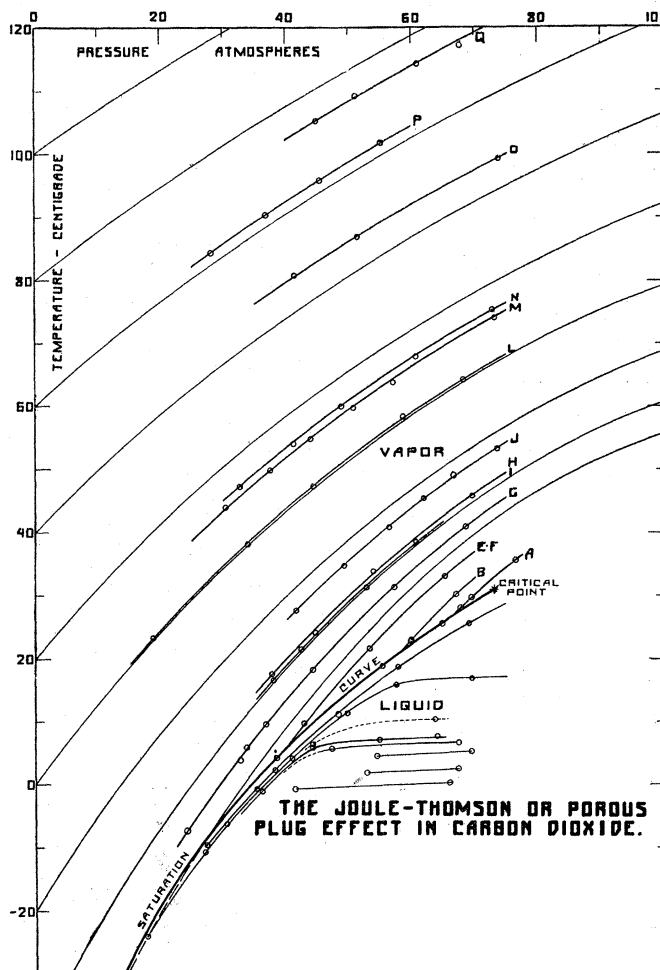


Fig. 2. Experimental isenthalpic or throttling curves; also curves computed from empirical formulation of 1913

analyses is that the volatile impurity found, which varied from about 0.25 per cent to 1.50 per cent by volume at atmospheric pressure, was mainly air in which the oxygen content was usually either normal or less than normal, ranging from 20 per cent down to 9 per cent, though one value of 24 per cent was obtained.

## REDUCTION OF THE OBSERVATIONS

*Sample set of observations.* Table I shows a sample set of observations as recorded in the log book under the headings mentioned in a previous paragraph; the other items are self-explanatory; averages are also included. This table shows that the initial-temperature variations of this particular run were not serious; also, on the whole, the pressure variations of this run were not disturbing. A vertical comparison of the means under  $R_1$  and  $H_1$  shows but slight departures from a fixed initial condition.

Table II assembles the means selected to represent the observations sampled in Table I. It also gives the complete corrected values of temperatures, temperature differences, and pressures, in degrees centigrade and atmospheres, respectively, according to the calibrations; and it gives the average initial temperature and the average initial pressure for the whole run. Column headed  $(T_1 - T_2)$  is added for comparison with the values of  $T_{\Delta}$ ; they should agree. Each line of Table II corresponds to the averages of one group of Table I and furnishes the data for one pair of points of an isenthalpic curve through the initial or high side point of the pair.

*Adjustment to standard initial point.* Deviations from the average for the run, of the initial points of the several pairs of points which serve to establish such a curve, imply corresponding deviations of greater or less magnitude of the low side points. An approximate corrective adjustment for these deviations is to shift the temperature and pressure of both points of a pair by amounts equal to the respective temperature and pressure deviations of its initial point from this average or standard initial point state. Table III shows the results of adjusting the data in this manner so that all low side points of a curve shall conform more closely to the isenthalp through a standard initial point. In columns 1 and 3 have been assembled the observed initial and low side temperatures, in columns 8 and 6 the observed initial and low side pressures, respectively, all transferred from Table II.  $T_1'$  and  $p_1'$  are the values selected as standard for the run. Column 2 gives  $(T_1' - T_1)$ , the temperature shifts, and column 7 gives  $(p_1' - p_1)$ , the pressure shifts to be added to columns 3 and 6 respectively to make their initial points approximately conform. The values of columns 4 and 5, the adjusted values, together with  $(T_1', p_1')$ , are the coordinates of the points plotted on the chart, Fig. 2, that are connected by the heavy-lined curve marked  $J$ ; the other heavy-lined curves of this chart were similarly obtained from their corresponding observations.

## THE EXPERIMENTAL ISENTHALPIC CURVES

A glance at Fig. 2 shows some of these curves intersecting the saturation curve for pure CO<sub>2</sub> near its upper end (see also Fig. 4). The observed values of pressure and temperature on the low side of the plug that fall below these intersections are distributed along the saturation curve but, to avoid confusion, are omitted from these charts. These relations show that if the porous plug expansion of CO<sub>2</sub> vapor starts from an initially superheated condition represented by any point near enough to the upper reaches of the saturation curve and be carried far enough, a part of the vapor will condense, so that the observed low side pressures and temperatures must be those of equilibrium between coexisting vapor and liquid phases. If the expansion be continued sufficiently far toward the region of low pressures the condensation of vapor will gradually decrease, re-evaporation of the condensate will ensue and eventually become complete; the isenthalp will emerge from the saturation curve at a certain low pressure and diverge therefrom toward the lower pressures and temperatures of the superheat field. This latter course of an isenthalp was not observed experimentally on account of the limitations set by the single-stage compressor available for this work; the charts do indicate however that such a course is undoubtedly the most likely one, and such a conclusion is supported by experimentally determined throttling curves for initially "wet" steam in the corresponding region of the steam field.<sup>3</sup> The charts show that there is one vapor isenthalp that just grazes the saturation curve at a point which it may be shown corresponds to that of maximum total heat of dry saturated CO<sub>2</sub> vapor.

The data for the liquid are much less satisfactory than are those for the vapor. It was much more difficult to control the experimental conditions when working with liquid CO<sub>2</sub>; more initial point variation occurred, requiring larger and more uncertain adjustments to group the data into the curves shown in the liquid field of the chart, Fig. 2. The effect of impurities more volatile than the liquid is of considerable moment in this region. Each liquid isenthalp appears to merge gradually into a saturation curve of its own corresponding to the particular mixture represented by its components—CO<sub>2</sub> and air.

*First formulation of experimental isenthalps.* The light-lined curves of Fig. 2 spaced 20° apart on the temperature axis are computed from an empirical relation derived by 1913 in the course of early and un-

<sup>3</sup> See particularly the discussion and application of the throttling experiments on steam of Peake, Grindley, Griessman, and Dodge, by H. N. Davis, Proc. Am. Acad. Arts and Sci. **45**, 241-411, 1910.



successful attempts to formulate an expression that would represent the data over the entire experimental field. The equations given below do represent very satisfactorily, however, the experimental isenthalps of the vapor field that do not intersect the saturation curve and they were of great assistance in later applying more complete and proper adjustments to all of the original data which they cover. The equation of one of these curves is

$$t = t_0 + \mu_0 p + m p^n \quad (3)$$

in which  $t$  is the temperature centigrade at the pressure  $p$  atmospheres;  $\mu_0$  is the slope of the curve at its intercept  $(t_0, p_0)$  with the temperature axis;  $m$  and  $n$  are constants;  $m$  is negative and differs for each curve;  $n$  has a value greater than unity, taken as  $5/3$  for all curves covered. The several equations of this form are connected by the following relations between their coefficients, in which  $T_0 = t_0 + 273$ ;

$$\mu_0 = 121,000/T_0^2 - 53/T_0; \quad m = -3350/T_0^2 + 0.0155 \quad (4)$$

#### LATER TREATMENT OF DATA

In the light of the studies outlined above, and of many others made then and since that are not detailed here, the original observations have been during 1922 once more subjected to the closest scrutiny. Some better average values have been obtained than those given in Table II. By the use of the 1913 empirical equations, supplemented where necessary, when possible, by graphical determination, these re-scrutinized original data have thus been better adjusted to conformity with fixed initial points than by the corrective approximation first used.

*Correction for effect of air impurity in the CO<sub>2</sub>.* Practically the only direct evidence bearing on the effect of impurities such as air on the determination of  $\mu$  for pure CO<sub>2</sub> vapor are the experiments of Kester<sup>4</sup> in 1905 and the original Joule and Thomson experiments on the cooling experienced by various mixtures of air and CO<sub>2</sub> when passed through a porous plug.<sup>5</sup> Kester's results in this regard are erratic and inconclusive. Joule and Thomson's values are also erratic but on the whole they show a definite variation of  $\mu$  with a progressive variation of the components of their mixtures.

From a study of their data the writer was led to the conclusion that approximately one per cent of the observed temperature drops as corrected and adjusted in this later treatment of the data should be, and

<sup>4</sup> Kester, F. E., Phys. Rev. (1) **21**, 260, 1905

<sup>5</sup> Joule, J. P., and Wm. Thomson, Collected Papers (Thomson), I, p. 333, or Scientific Papers (Joule), II, p. 216; or Harper's Scientific Memoirs, Thermal Effects of Fluids in Motion, by Joule and Thomson.

therefore has been, added thereto for each one per cent of air content in the CO<sub>2</sub> vapor which he used. Since no definite knowledge of the impurity effect as a function of temperature and none at all of it as a function of pressure is available, no correction on the latter bases could be attempted. For similar reasons no attempt was made to apply proportional corrections to the temperature drops observed on passing liquid CO<sub>2</sub> through the plug.

Table IV presents in descending order of pressure and temperature magnitudes the finally acceptable values for all the runs, arranged in the order of the proximity of their graphs to the critical point. The

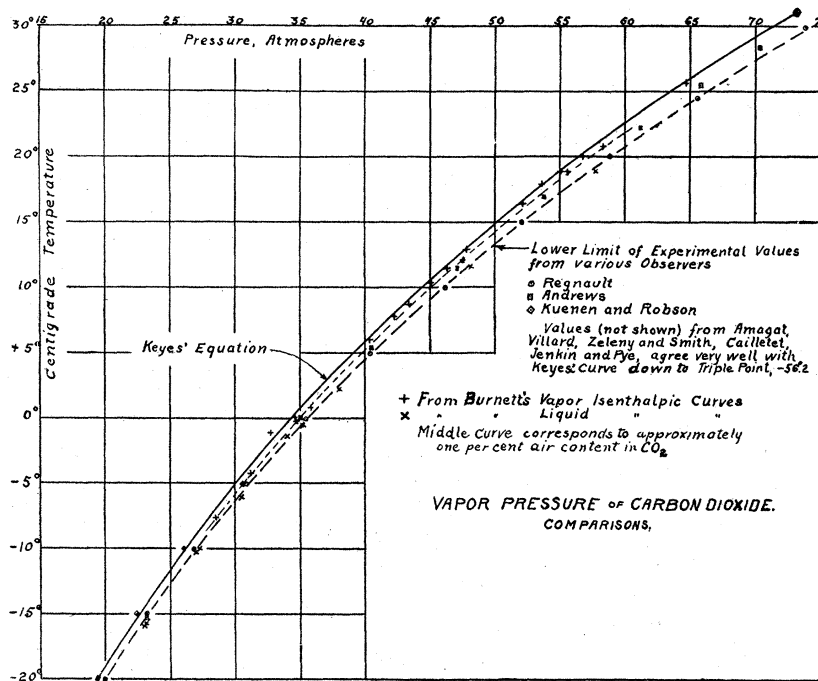


Fig. 3.

column headings are self-explanatory. The  $\pm$  values were determined by comparison of  $(T_1 - T_2)$  with  $T_{\Delta}$ , which should agree. In the following Table V are grouped, on the basis of percentage of impurity, the uncorrected observed values of pressure and temperature for the experimental points that are found to lie along the saturation curve; these values are compared in Fig. 3 with the results of other observers; they are omitted from the chart, Fig. 4.

Table IV furnishes the values which are plotted as crosses (+) on the chart, Fig. 4. Of the writer's liquid curves shown thereon, the first two points only are plotted.

*Throttling experiments of Jenkin and Pye.* There are also shown on this chart, by circles (o) points corresponding to the throttling curves for CO<sub>2</sub> vapor and liquid from the experiments of Jenkin and Pye.<sup>6</sup>

The liquid "curves" of Jenkin and Pye are but two-point chords that extend much closer to the saturation curve than do the "first-two-point" chords of the writer's data. The volatile impurity (air) in their CO<sub>2</sub> was never more than 0.11 per cent by volume, about one tenth as much as was present in the CO<sub>2</sub> used by the writer. It appears most likely therefore that the trend of their liquid chords near the saturation curve is more nearly the trend for pure CO<sub>2</sub> than is that shown by the writer's liquid curves for his less pure CO<sub>2</sub> as represented on the chart, Fig. 2. The agreement of the slopes of the Jenkin and Pye liquid chords with those of the writer's "first-two-point" chords which are the more remote from the saturation curve where the effect of volatile impurity is much less, is further evidence that for pure CO<sub>2</sub> the trend of the liquid isenthalps approaching the saturation curve is of the order of that shown by Fig. 4 rather than of that shown by Fig. 2. Further developments herein are based upon that conclusion.

This close agreement of the values of Jenkin and Pye for liquid CO<sub>2</sub> as well as the close agreement of the general trend of the curves through their points for CO<sub>2</sub> vapor with that of the writer's curves in the vapor field, especially in the sections common to both, indicates that the two entirely independent sets of data are mutually concordant.

The experimental throttle-valve and other arrangements by which the observations of Jenkin and Pye were obtained are, in the opinion of the writer, inherently much more likely to introduce uncertainties in the accuracy of the observations than are those of the radial flow plug used by the writer. But in view of the concordance noted in these two sets of data as shown by the comparisons of Fig. 4 there appears to be no reason for assuming that either set is less reliable than the other; consequently from this point on both are used as a guide to the complete formulation from which the smooth curves of the chart, Fig. 4, and those following, have been computed.

#### THE COMPLETE FORMULATION

*Choice of equation for isenthalps.* The most direct method of attack is to select one form of equation between pressure and temperature to represent the course of each individual smooth curve drawn through the several points corresponding to each of the various runs represented

<sup>6</sup> Thermal Properties of Carbon Dioxide at Low Temperatures. Phil. Trans. A **213**, 67-118, 1914; A **214**, 353-382, 1915.

by the plots of Fig. 4, determine the coefficients of these several equations, and then find a cross relation between these coefficients and the temperature intercepts of their graphs on some constant pressure line such as  $p=0$ ,  $p=1$ ,  $p=p_c$ , the critical pressure, or  $p$  equal to some pressure greater than the critical pressure and therefore not involved with abrupt

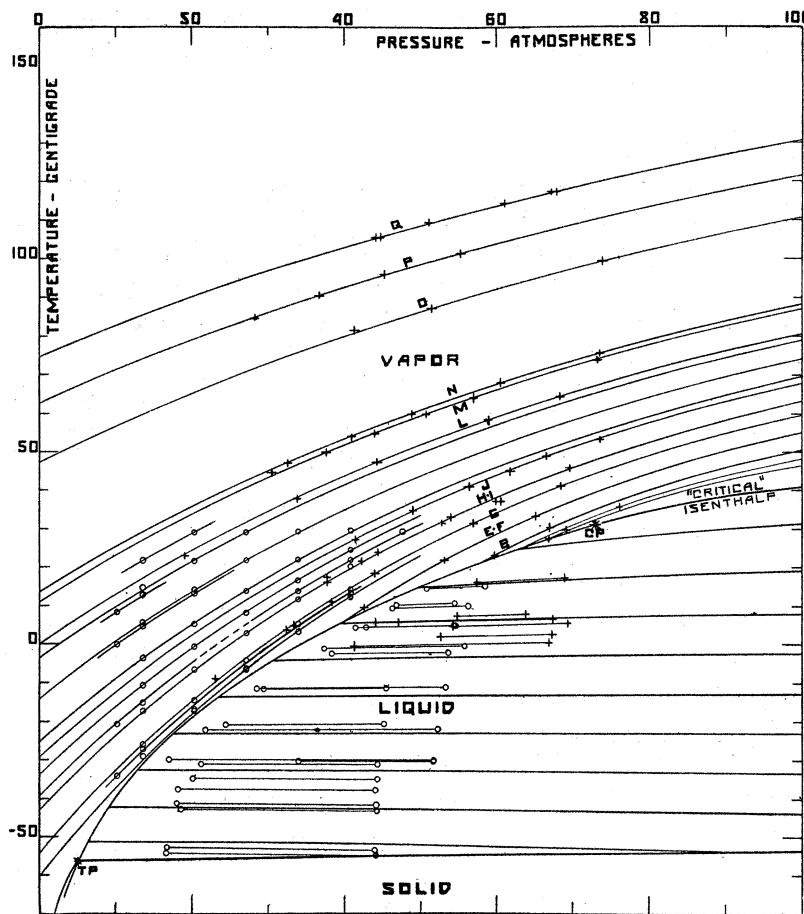


Fig. 4. Isenthalpic or throttling curves. Computed from an empirical formation by E.S. Burnett, 1922, based on data from experiments [+], by Burnett in 1910, and from later independent experiments [o] by Jenkin and Pye in 1914-1915

phase changes. The critical pressure line was logically chosen as the reference pressure line since it is the first one in the direction of increasing pressures that is intercepted at any temperature (except at the critical point) by one and only one isenthalp.

It was found after considerable study that the various characteristic equations of state that have been proposed for fluids would not yield

expressions for isenthalpic curves or their derivatives that would satisfy the data. Effort was therefore concentrated on purely empirical forms of equations but with some regard to ease of modifying them to conform with additional data beyond the present experimental limits when such data be available.

Consideration was given to the probable courses of these curves when extended toward both higher and lower pressure limits; but in view of the absolute lack of any definite experimental controls for these external extensions the writer finally selected a form of equation for the isenthalps which continues undisturbed into the low pressure field their apparent trend as they approach from the higher pressure region, and which carries, in the direction of increasing pressures those isenthalps which cross the critical isobar above  $-24^{\circ}\text{C}$ , and in the opposite direction those which cross it below that temperature, asymptotically toward finite temperature limits above which it seems likely that the true isenthalps will not rise.

The equation selected to represent each isenthalp is of an exponential form with two constants; it is obtained by integrating its derivative which expresses  $\mu$ , the slope of the isenthalp, as a function of pressure, for it was observed that  $\log \mu$ , along an isenthalp, plots as a linear function of the corresponding pressure, whence,

$$\log (\mu/\mu')_o = b(p-p') \quad (5)$$

which is equivalent to

$$\mu = \mu' e^{b(p-p')} \quad (6)$$

in which  $\mu'$  is the slope of the isenthalp at its intercept with the pressure line  $p=p'$ , and  $b$  is a parameter.

Putting  $(\partial t/\partial p)_o$  for  $\mu$  in Eq. (6) its integration yields

$$T - T' = (\mu'/b)[e^{b(p-p')} - 1] \equiv (1/b)(\mu - \mu') \quad (7)$$

from which it is evident that along an isenthalp  $\mu$  is by this equation represented as a linear function of the temperature as shown in Fig. 6, for on re-arranging Eq. (7) becomes

$$\mu = b(T - T') + \mu' \equiv bT + (\mu' - bT') \quad (8)$$

Also, solving Eq. (7) for  $p$ , we obtain

$$p - p' = \frac{1}{b} \log_e \left[ \frac{b}{\mu'} (T - T') + 1 \right] \quad (9)$$

These several equations have a number of characteristics that make them particularly applicable to the limited data to which they are fitted; but the reader is referred to the complete account of this work to be published elsewhere<sup>7</sup> for an outline of these characteristics.

<sup>7</sup> Bulletin of The University of Wisconsin, Engineering Series, 1924

In expressing the relation found for  $\mu'$  as a function of  $T'$  along the critical isobar  $p' = p_c$ , the critical pressure, the critical temperature and the slope  $(dt/dp)_s$  of the saturation curve at the critical point, are all involved; the course of the saturation curve itself is also involved in locating the intersections of the isenthalps therewith. The values here used for these several quantities are taken from Keyes' formulations<sup>8</sup> based upon his consideration of data then available. They are:

$$p_c = 72.9 \text{ atm.}; T_c = 304.1^\circ \text{ K (31.0}^\circ \text{ C)}; \mu_c = (dt/dp)_s = 0.6050^\circ \text{ C/atm.} \quad (10)$$

The last value, and the pressure-temperature values along the saturation curve, are from his equation,

$$\log_{10} p = 12.0722 - 1496.7/T - 2.8458 \times 10^{-2} T + 3.64 \times 10^{-5} T^2 \quad (11)$$

in which  $p$  is in atmospheres, and  $T$  is in centigrade degrees of the absolute temperature scale. Keyes' formulations are used because they are the only ones known to the writer which express in continuous though empirical assemblies, from the triple point ( $-56.2^\circ \text{ C}$ , 5.15 atm.), to the critical point, all of the saturation properties of  $\text{CO}_2$ .

The relation found to represent  $\mu'$  as a function of the absolute temperature  $T'$  along the critical isobar is as follows:

$$\mu' = \mu_c \left\{ e^{2.3026(T_c/T')^2[0.1700 - 0.0765(T' - T_c)^{3/13}(T' - T_c)^{1/3}]} \right\} - [(T' - T_c)/T']^{52/15} \quad (12)$$

in which the values are as previously defined.

This expression makes  $\mu'$  zero at  $T' = 249.1^\circ \text{ K}$  ( $-24.0^\circ \text{ C}$ ); also at about  $1642^\circ \text{ K}$ , far beyond these experimental limits, but near the point where we have some reason for expecting to find an inversion temperature for the sign of  $\mu$ . Between these two temperatures  $\mu'$  is positive, and has a maximum value of 0.7635 deg. per atm. slightly above the critical temperature at about  $307.1^\circ \text{ K}$ ; elsewhere  $\mu'$  is negative; its rate of change with temperature is infinite at the critical point; nowhere is its rate of change zero except as infinitely high temperatures are approached, which is without significance here.

*Formulation of  $b$  as a function of  $T'$ .* The relation between  $b$  and  $T'$  which was found to satisfy certain arbitrary requirements as well as the "normal" ones expressed in equations (5) to (9) is given in the following equation

$$b = b_c \left( \frac{T'}{T_c} \right)^5 e^{-0.37(T' - T_c)^{\frac{1}{2}}} + 0.0337 \left[ \frac{T' - T_c}{T'} \right]^{96/49} \quad (13)$$

in which  $b_c = -0.04267$ ,  $T_c = 304.1^\circ \text{ K}$ , and  $T'$  has the values previously defined.

<sup>8</sup> Keyes, F. G., and A. W. Kenney, Thermodynamic Properties of Carbon Dioxide, Am. Soc. Refr. Eng. Journ. 3, 17-43, 1917.

One intended consequence of these relations is that all of the isenthalpic curves of the vapor field which intersect the saturation curve at all, shall do so twice, entering at a higher pressure and leaving at a lower pressure when viewed in the latter direction. The "critical" isenthalp enters at the critical point and leaves at the null point. Thus the vapor field is entirely covered by all of the curves above the critical isenthalp, and the liquid field by all of those below it.

At  $T' = 249.1^\circ \text{K}$  ( $-24.0^\circ \text{C}$ ) the isenthalp is a line of constant temperature—the inversion temperature of the liquid field, for which  $\mu$  is zero at all pressures of the chart, Fig. 4, since the data are insufficient to disclose a variation of the inversion temperature with pressure. Below this temperature the liquid isenthalps have negative slopes, and eventually meet in the direction of increasing pressures, their limits at the liquid-solid phase-boundary<sup>9</sup> which crosses the field from the triple point [ $p = 5.15$  atm.,  $T = 216.9^\circ \text{K}$  ( $-56.2^\circ \text{C}$ )] through the point [ $p' = 72.9$  atm.,  $T' = 218.5^\circ \text{K}$ ].

Table VI presents values of  $\mu'$  and  $b$  computed from equations (12) and (13) as functions of  $T'$ . Values of  $(db/dT')/b$  and  $(d\mu'/dT')/\mu'$  as functions of  $T'$  are also given since they are of value for future operations. Most of the values given in Table VI were computed by use of six place logarithms, and are given to four or five significant figures for the sake of securing smoothness in the progressive variations of other magnitudes computed therefrom. A few were read from a large scale plot of the others.

The complete general equations for the whole field involved are of course obtained by combining equations (12) and (13) with equations (5) to (9), which combination yields admittedly cumbersome and unwieldy expressions that also involve transcendental relations. It is a matter of regret that the writer was unable to establish a simpler and more easily usable formulation. Every effort was made to obtain simplicity but the data cannot be simply represented.

Corresponding values of  $T$ ,  $p$  and  $\mu$  have been computed from this formulation for isenthalps spaced  $10^\circ$  or less apart on the critical pressure line and are presented in Table VII. Most of the computed values in this table were obtained by use of a circular slide-rule accurate to four significant figures and are so given for the reasons stated above. The isenthalps themselves are shown on the chart Fig. 5.

In Fig. 6 the curves depict  $\mu$  as an *isobaric* function of temperature, and the straight lines as an *isenthalpic* function of temperature, both sets of loci being plotted from the values presented in Table VII. Values

<sup>9</sup> Tammann, *Kristallisiern und Schmelzen*, A. J. Barth, Leipzig, 1903, p 296

of  $\mu$  as an *isothermal* function of pressure, obtained by cross-reading a large-scale plot of Fig. 6, are presented in Table VIII and Fig. 7.

Inspection of these several charts reveals at once that the relations disclosed are not simple. Attention is called to the reversion of the order of the curves of Fig. 6 at pressures up to 60 atm. between about 275° and 300° K (from 0° to 25° C). It is in this particular region that much of the work of previous investigators was done, and it is

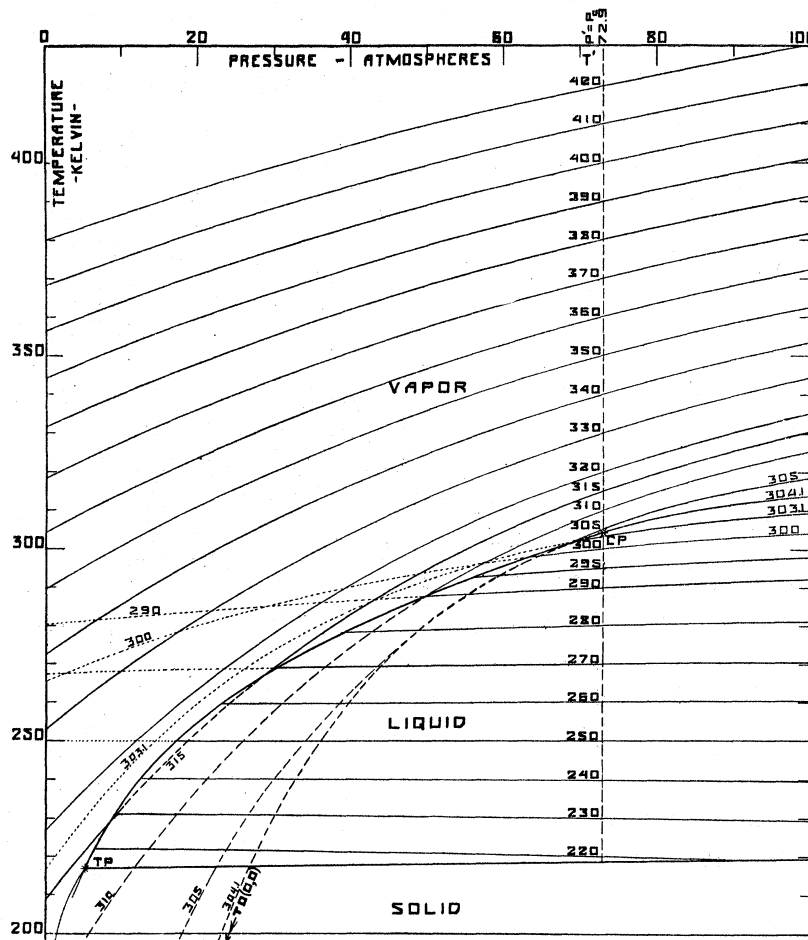


Fig. 5. Isenthalpic curves computed according to latest formulation

evident that here even slight variations in experimental results might lead to entirely discordant conclusions as to the character or magnitude of the true variation of Joule-Thomson effect, so that the discrepancies noted between the results of Joule and Thomson, Natanson, and Kester are not surprising.



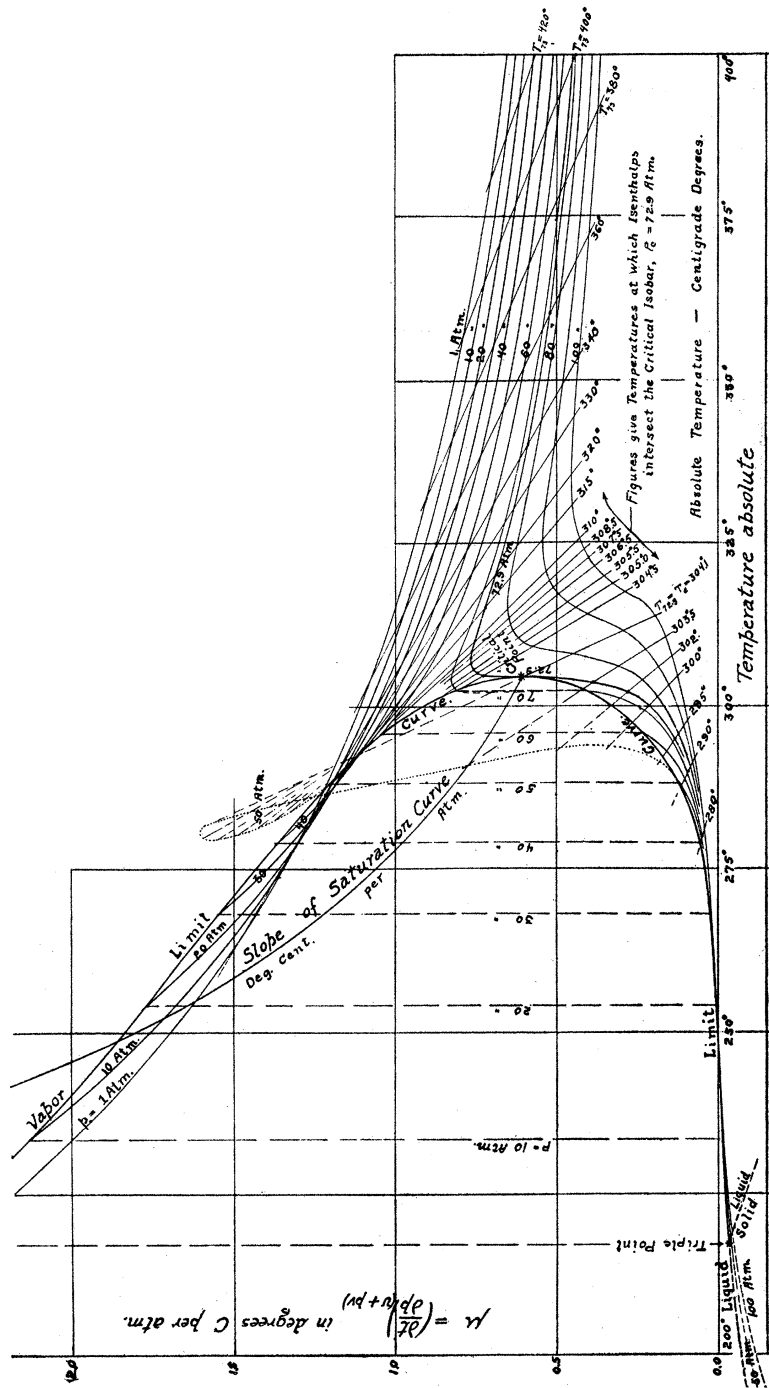


Fig. 6. Curves show  $\mu$  as an isobaric function of temperature; straight lines show  $\mu$  as an isenthalpic function of temperature.

COMPARISON OF VARIOUS RESULTS

Fig. 8 furnishes some comparisons of the results of these previous investigators with the results from the present formulations which are based upon the experimental observations of the writer combined with those of Jenkin and Pye.<sup>6</sup> On the temperature basis of comparison, Kester's<sup>4</sup> values of  $\mu$  are considerably higher than those of Joule and

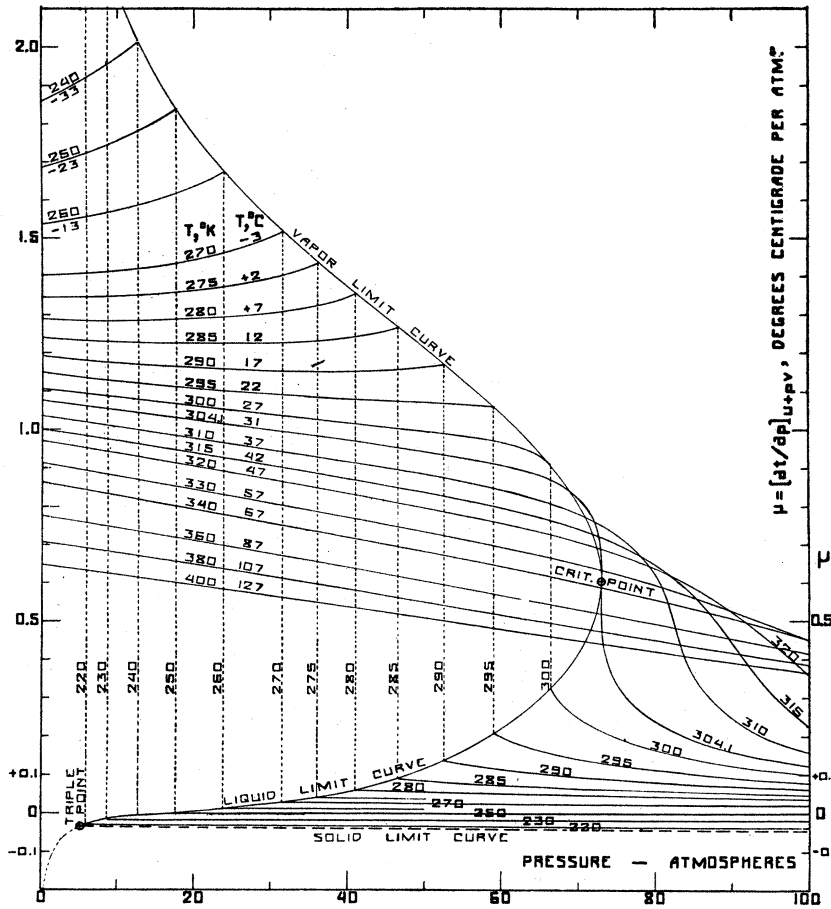


Fig. 7. Isothermal variation of  $\mu$  with pressure

Thomson,<sup>5</sup> these are all for low pressures up to 15 atm. The writer's extrapolated values for 1 atm. and 10 atm. are seen to fall about midway between those of Kester and those of Joule and Thomson, but to favor the latter at the lower temperatures and the former slightly at the higher temperatures. None of their values was used by the writer as a guide in his formulation, so that it is reassuring that the rather wide

extrapolation over some 10 atm. at the lower temperatures of this comparison to some 40 atm. at the higher temperatures, yields values consistent with the only previously determined values of other investigators that are available for comparison.

Fig. 8 also shows some comparisons of the variation of  $\mu$  with pressure at constant temperature. Natanson's<sup>10</sup> and Kester's results, where

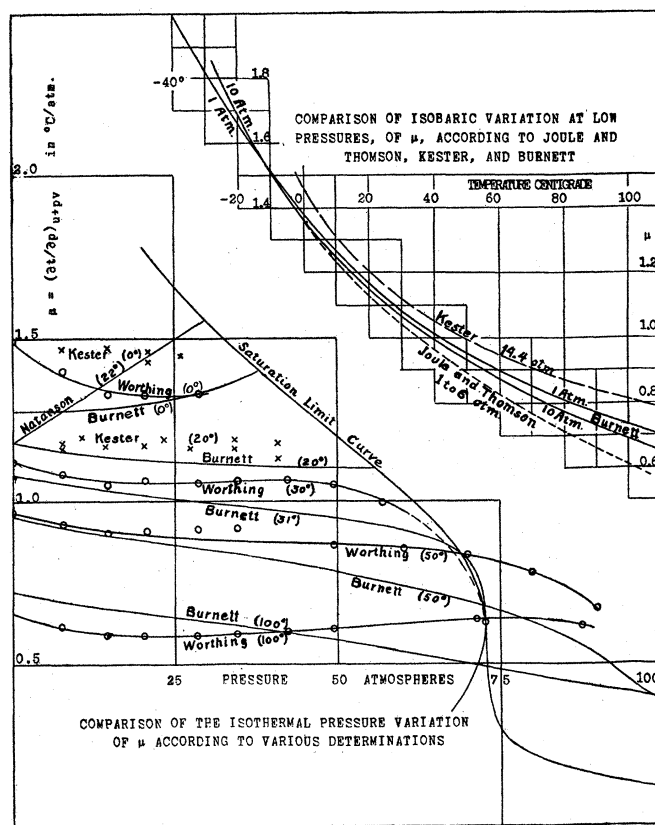


Fig. 8

comparable, are either mutually discordant or indeterminate. Worthing<sup>11</sup> computed  $\mu$  from its thermodynamic relations to other known or assumed data on the properties of  $\text{CO}_2$  including his own experimental determination of the ratio of its constant pressure and constant volume specific heats. His isotherms of  $\mu$  thus determined show in some sections of the field a striking similarity of form to those of the writer, although the

<sup>10</sup> Natanson, Wied. Ann. **31**, 502, 1887

<sup>11</sup> Worthing, Phys. Rev. **33**, 256, 1911

agreement as to location throughout their courses is not so good. His computations, however, involve considerable uncertainty in some of the data used as well as some small difference factors between large and somewhat uncertain quantities. The comparison is of interest chiefly because of the similarity of form which it discloses.

Other comparisons are made in the detailed account of the development of the writer's present formulation, to which reference has been made<sup>7</sup> which further tend to support confidence in the belief that this formulation, besides representing within the limits of experimental uncertainty the facts disclosed by the data over their actual range, does also indicate with a close approximation to the probable truth the pressure and temperature variation of the Joule-Thomson effect in CO<sub>2</sub> over the extended range of these charts which is from zero to 100 atmospheres in pressure range, and from under 200° to over 400° in range of absolute temperature (°K).

By means of this formulation the variation along the isenthalps of the specific heat at constant pressure has been determined, and, by combination with absolute values of specific heats and other data for CO<sub>2</sub> determined from other sources, charts and tables have been prepared showing the variation of specific heat at constant pressure as a function of pressure and temperature, and also the variation of the heat-content of CO<sub>2</sub> liquid and vapor with pressure and temperature. Discussion of these and additional developments will be presented in subsequent papers.

The experimental work leading up to and including that herein described was conducted by the writer at the University of Wisconsin under the joint auspices of the College of Engineering and the Department of Physics of the University during the years 1905-1910; it was financed by University funds, assisted toward the end of that period by grants from the Count Rumford Research Fund.

MADISON, WISCONSIN,  
April 21, 1923.

TABLE I  
SAMPLE SET OF OBSERVATIONS  
*Resistances are expressed in bridge box units; pressures in cm of Hg*  
Date: Wed. P. M., Aug. 17, 1910. *Zero of manometer column, +1.50 cm*

Time	$R_1$	Time	$R_2$	Time	$R_\Delta$	Time	$H_1$	Time	$H_2$
2:51	53.08	2:56	28.19	2:58	24.83	2:56	113.04	2:54	63.54
3:01	53.12	3:03	28.24	3:04	24.84	3:00	113.04	3:06	63.65
3:06	53.11	3:08	28.40	3:09	24.95	3:08	113.06	3:12	63.80
3:10	53.11	3:12	28.39	3:13	24.91	3:15	113.05	3:18	63.84
3:15	53.15	3:17	28.39	3:18	24.75	3:23	113.05	3:21	63.86
3:21	53.15	3:22	28.43	3:24	24.75	3:24	113.04	3:27	63.90
3:25	53.13	3:27	28.45	3:29	24.68	3:29	113.08	3:30	63.90
Means	53.12		28.36		24.82		113.05		63.78
3:38	53.17	3:42	35.57	3:44	17.57	3:38	113.05	3:43	75.58
3:45	53.17	3:47	35.58	3:48	17.57	3:48	113.04	3:50	75.58
3:49	53.17	3:50	35.58	3:51	17.57	3:53	112.95	3:54	75.55
3:53	53.16	3:55	35.60	3:56	17.56	3:59	112.94	3:56	75.55
3:58	53.16	4:00	35.62	4:03	17.56	4:03	112.86	4:00	75.52
Means	53.17		35.59		17.57		112.97		75.56
4:08	53.18	4:12	41.82	4:14	11.36	4:13	113.05	4:11	86.70
4:16	53.17	4:17	41.82	4:18	11.36	4:19	113.05	4:17	86.70
4:19	53.17	4:20	41.82	4:22	11.36	4:22	113.05	4:23	86.70
Means	53.17		41.82		11.36		113.05		86.70
4:32	53.17	4:36	46.17	4:38	6.84	4:32	113.00	4:35	95.20
4:45	53.18	4:48	46.37	4:50	6.90	4:43	112.94	4:46	94.82
4:53	53.21	4:54	46.23	4:55	6.85	4:51	112.62	4:53	95.02
4:58	53.14	4:58	46.23	4:59	6.87	4:56	113.00	4:57	95.02
5:00	53.14	5:01	46.19	5:03	6.88	5:03	112.97	4:59	95.03
5:04	53.15	5:05	46.20	5:06	6.86	5:07	113.00	5:04	94.82
5:07	53.11	5:08	46.17	5:10	6.92	5:10	112.93	5:09	95.02
Means	53.17		46.22		6.87		112.89		94.99
5:22	53.10	5:25	49.84	5:27	3.29	5:23	113.10	5:26	102.40
5:28	53.15	5:29	49.84	5:30	3.29	5:28	113.06	5:30	102.35
5:33	53.16	5:34	49.84	5:35	3.29	5:35	113.05	5:36	102.28
5:36	53.16	5:37	49.84	5:38	3.29	5:38	113.05	5:40	102.22
5:40	53.16	5:41	49.84	5:42	3.30				
Means	53.14		49.84		3.29		113.06		102.33

Temperature of box varied from 26.6° to 27.25°; temperature of mercury column from 29.0° to 29.5°.

TABLE II  
MEAN VALUES FROM TABLE I  
*Temperatures in degrees C; pressures in atmospheres*

$R_1$	$T_1$	$R_2$	$T_2$	$R_\Delta$	$T_\Delta$	$T_1 - T_2$	$H_1$	$p_1$	$H_2$	$p_2$	$p_1 - p_2$
53.12	53.26	28.36	27.47	24.82	25.75	25.79	113.05	73.48	63.78	41.46	32.02
53.17	53.31	35.59	34.80	17.57	18.16	18.51	112.97	73.43	75.56	49.12	24.31
53.17	53.31	41.82	40.93	11.36	12.42	12.38	113.05	73.48	86.70	56.35	17.13
53.17	53.31	46.22	45.35	6.87	8.00	7.96	112.89	73.38	94.99	61.74	11.64
53.14	53.28	49.84	49.00	3.29	4.32	4.28	113.06	73.49	102.33	66.51	6.98
Means	53.29							73.45			



TABLE IV B  
LIQUID ISENTHALPS; EXPERIMENTAL VALUES  
*Pressure in atmospheres; temperature in degrees centigrade*

Curve	Percent impurity	Adjusted values		Observed values, unadjusted			
		$p$	$t$	$p_1$	$t_1$	$p_2$	$t_2$
<i>a</i> Sept. 18	0.30			71.92	31.25	55.53	18.77 ± 0.14
				72.22	31.22	53.68	17.83 0.59
				72.22	30.38	43.38	8.65 0.19
<i>b</i> Aug. 19 combined with Sept. 18	1.08	68.90	25.70				
		57.65	18.79 ± 0.04	68.92	25.65	57.65	18.73 ± 0.04
		48.90	11.12 0.08	68.84	26.07	48.09	11.52 0.08
		38.00	+ 2.41 0.11	67.68	24.80	38.00	+ 2.23 0.11
		35.09	- 0.72 0.15	69.26	26.16	35.09	- 0.54 0.15
		27.25	- 9.65 0.30	69.72	25.70	27.25	-10.06 0.30
<i>c</i> Sept. 25	0.90	69.30	17.00				
		57.32	15.09 ± 0.00	68.93	17.09	57.32	15.97 ± 0.00
		49.55	11.35 0.08	68.96	17.09	49.55	11.37 0.08
		40.69	+ 4.16 0.14	69.62	16.99	40.69	+ 4.16 0.14
		30.38	- 6.27	68.83	16.41	30.38	- 6.22
		26.97	-10.66 0.26	69.22	14.64	26.97	-10.78 0.26
		17.63	-24.17 0.17	70.02	15.94	17.63	-24.21 0.17
<i>d</i>	0.50	Sept. 19		56.30	11.70	34.00	- 1.35 ± 0.02
<i>e</i>	0.80	Sept. 23		63.50	11.40	44.10	+ 6.45 0.20
<i>f</i> Sept. 23	0.85	63.80	7.75				
		54.77	7.10 ± 0.05	63.84	7.87	54.77	+ 7.26 ± 0.05
		44.03	+ 5.93 0.12	63.73	7.69	44.03	+ 5.84 0.12
		35.94	- 1.10 0.02	63.81	7.75	35.94	- 1.10 0.02
		23.21	-15.30 0.86	63.82	7.74	23.21	-15.30 0.86
<i>g</i> to Sept. 23	0.4 to 0.2			67.30	6.70	47.10	5.60 ± 0.03
				69.35	5.40	54.25	4.60 0.04
				67.20	2.55	52.60	+ 1.90 0.07
				66.80	+0.25	41.25	- 0.70 0.03
				62.35	-0.20	23.05	-15.95 0.10
				65.25	-0.40	31.55	- 5.70 0.03
				61.45	-0.90	23.25	-15.80 0.21

TABLE V  
SATURATION VALUES; EXPERIMENTAL

Average Impurity	Pressure atm.	Temperature degrees C
1.11%	65.54	25.55 ± .01
	58.34	20.68 .02
	57.65	18.79 .04
	48.90	11.12 .08
	47.56	12.05 .14
	46.68	12.78 .05
	40.31	6.00 .38
	38.00	+ 2.41 .11
	35.80	+ 0.80 .25
	35.09	- 0.72 .15
	34.67	- 0.25 .17
	34.60	0.0 .16
	32.76	- 1.16 .34
	31.22	- 4.28 .17
	28.48	- 7.67 .19
	27.25	- 9.65 .30

TABLE V—Continued

Average Impurity	Pressure atm.	Temperature degree C
0.87%	44.08	6.46 ± .20
	40.69	+ 4.16 .14
	35.94	- 1.10 .02
	30.38	- 6.22 .02
	26.97	-10.78 .26
	23.21	-15.30 .86
	17.63	-24.21 .17
0.60%	56.68	20.00 ± .01
	55.08	18.77 .05
	52.08	16.28 .06
	47.86	12.84 .10
	46.33	11.39 .06
	45.02	10.23 .11
	42.28	7.73 .05
0.30%	34.00	- 1.35 .02
	55.53	18.77 .14
	53.68	17.83 .59
	43.38	8.65 .10

TABLE VI  
VALUES DERIVED FROM EQS. (12 AND 13)

$T'(p=p_0)$	$\mu'$	$\frac{1}{\mu'} \left( \frac{d\mu'}{dT'} \right)$	$b$	$\frac{1}{b} \left( \frac{db}{dT'} \right)$
200°K	-0.10394	-0.05070	+0.009137	-0.02958
210	-0.06174	-0.05365	+0.006580	-0.03436
220	-0.03528	-0.05626	+0.004527	-0.04126
230	-0.01867	-0.06956	+0.002803	-0.05700
240	-0.007736	-0.11568	-0.001291	-0.11190
245	-0.003376	-0.24875	+0.000578	-0.24540
250	+0.000730	+1.1279	-0.000131	+1.0895
255	+0.004969	+0.17832	-0.000855	+0.17316
260	+0.009732	+0.10630	-0.001630	+0.09709
265	+0.01548	+0.08306	-0.002456	+0.07196
270	+0.02278	+0.07266	-0.003401	+0.05997
280	+0.04543	+0.06720	-0.005887	+0.05229
290	+0.09091	+0.07220	-0.010152	+0.05682
295	+0.13243	+0.08171	-0.013658	+0.06567
300	+0.021266	+0.11453	-0.019944	+0.09175
302	+0.27742	+0.15868	-0.02464	+0.12542
303.5	+0.3804	+0.31550	-0.03156	+0.23482
303.8	+0.4265		-0.03419	
304.1	0.6050	+∞	-0.04267	±∞
304.2	0.6922	+0.44701	-0.03742	-0.57456
304.3	0.7081	+0.25817	-0.03572	-0.38557
304.5	0.7264	+0.07519	-0.03357	-0.25718
305	0.7468		-0.03045	
305.5	0.7560	+0.16857	-0.02841	-0.12005
306.5	0.7628	+0.003387	-0.025614	-0.08480
307.5	0.7630	-0.000646	-0.02385	-0.06694
308.5	0.7603	-0.004870	-0.02243	-0.05596
310	0.7533	-0.007072	-0.020792	-0.04559
315	0.7223	-0.009074	-0.017458	-0.028334
320	0.6900	-0.009052	-0.015448	-0.020562
330	0.6331	-0.008696	-0.013108	-0.013190
340	0.5872	-0.006992	-0.011675	-0.009780
360	0.5200	-0.005252	-0.009982	-0.007630
380	0.4742	-0.004074	-0.008876	-0.005295
400	0.4410	-0.003241	-0.008042	-0.004632
420	0.4154	-0.002785	-0.007308	-0.004289



TABLE VII  
 ISENTHALPIC VALUES FROM 1922 FORMULATION  
 Pressures in atmospheres; temperatures in °K;  $\mu$  in °K per atm.

$p$	0	1	20	40	60	72.9	80	100
<i>Vapor Isenthalps</i>								
$T$	379.94	380.63	393.12	404.56	414.39	420.00	422.88	430.22
$\mu$	0.7080	0.7029	0.6118	0.5284	0.4564	0.4154	0.3944	0.3407
$T$	356.30	357.10	370.92	383.40	394.00	400.00	403.05	410.74
$\mu$	0.7924	0.7860	0.6748	0.5745	0.4892	0.4410	0.4165	0.3546
$T$	331.40	332.30	347.99	361.90	373.52	380.00	383.27	391.43
$\mu$	0.9054	0.8974	0.6582	0.6348	0.5317	0.4742	0.4452	0.3728
$T$	304.30	305.35	323.77	339.76	352.85	360.00	363.57	372.35
$\mu$	1.0760	1.0655	0.8816	0.7220	0.5914	0.5200	0.4844	0.3967
$T$	272.42	273.88	297.03	316.46	331.83	340.00	344.00	353.64
$\mu$	1.3750	1.3590	1.0885	0.8620	0.6826	0.5872	0.5405	0.4280
$T$	226.91	229.09	263.56	290.42	310.15	320.00	324.63	335.27
$\mu$	2.1272	2.0948	1.5620	1.1470	0.8422	0.6900	0.6184	0.4540
$T$	208.69	211.26	[252.26]	282.91	304.56	315.00	319.82	330.59
$\mu$	2.5786	2.5338	[1.8181]	1.2826	0.9046	0.7223	0.6381	0.4501
$T$	181.28	[184.70]	237.43	274.42]	298.85	310.00	314.97	325.60
$\mu$	3.4295	[3.3588]	2.2620	1.4928]	0.9850	0.7533	0.6500	0.4290
$T$	157.40	[161.24]	226.49	269.35	295.97]	307.50	312.48	322.77
$\mu$	4.343	[4.2514]	2.6950	1.6727	1.0380]	0.7630	0.6442	0.3998
$T$	120.90	[126.80]	212.44	264.32	293.71]	305.50	310.36	319.77
$\mu$	6.000	[5.832]	3.400	1.926	1.091]	0.7560	0.6179	0.3508
$T$	76.00	[81.40]	198.40	260.85	292.77]	304.50	309.09	317.42
$\mu$	8.396	[8.114]	4.288	2.1915	1.1200]	0.7264	0.5724	0.2926
<i>Critical Isenthalp</i>								
$T$	0.00	[13.38]	182.77	260.56	293.70	304.10]	307.80	313.82
$\mu$	13.580	[.13.01]	5.783	2.463	1.049	0.6050]	0.4470	0.1906
<i>Liquid Isenthalps</i>								
$T$	[195.21	198.25	251.57	281.51	297.44]	303.50	305.92	310.43
$\mu$	[3.7974	3.6800	2.0194	1.0744	0.5716]	0.3804	0.3041	0.1618
$T$	[245.42	247.07	271.83	287.94	297.79]	302.00	303.81	307.48
$\mu$	[1.6720	1.6312	1.0210	0.6239	0.3812]	0.2774	0.2329	0.1423
$T$	[265.03	265.92	280.04	290.11	296.87]	300.00	301.41	304.45
$\mu$	[0.9102	0.8924	0.6108	0.4099	0.2751]	0.2127	0.1846	0.1239
$T$	[275.86	275.93	277.16]	278.34	279.39	280.00	280.32	281.14
$\mu$	[.06978	.06936	.06202]	.05514	.04901	.04543	.04357	.03873
$T$	[259.24	259.26	259.46]	259.67	259.88	260.00	260.07	260.26
$\mu$	[.01096	.01094	.01064]	.01027	.00993	.00973	.00962	.00931
$T$	[240.54	240.53]	240.40	240.29	240.10	240.00	239.94	239.79
$\mu$	[-.00704	-.00705]	-.00723	-.00742	-.00761	-.00773	-.00781	-.00801
$T$	[222.19	222.17]	221.66	221.08	220.44	220.00	219.74	218.98
$\mu$	[-.02537	-.02548]	-.02778	-.03040	-.03329	-.03528	-.03464	-.03989

TABLE VII—Continued

Supplementary values at graphically determined intersections of the isenthalps with the saturation curve

$T'$	$\mu'$	$b$	$p_1$	$T_1$	$\mu_1$	$p_2$	$T_2$	$\mu_2$	Remarks
315.85	0.7166	-0.01705	17.1	249.1	1.855	17.1	249.1	1.855	Tangent or grazing point
315.0			27.15	264.6	1.606	8.4	228.7	2.226	
313.88	0.7296	-0.01803	33.75	272.55	1.478	5.15	216.9	2.475	Lower point is triple point
312.75	0.7369	-0.01870	39.5	278.5	1.376	3.3	197.5	2.707	Lower point is on saturation curve
310.0			50.45	288.35	1.2015				extension below the triple point
307.5			59.3	295.25	1.0550				
305.5			66.5	300.15	0.9068				
304.5			70.7	302.75	0.7820				
304.1	0.6050	-0.04267	72.9	304.1	0.6050	0.0	0.0	13.580	Upper point is critical point, lower point is the null point (arbitrary)
303.5			69.9	302.3	0.4182				
302.0			66.3	300.0	0.3280				
300.0			62.6	297.5	0.2610				
280.0			39.25	278.25	0.0554				
260.0			23.5	259.5	0.0105				
249.1	0.0	0.0	17.1	249.1	0.0				Inversion temperature of the J-T effect for liquid carbon dioxide
240.0			12.8	240.4	-0.0072				
220.0			6.5	222.0	-0.0261				
(214.1)	(-0.0496)	(+0.0568)	5.15	216.9	-0.03375				Triple point; ( $T'$ , $p'$ ) for this isenthalp is a point of solid phase

NOTE: Values between brackets [] in the main part of this table indicate "mathematical" courses of the curves when both liquid and vapor phases are present; these are shown by the broken lined portions of a few of the curves of the chart Fig. 5. Physically and experimentally the temperatures and slopes observed are those of the saturation curve for the pressures corresponding to the values within the brackets.

TABLE VIII

*Isothermal and isobaric values of  $\mu$  corresponding to the charts of Figs. 6 and 7, expressed in deg. C per atm.*

Temp. °K	Pressure in atmospheres											
	0	1	10	20	40	60	72.9	80	100			
Vapor phase above line												
400.0	0.6475	0.6440	0.6210	0.5950	0.5375	.4790	.4410	.4225	.3635			
390.0	0.6755	0.6725	0.6485	0.6200	0.5595	.4965	.4560	.3850	.3235			
380.0	0.7080	0.7045	0.6780	0.6475	0.5835	.5165	.4742	.4505	.3855			
370.0	0.7415	0.7335	0.7100	0.6775	0.6160	.5405	.4952	.4705	.3995			
360.0	0.7790	0.7750	0.7455	0.7110	0.6420	.5685	.5200	.4930	.4155			
350.0	0.8195	0.8150	0.7850	0.7500	0.6780	.6020	.5500	.5210	.4340			
340.0	0.8640	0.8595	0.8290	0.7950	0.7205	.6425	.5872	.5550	.4500			
330.0	0.9140	0.9095	0.8795	0.8450	0.7720	.6925	.6331	.5945	.4490			
325.0	0.9425	0.9375	0.9075	0.8745	0.8025	.7230	.6605	.6165	.4220			
320.0	0.9710	0.9665	0.9380	0.9050	0.8360	.7570	.6900	.6380	.3570			
315.0	1.0020	0.9985	0.9705	0.9395	0.8735	.7970	.7223	.6500	.2210			
310.0	1.0360	1.0320	1.0055	0.9765	0.9160	.8435	.7554	.6100	.1585			
305.0	1.0710	1.0675	1.0445	1.0155	0.9640	.9000	.7468	.2890	.1270			
304.1	1.0775	1.0740	1.0505	1.0240	0.9735	.9100	.6050	.2420	.1215			
300.0	1.1070	1.1045	1.0840	1.0600	1.0175	.9675	.2147	.1650	.1005			
295.0	1.1480	1.1455	1.1270	1.1090	1.0805	.1990	.1324	.1134	.0794			
290.0	1.1920	1.1900	1.1750	1.1635	1.1525	.1156	.9999	.0815	.0619			
285.0	1.2395	1.2385	1.2280	1.2245	1.2400	.0761	.06355	.0586	.0478			
280.0	1.2900	1.2900	1.2845	1.2915	1.3470	.0515	.0454	.0425	.0364			
275.0	1.3455	1.3455	1.3470	1.3645	0.0414	.0355	.0324	.0309	.0275			
270.0	1.4050	1.4060	1.4155	1.4455	0.0274	.0246	.0228	.0221	.0202			
260.0	1.5375	1.5405	1.5735	1.6375	0.0106	.0101	.00973	.0096	.0090			
250.0	1.6885	1.6954	1.7570	0.0735	0.0733	.0731	.0730	.0729	.0727			
240.0	1.860	1.870	1.974	-0.00723	-0.00742	-.00761	-.00774	-.00781	-.00801			
230.0	2.060	2.070	-0.0168	-0.0171	-0.0177	-.0183	-.0187	-.0190	-.0195			
220.0	2.2855	2.3035	-0.0294	-0.0304	-0.0323	-.0341	-.0353	-.0359	-.0375			
Liquid phase below line												
Supplementary values at graphically determined intersections of isotherms and isobars of $\mu$ with the saturation curve												
$p$	1	5	10	15	20	30	40	50	60	65	70	72.9
$T$	(193.5)	216.2	233.4	245.05	254.1	268.15	279.0	288.0	295.7	299.15	302.35	304.1
$\mu_v$	(3.055)	2.510	2.135	1.922	1.773	1.545	1.371	1.211	1.043	0.937	0.801	0.6050
$\mu_l$	(?)	-0.0346	-0.0083	-0.0031	0.0046	0.0245	0.0575	0.1182	0.2225	0.2985	0.418	0.6050
$T$	216.9	220.0	230.0	240.0	250.0	260.0	270.0	280.0	285.0	290.0	295.0	300.0
$p$	5.15	5.95	8.8	12.65	17.6	23.9	31.55	41.0	41.0	52.55	59.0	61.3
$\mu_v$	2.475	2.410	2.200	2.020	1.841	1.675	1.515	1.354	1.354	1.174	0.961	0.914
$\mu_l$	-0.3375	-0.0290	-0.0167	-0.0074	+0.0007	+0.0115	0.0285	0.0625	0.0938	0.1386	0.2095	0.3235
Values below correspond to regions of rapid rates of change of $\mu$ along isotherms.												
$T$	220.0	230.0	304.1	304.1	304.1	304.1	304.1	310.0	310.0	315.0	315.0	315.0
$p$	5.0	5.0	70.0	72.0	74.0	76.0	90.0	85.0	90.0	85.0	90.0	95.0
$\mu$	2.387	2.132	0.822	0.767	0.382	0.310	0.159	0.360	0.250	0.569	0.443	0.312