DECEMBER 15, 1931 PHYSICAL REVIEW VOLUME 38

# SOME PHYSICAL PROPERTIES OF COMPRESSED GASES. II, CARBON MONOXIDE

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(Received September 5, 1931)

## Abstract

The writers have adjusted and extrapolated the compressibility data obtained by Bartlett and his collaborators on carbon monoxide, so that accurate $p-v-T$ relations from $-70°$ to $400°$ and up to 1200 atm. are available. The relatively low pressure isotherms of Scott at 25° and of Goig-Botella at 0°, 12.44°, and 20.22° are included. Derivatives are obtained by the graphical scheme used for similar calculations on nitrogen. The specific volume, density, expansion coefficients $-(p/v)(dv/dp)_T$ and $(T/v)(dv/dT)_p$ fugacity, $C_p$, $C_p-C_v$, $C_v$, Joule-Thomson coefficient $\mu$ are calculated and shown in curves and a table for 14 pressures and 11 temperatures in the range $-70°$ to $400°$ and 25 to 1200 atm. In particular, $C_p$ vs. $p$ isotherms, $C_v$ vs. $t$ isobars, $t$ vs. $p$ $\mu=$const. graphs are shown; among the last, the $\mu=0$ curve is the inversion curve. There are no direct experimental data for comparison. On account of similarity in the molecular structure and the spectra of the molecules CO and $N_2$, one might look for some correspondence in the physical properties of the two gases. In general, the trends of the two are qualitatively similar. The $C_p-C_v$ vs. $p$ isotherms all show a maximum. This maximum is very flat at the highest temperatures and comes at about 700 atm. As the temperature decreases, the maximum becomes pronounced and moves to lower pressures; it comes at about 200 atm. along the $-50°$ and $-70°$ curves. Along the $-70°$ isotherm a second maximum appears at about 550 atm., but it is not evident at higher temperatures. $C_p-C_v$ approaches $R$, of course, along all isotherms as the pressure is decreased to zero. $C_p$ is obtained by adding $\Delta C_p$ to $C_p^*$. $C_p^*$ denotes the heat capacity for a given temperature at zero pressure; $\Delta C_p$ is the change in $C_p$ with pressure along a given isotherm. It is evaluated thru $\int_0^p -T(d^2v/dT^2)_p dp$. The derivative occurring under the integral sign is obtained by the authors' graphical scheme at a sufficient number of points for mechanical integration under the isotherm. Along isotherms at 50° and lower, $C_p$ increases rapidly with pressure and reaches a maximum at about 300 atm. Changes in pressure above 500 atm. cause only relatively small changes in $C_p$ at any temperature. Above 200 atm. and below 0°, $C_p$ increases rapidly as the temperature is lowered. The $C_v$ vs. $t$ isobars show that from 300 to 1200 atm. $C_v$ has a minimum at about 100°. On the low temperature side of this minimum the curves are very steep; along the 1200 atm. isobar $C_v$ drops from $4.4\,R$ at $-70°$ to $2.57\,R$ at 100°. Above 100°, $C_v$ is only a few hundredths cal./mole deg. higher than $C_v^*$ for pressures up to 400 atm; further increase in pressure to 1200 atm. raises $C_v$ only a few tenths. Below 25°, $C_v$ for $p=25$ is slightly less than $C_v^*$. Below 0°, $C_v$ at 100, 150, and 200 atm. drops far below $C_v^*$ as the temperature is lowered. A graph showing $\Delta\equiv v(pv/RT-1)$ vs. $\rho$ isotherms and isobars is shown, the data for which are listed in the table. This graph is very convenient for interpolating $p-v-T$ data. Having given two of the three $p-v-T$ coordinates, the third is quickly estimated from the graph, or is readily computed more exactly by reading the ordinate $\Delta$ and solving $\Delta=v(pv/RT-1)$ for the unknown desired. Values for the second virial coefficient are found. They are expressible by $B=58.03-19.84\ T^{-1}$ cc/mole between $-70°$ and $400°$.

FAIRLY complete compressibility data for several gases over considerable range of pressure and temperature are now available. The work of Bartlett and his collaborators and of others on nitrogen, hydrogen, and their mixtures,[1] carbon monoxide,[2] methane,[3] and helium[4] form valuable extensions of hitherto existing data. A method of determining derivatives such as $(dv/dp)_T$, $(dv/dT)_p$, $(d^2v/dT^2)_p$ from compressibility data enables various physical properties to be computed. The writers have been using a graphical scheme for evaluating derivatives. Curves and a table showing specific volume, density, fugacity, expansion coefficients $-(p/v)(dv/dp)_T$ and $(T/v)(dv/dT)_p$, $\Delta C_p$, $C_p$, $C_p - C_v$, $C_v$, and $\mu$ for nitrogen over the range −70° to 600° and from 20 to 1200 atm. have been published.[5] In the present paper we give the results for carbon monoxide.

This graphical scheme depends on the fact that

$$\Delta \equiv v(pv/RT - 1) \tag{1}$$

and

$$\alpha \equiv RT/p - v \tag{2}$$

and their derivatives with respect to $p$, $v$, $T$ express the deviation from Boyle's law; and that any departure of $-(p/v)\ (dv/dp)_T$ and $(T/v)\ (dv/dT)_p$ from unity is evidenced by $\Delta$ and $\alpha$ and their derivatives being different from zero. In addition to the relations between the derivatives of $v$, $\Delta$, and $\alpha$ given by Eqs. (3) to (10), we shall need[6]

$$(T/v)(dv/dT)_p = \frac{pv/RT - (d\Delta/dT^{-1})_p/vT}{1 + 2\rho\Delta} \tag{15}$$

$$(T/v)(dv/dT)_p = pv/RT[\rho^2(d\Delta/d\rho)_p + (1 + 2\rho\Delta)] \tag{16}$$

$$(T/v)(dv/dT)_p = (d\alpha/dT^{-1})_p/vT + RT/pv \tag{17}$$

$$-\ T(d^2v/dT^2)_p = \frac{T}{v}\left\{\left(\frac{dv}{dT}\right)^2 - \frac{1}{p}\,\frac{d}{dT}\left(pv\frac{dv}{dT}\right)\right\}_p, \tag{18}$$

[1] Bartlett, J. Amer. Chem. Soc. **49,** 687 (1927); **49,** 1955 (1927); Bartlett, Cupples, Tremearne, ibid. **50,** 1275 (1928); Bartlett, Hetherington, Kvalnes, Tremearne, ibid. **52,** 1363 (1930).

[2] Bartlett, Hetherington, Kvalnes, Tremearne, J. Amer. Chem. Soc., **52,** 1374 (1930); G. A. Scott, Proc. Roy. Soc. **125 A,** 330 (1929); Severian Goig-Botella, Anales soc. espan. fis-quim **27,** 315 (1929); one set of his measurements at 0° is published in duplicate in the Comptes Rendus **189,** 246 (1929).

[3] Kvalnes and Gaddy, J. Amer. Chem. Soc. **53,** 394 (1931). This publication gives data from −70° to 200° and up to 1000 atm. Isotherms at 300° and 400° will soon be undertaken by Dr. Wiebe on the same apparatus.

[4] Wiebe, Gaddy, Heins, J. Amer. Chem. Soc. **53,** 1721 (1931). This publication gives data from −70° to 200° and up to 1000 atm. Isotherms at 300° and 400° will soon be undertaken by Dr. Wiebe on the same apparatus.

[5] W. Edwards Deming and Lola E. Shupe, Phys. Rev. **37,** 638 (1931).

[6] In this paper, the equations, figures, and tables will be numbered as continuations from those in the paper on nitrogen.

because it is more accurate to use Δ and $\alpha$ in isobars against $T^{-1}$ than against $T$, and because the second derivative is conveniently found from $pv(dv/dT)_p$ vs. $T$ isobars, as will be explained later.

After Bartlett's[2] data on carbon monoxide were published a recalibration of his thermocouple showed that the temperatures recorded as −25°, −50°, −70° should have been −24.99°, −49.93°, −69.90°. The slight corrections necessary at these temperatures were made, and then Δ vs. $p$ isotherms were plotted from Bartlett's data at −70°, −50°, −25°, 0°, 25°, 50°, 100°, 150°, 200° to 1000 atm., and from Scott's 25° isotherm, which goes to 170 atm., and from Goig-Botella's isotherms at 0°, 12.44°, and 20.22°, which go from 50 to 130 atm. The low pressure portion of these isotherms are shown in Fig. 7. We also plotted Δ vs. $T^{-1}$ isobars obtained from Bartlett's data, at 25, 50, 75, 100, 150, 200, 300, 400, 500, 600, 800, 1000 atm., from −70° to 200°. On these curves were also placed points from Scott's and Goig-Botella's data where they could be used. By trial and error smooth isotherms and isobars were finally placed so that the same value of Δ would be read from a curve on either plot at a given temperature and pressure. This is equivalent to fixing a smooth Δ, $p$, $T^{-1}$ surface in space.

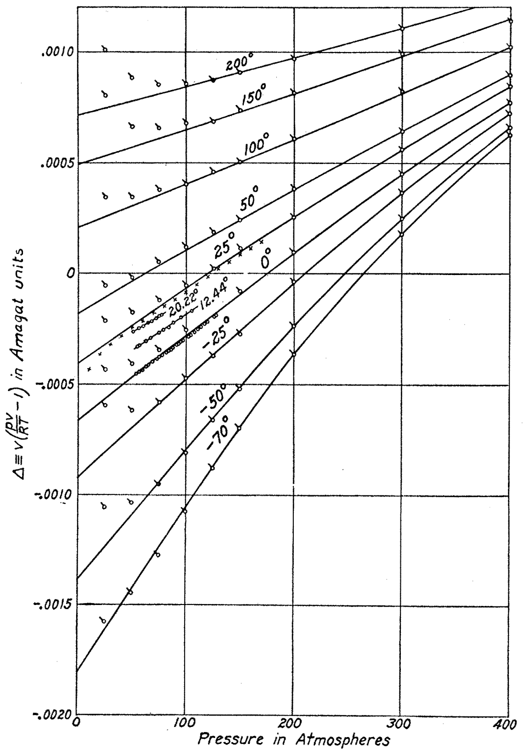

Fig. 7. Δ vs. $p$ isotherms for carbon monoxide to 400 atmospheres. Bartlett's points are flagged circles, Goig-Botella's are circles, Scott's are crosses. Scott's isotherm is at 25°, Goig-Botella's are at 0°, 12.44°, and 20.22°. The data were smoothed according to the curves.

The $pv/(pv)_s$ value for 800 atm. and 25° was misprinted in Bartlett's paper as 1.9915. It should be 1.0115.

Bartlett's isobars were extrapolated to 1200 atm. and his isotherms to 400°; this is a 20 percent extrapolation with regard to pressure and a 22 percent extrapolation with regard to $T^{-1}$. Since Bartlett gives nine isotherms and twelve isobars in the range $25 \leqq p \leqq 1000$ atm. and $0.002113 \leqq T^{-1} \leqq 0.004922$, extrapolation to 1200 atm. and to $0.001485°K^{-1}$ should be trustworthy. The value of these extrapolations, if they are any where near as reliable as we think they are, must be considerable; to extend the $p$-$v$-$T$ observations to 300° and 400° and to 1200 atm. would require some changes in the apparatus; in fact serious difficulties would have to be overcome in experiments with carbon monoxide at 300° and 400° under high pressure.

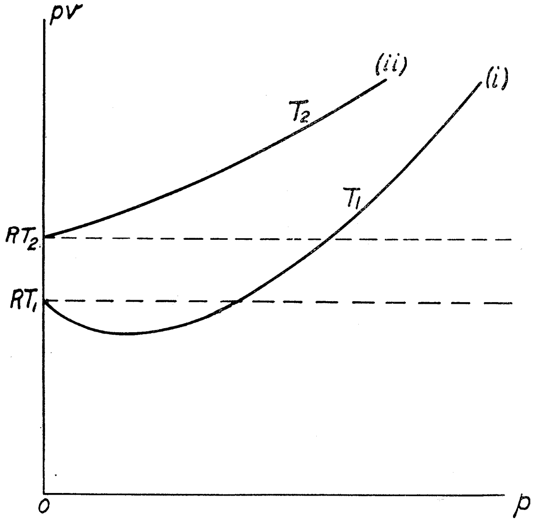

Fig. 8. The isothermal variation of $pv$ with $p$ at low pressure for an actual gas. Carbon monoxide takes the form of (*i*) at 50° or lower, and takes the form of (*ii*) at 100° or higher.

As with nitrogen, the close proximity of the plotted (experimental) values of $\Delta$ to the final smooth curves, on which lie the adjusted values of $\Delta$, attests to the high precision of the compressibility data and gives promise that the derived calculations should be reliable. An exception occurs at Bartlett's low pressure observations, as is seen in Fig. 7. The curves shown were drawn from the following considerations.

Holborn and Otto[7] found that the expression

$$pv = RT + ap + bp^2 + cp^4 \tag{19}$$

is capable of following the data of most of the permanent gases along an isotherm from about 20 to 100 atm. Recently William Wild[8] has observed that

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[7] Holborn and Otto, Zeits. f. Physik **33,** 1 (1925).

[8] William Wild, Phil. Mag. **12,** 41 (1931).

this power series, when used with constants obtained from data between roughly 20 and 100 atm., extrapolated to 1 atm. gives the "compressibility" (usually denoted by $1+\lambda$, the ratio of the $pv$ product at zero pressure to the product at 1 atm., both at 0°C) in agreement better than 1 in 10,000 with the value obtained from low pressure data where a linear equation $pv=RT+ap$ suffices. These facts mean that the series (19) is capable of expressing the trends of the isotherms from zero pressure up to 50 or 100 atm.

From Eq. (19),

$$\Delta = a + (a^2/RT + b)p + (2ab/RT)p^2 + (b^2/RT + c)p^3 + \cdots \quad (20)$$

A $pv$ vs. $p$ isotherm will take the form (*i*) or (*ii*) in Fig. 8, depending on whether the temperature is below or above the Boyle temperature; at the Boyle temperature $pv=RT$ and the curve is a horizontal line, at least for some distance. Along (*ii*) $a>0$ and $b>0$, hence the corresponding $\Delta$ vs. $p$ graph will begin as a straight line with a positive intercept and positive slope and will then curve upward as indicated in Fig. 9, since the coefficients of $p$ and $p^2$ in (20) are positive. Along (*i*) $a<0$ and $b>0$, so the corresponding $\Delta$ curve will begin as a straight line with a negative intercept and positive slope and will then curve downward as shown, since in (20) the coefficients of $p$ and $p^2$ are positive and negative respectively. The trends thus predicted for the $\Delta$ curves are beautifully followed by Goig-Botella's and Scott's points in Fig. 7, but not by Bartlett's. Goig-Botella's and Scott's apparatuses were designed for the low pressure region, but Bartlett's was designed primarily for

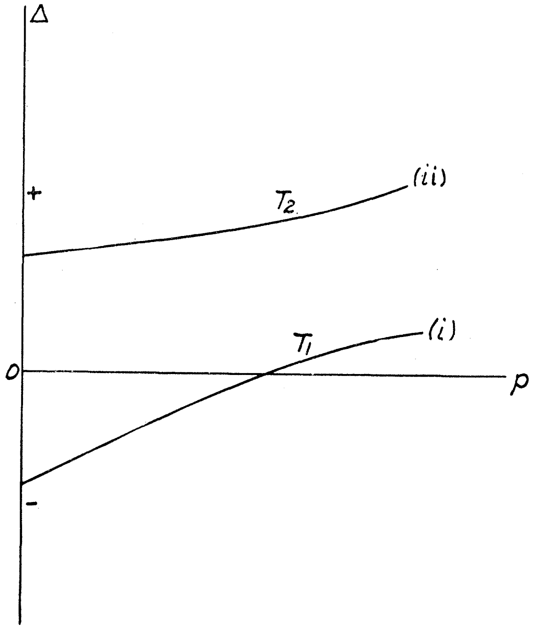

Fig. 9. The graphs of $\Delta$ vs. $p$ corresponding to the $pv$ vs. $p$ isotherms in Fig.6.

work from 100 to 1000 atm., and the upward curl of his points may come from a small systematic error, active only at low pressure. This explanation of the deviation is satisfactory according to a private communication from Dr. Bartlett.

It should be noted that this discrepancy is only slight. The $\Delta$ curves are magnified residuals; further, $(dp/d\Delta)_{v,T}=RT\rho^2$ is very small at the low pressure (or low density) end—at 25 atm. and 0° a change in $\Delta$ of 0.0001 Amagat units affects the calculated pressure only 0.06 atm.; therefore the points in Fig. 7, instead of showing the data to be unreliable, really show them to be remarkably systematic.

The family of $\Delta$ *vs.* $T^{-1}$ isobars (not shown) become nearly straight lines at the higher temperatures and at the lower pressures. The zero pressure isobar is fitted well enough by a straight line, and

$$\Delta = b - (a/R)T^{-1} \tag{21}$$

may be taken for its equation. When $\Delta$ is replaced by $v(pv/RT-1)$, this becomes closely

$$(p + a/v^2)(v - b) = RT, \tag{22}$$

which is van der Waals' equation. From this,

$$- T(d^2v/dT^2)_p = 2a/RT^2 \text{ at } p = 0. \tag{23}$$

The slope $-a/R$ of the zero pressure isobar is $-0.8856$ Amagat units, so

$$\begin{aligned} - T(d^2v/dT^2)_p &= 2 \times 0.8856T^{-2} \text{ Amagat units} \\ &= 960.7T^{-2} \text{ cal./mole atm. deg.} \end{aligned} \tag{24}$$

This quantity will be used later in calculating the heat capacities. It is the value of $(dC_p/dp)_T$ at zero pressure. A more accurate equation of state would give the same result for this purpose, since we need the derivative $-T(d^2v/dT^2)_p$ only at zero pressure.

Eq. (1) can be rewritten as

$$pv/RT = 1 + \Delta\rho. \tag{25}$$

$\Delta$ at low pressures is then the second virial coefficient, usually denoted by $B$; so the $\Delta$ vs. $T^{-1}$ zero pressure isobar is really a plot of $B$. It is expressed by statistical theory in terms of the interaction energy $\epsilon$ of two molecules, and the temperature, by

$$B = 2\pi N \int_0^\infty (1 - e^{-\epsilon/kT})r^2dr. \tag{26}$$

According to London,[9] $-\epsilon$ lies between $3\alpha^2V_a/4r^6$ and $3\alpha^2V_i/4r^6$. $\alpha$ here denotes the polarizability of the molecule, and is not the $\alpha$ of Eq. (2). $V_a$ and $V_i$ are the excitation and ionization energies, and $r$ is the molecular separation.

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[9] Eisenschitz and London, Zeits. f. Physik **60**, 491 (1930); London, Zeits. f. Physik **63**, 245 (1930).

Margenau[10] evaluated the above integral by assuming that $\epsilon = \infty$ for $r \leqq d$, and $-\epsilon = 3\alpha^2 V_i / 4r^6$ when $r > d$. His result is

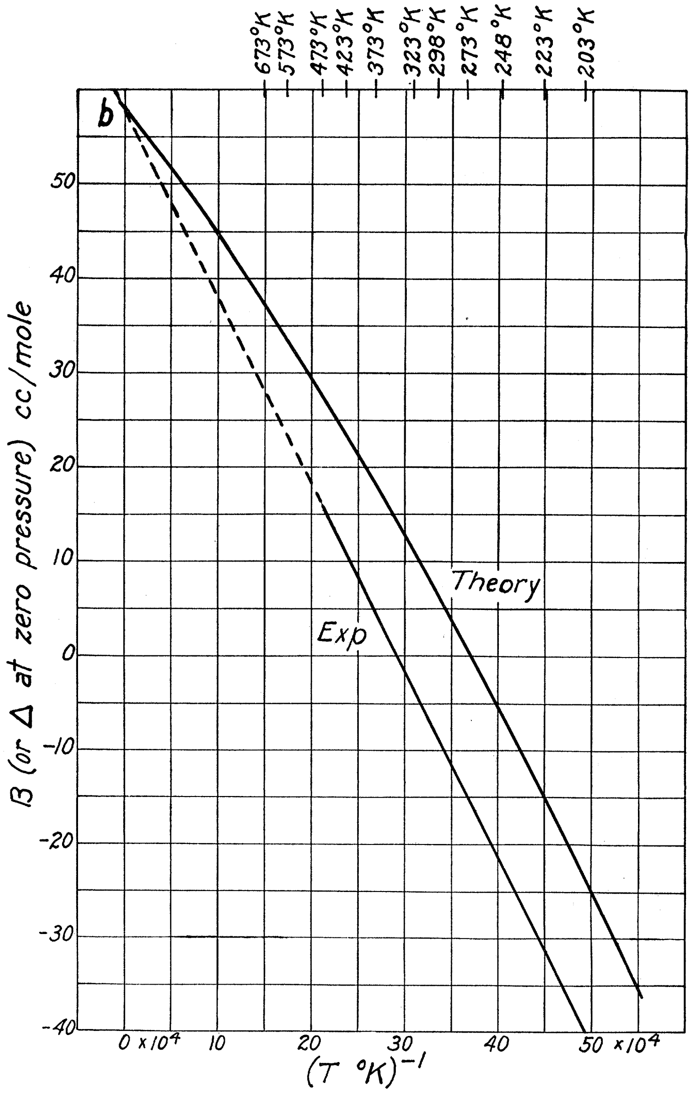

Fig. 10. Carbon monoxide. The curve marked "Exp." shows the experimental values of the second virial coefficient from −70° to 200°C. The extrapolation (dashed) gives $b = 58.03$ cc/mole. This value in Eq. (27) gives the curve marked "Theory".

$$B = b(1 - 0.75y - 0.094y^2 - 0.014y^3 - 0.0019y^4 - 0.00022y^5 - 0.000022y^6 - \cdots) \quad (27)$$

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[10] H. Margenau, Phys. Rev. **36**, 1782 (1930).

where

$$b = 2\pi N d^3/3, \quad y = \alpha^2 V_i/d^6 kT = 4\pi^2 N^2 \alpha^2 V_i/9kb^2 T.$$

$b$ is thus four times the volume of $N$ spheres of diameter $d$. If $N$ is the number of molecules per mole, $b$ is in cc/mole. $b$ can be evaluated by extrapolating the zero pressure $\Delta$ vs. $T^{-1}$ isobar back to $T^{-1}=0$. The value so obtained is $b=0.002590$ Amagat units or $22403\times 0.002590=58.03$ cc/mole. Zahn and Miles[11] give information from which it is possible to deduce that the polarizability of CO is $1.97\times 10^{-24}$cc per molecule. John T. Tate and P. T. Smith[12] found 14.20 electron volts for the ionization potential of CO.

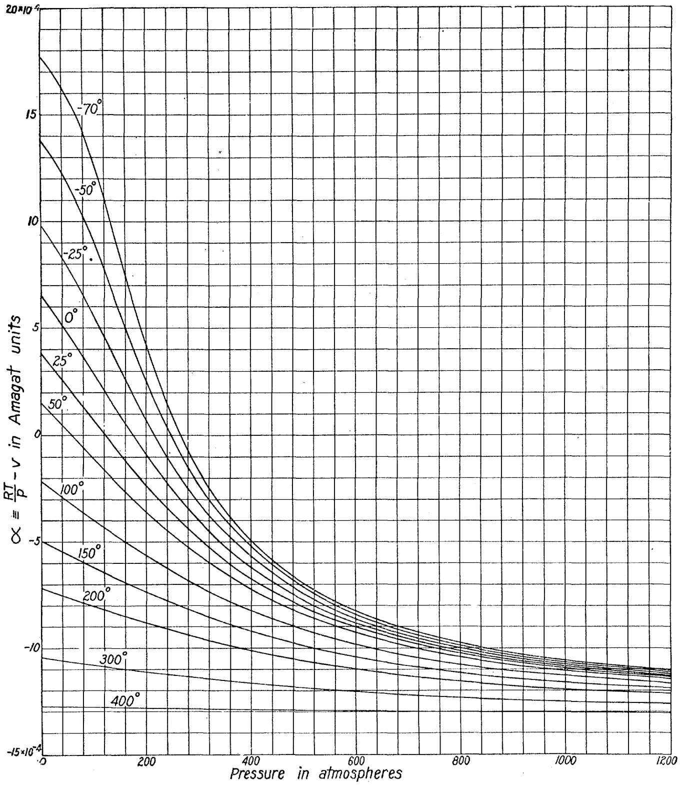

Fig. 11. $\alpha$ vs. $p$ isotherms for carbon monoxide.

With these, $y=177.7T^{-1}$. The curve given by the series (27) is marked "Theory" in Fig. 10. The curve marked "Exp." is our $\Delta$ vs. $T^{-1}$ zero pressure isobar. The agreement is fairly good. The theoretical curve has a perceptible curvature over the range of experiment, $-70° \leqq t \leqq 200°$, while the other does not. According to a recent paper by Kirkwood and Keyes,[13] the second virial

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[11] C. T. Zahn and J. B. Miles Jr., Phys. Rev. **32,** 497 (1928).

[12] From a paper read at the Washington meeting of the American Physical Society, May 2, 1931.

[13] J. G. Kirkwood and F. G. Keyes, Phys. Rev. **37,** 832 (1931).

coefficient for He goes through a maximum at about $-100°$, and the same phenomenon should appear at sufficiently high temperatures for other gases. This would imply that the experimental curve should not be extrapolated as a straight line to $T^{-1}=0$ and that $b<58.03$; also that the assumptions underlying the development of Eq. (27) are not fully valid at high temperatures, and that perfect agreement of the curves in Fig. 10 is not to be expected. The experimental curve in Fig. 10, or the list of $\Delta$ at zero pressure at the bottom of Table II are probably as good values for the second virial coefficient from $-70°$ to 400° as can be gotten from the data available.

The $\alpha$ vs. $p$ isotherms of Fig. 11 might be of some interest. There has been some conjecture[14] concerning the shape of these curves for a real gas, and Fig. 11 is probably the first publication for an extended range for any gas.[14a] The areas under the curves are used in determining fugacities by Eq. (28).

The tables published by Bartlett and others show compressibility factors $pv/(pv)_s$ at the different pressures and temperatures. The denominator $(pv)_s$ is the value of $pv$ at S. T. P. Baxter[15] gives 1.00048 for $pv/(pv)_s$ at zero pressure. Using Birge's value 22414.1 cc for the volume of a mole of an ideal gas at S. T. P. we have $22414.1/1.00048=22403.3$ for the factor to convert Amagat units of volume into cc/mole. Multiplication of densities in mole/cc by 28.006 converts them into g/cc. We also use $R=82.0489$ cc atm./mole deg. or 1.9864 cal./mole deg., and 273.18° for the ice point, after Birge.

The final values of the physical properties are shown in Table II and in the figures. Care has been taken in each entry to give only as many figures as we consider significant; the last figure is considered doubtful. No points are shown on the curves because they are drawn through the plotted point in every case. Each physical property listed will now be discussed.

### Specific volume v, column 2; density $\rho$, column 3; $\Delta$, column 10 and Fig. 12.

The values of $\Delta$ were read from the $\Delta$ vs. $p$ isotherms or from the $\Delta$ vs. $T^{-1}$ isobars. Those for zero pressure or zero density constitute the second virial coefficient, and are shown at the bottom of the table and in Fig. 10. Eq. (1) solved for $v$ then gives the specific volume for any pressure and temperature at which $\Delta$ is known. The densities in column 3 are in g/cc and were obtained by dividing 28.006 by the corresponding $v$ in cc/mole.

The $\Delta$ vs. $\rho$ isotherms and isobars of Fig. 12 are convenient for exhibiting and interpolating the $p$-$v$-$T$ data, as is described in the title to the figure. Any one of the $p$-$v$-$T$ coordinates can be quickly estimated when the other two are given; when greater accuracy is desired, the value of $\Delta$, as read from the graph corresponding to the two given coordinates ($\rho$ and $T$, $v$ and $p$, etc.), is substituted in Eq. (1) to obtain the third coordinate. The values of $\Delta$ are listed so that anyone desiring to make interpolations in the $p$-$v$-$T$ data with more accuracy than can be gotten from the Fig. 12 appearing here can construct a

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[14] Lewis and Randall, Thermodynamics, p. 195 (McGraw-Hill Book Company, 1923).

[14a] Added in proof. Since this was written, a table of $\alpha$ for nitrogen from $-148°$ to 300° and to about 100 atm. has appeared in a paper by George Tunell, J. Phys. Chem. **35**, 2885 (1931).

[15] Baxter *et al.*, J. Amer. Chem. Soc. **53**, 1627 (1931).

TABLE II. *Some physical properties of compressed carbon monoxide derived from experimental data on compressibility.*

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| $p$ | $v$ | $\rho$ | $f$ | $-\frac{p}{v}\left(\frac{dv}{dp}\right)_T$ | $\frac{T}{v}\left(\frac{dv}{dT}\right)_p$ | $\Delta C_p$ | $C_p$ | $C_v$ | $\Delta$ |
| atm. | cc/mole | g/cc | atm. | | | calories/mole degree | | | cc/mole |
| $t=-70°$ $C_p^*=6.953$, $C_v^*=4.967$ cal./mole deg. | | | | | | | | | |
| 25 | 629.0 | .04453 | 23.59 | 1.057 | 1.220 | .63 | 7.58 | 4.94 | −35.62 |
| 50 | 298.1 | .09395 | 44.67 | 1.100 | 1.465 | 1.37 | 8.32 | 4.86 | −31.57 |
| 75 | 189.8 | .1475 | 63.68 | 1.118 | 1.710 | 2.21 | 9.16 | 4.71 | −27.71 |
| 100 | 138.3 | .2025 | 81.13 | 1.076 | 1.899 | 3.11 | 10.06 | 4.54 | −23.64 |
| 150 | 92.40 | .3031 | 113.4 | .881 | 1.943 | 4.57 | 11.53 | 4.45 | −15.57 |
| 200 | 73.95 | .3787 | 144.9 | .667 | 1.706 | 5.38 | 12.34 | 4.64 | −8.33 |
| 300 | 59.32 | .4721 | 214.5 | .446 | 1.188 | 5.76 | 12.72 | 6.01 | 4.01 |
| 400 | 52.77 | .5307 | 299.5 | .366 | .888 | 5.52 | 12.47 | 7.05 | 14.05 |
| 500 | 48.91 | .5726 | 405.9 | .320 | .780 | 5.26 | 12.21 | 6.67 | 22.85 |
| 600 | 46.23 | .6058 | 539.7 | .293 | .708 | 5.31 | 12.26 | 6.62 | 30.69 |
| 800 | 42.69 | .6561 | 917.8 | .257 | .552 | 5.52 | 12.47 | 7.63 | 44.76 |
| 1000 | 40.35 | .6941 | 1509 | .238 | .467 | 5.62 | 12.57 | 8.17 | 57.31 |
| 1100 | 39.43 | .7103 | 1917 | .231 | .426 | 5.65 | 12.60 | 8.54 | 63.16 |
| 1200 | 38.62 | .7252 | 2422 | .223 | .396 | 5.67 | 12.62 | 8.75 | 68.73 |
| $t=-50°$ $C_p^*=6.953$, $C_v^*=4.967$ cal./mole deg. | | | | | | | | | |
| 25 | 703.6 | .03980 | 24.00 | 1.038 | 1.168 | .51 | 7.46 | 4.95 | −27.69 |
| 50 | 339.9 | .08239 | 46.22 | 1.062 | 1.352 | 1.07 | 8.02 | 4.85 | −24.40 |
| 75 | 220.6 | .1269 | 67.00 | 1.064 | 1.500 | 1.67 | 8.63 | 4.83 | −21.24 |
| 100 | 162.9 | .1719 | 86.70 | 1.037 | 1.619 | 2.28 | 9.23 | 4.77 | −17.99 |
| 150 | 109.3 | .2561 | 124.3 | .909 | 1.655 | 3.28 | 10.23 | 4.87 | −11.40 |
| 200 | 86.02 | .3256 | 161.7 | .751 | 1.528 | 3.87 | 10.82 | 5.02 | −5.20 |
| 300 | 66.20 | .4231 | 242.9 | .551 | 1.172 | 4.16 | 11.11 | 5.74 | 5.60 |
| 400 | 57.44 | .4876 | 339.4 | .433 | .942 | 4.01 | 10.96 | 5.86 | 14.63 |
| 500 | 52.60 | .5325 | 457.9 | .374 | .810 | 3.86 | 10.81 | 5.80 | 22.94 |
| 600 | 49.36 | .5674 | 604.6 | .337 | .710 | 3.88 | 10.83 | 6.02 | 30.47 |
| 800 | 45.00 | .6224 | 1010 | .291 | .569 | 4.02 | 10.97 | 6.63 | 43.46 |
| 1000 | 42.16 | .6643 | 1624 | .271 | .484 | 4.08 | 11.03 | 7.08 | 54.91 |
| 1100 | 41.07 | .6819 | 2038 | .262 | .447 | 4.10 | 11.05 | 7.31 | 60.27 |
| 1200 | 40.13 | .6979 | 2544 | .251 | .417 | 4.11 | 11.06 | 7.44 | 65.42 |
| $t=-25°$ $C_p^*=6.954$ $C_v^*=4.968$ cal./mole deg. | | | | | | | | | |
| 25 | 794.6 | .03524 | 24.36 | 1.022 | 1.124 | .40 | 7.36 | 4.96 | −19.33 |
| 50 | 389.7 | .07186 | 47.62 | 1.032 | 1.245 | .82 | 7.78 | 4.93 | −16.76 |
| 75 | 256.4 | .1092 | 70.01 | 1.029 | 1.348 | 1.26 | 8.22 | 4.90 | −14.23 |
| 100 | 191.3 | .1464 | 91.80 | 1.007 | 1.421 | 1.69 | 8.64 | 4.90 | −11.58 |
| 150 | 128.9 | .2173 | 134.5 | .925 | 1.454 | 2.36 | 9.31 | 5.00 | −6.50 |
| 200 | 100.3 | .2791 | 177.5 | .808 | 1.392 | 2.76 | 9.71 | 5.02 | −1.46 |
| 300 | 74.75 | .3747 | 270.5 | .629 | 1.152 | 2.99 | 9.95 | 5.31 | 7.84 |
| 400 | 63.62 | .4403 | 378.8 | .509 | .969 | 2.93 | 9.88 | 5.30 | 15.88 |
| 500 | 57.35 | .4883 | 509.2 | .437 | .833 | 2.84 | 9.80 | 5.36 | 23.41 |
| 600 | 53.26 | .5258 | 667.6 | .393 | .724 | 2.83 | 9.78 | 5.61 | 30.33 |
| 800 | 47.86 | .5852 | 1094 | .342 | .591 | 2.86 | 9.81 | 5.99 | 42.14 |
| 1000 | 44.45 | .6301 | 1720 | .314 | .504 | 2.87 | 9.82 | 6.31 | 52.58 |
| 1100 | 43.13 | .6494 | 2132 | .303 | .469 | 2.88 | 9.83 | 6.48 | 57.35 |
| 1200 | 42.01 | .6666 | 2628 | .285 | .441 | 2.88 | 9.84 | 6.48 | 62.01 |
| $t=0°$ $C_p^*=6.956$, $C_v^*=4.970$ cal./mole deg. | | | | | | | | | |
| 25 | 884.0 | .03168 | 24.62 | 1.012 | 1.094 | .33 | 7.28 | 4.96 | −12.55 |
| 50 | 437.6 | .06400 | 48.60 | 1.015 | 1.183 | .66 | 7.62 | 4.94 | −10.44 |
| 75 | 290.3 | .09649 | 72.13 | 1.008 | 1.255 | 1.00 | 7.95 | 4.94 | −8.33 |
| 100 | 217.8 | .1286 | 95.38 | .989 | 1.305 | 1.32 | 8.27 | 4.95 | −6.25 |
| 150 | 147.4 | .1900 | 141.7 | .926 | 1.334 | 1.83 | 8.79 | 5.02 | −2.02 |
| 200 | 114.2 | .2453 | 189.0 | .843 | 1.299 | 2.14 | 9.10 | 5.05 | 2.15 |
| 300 | 83.71 | .3346 | 290.8 | .674 | 1.135 | 2.36 | 9.32 | 5.07 | 10.08 |
| 400 | 69.96 | .4003 | 408.3 | .566 | .980 | 2.35 | 9.31 | 5.10 | 17.39 |
| 500 | 62.19 | .4504 | 547.6 | .493 | .851 | 2.31 | 9.27 | 5.22 | 24.08 |
| 600 | 57.13 | .4902 | 714.1 | .443 | .748 | 2.27 | 9.23 | 5.39 | 30.24 |
| 800 | 50.72 | .5521 | 1152 | .380 | .616 | 2.20 | 9.16 | 5.57 | 41.11 |
| 1000 | 46.72 | .5995 | 1778 | .352 | .531 | 2.16 | 9.12 | 5.81 | 50.65 |
| 1100 | 45.18 | .6199 | 2183 | .340 | .496 | 2.15 | 9.11 | 5.93 | 55.00 |
| 1200 | 43.90 | .6380 | 2663 | .319 | .467 | 2.15 | 9.10 | 5.92 | 59.28 |
| $t=25°$ $C_p^*=6.959$, $C_v^*=4.973$ cal./mole deg. | | | | | | | | | |
| 25 | 971.8 | .02882 | 24.80 | 1.005 | 1.073 | .27 | 7.23 | 4.97 | −6.72 |
| 50 | 484.2 | .05784 | 49.31 | 1.003 | 1.140 | .54 | 7.50 | 4.96 | −5.04 |
| 75 | 322.8 | .08675 | 73.64 | .994 | 1.193 | .81 | 7.77 | 4.96 | −3.32 |
| 100 | 243.1 | .1152 | 97.94 | .977 | 1.229 | 1.07 | 8.02 | 4.98 | −1.52 |
| 150 | 165.1 | .1696 | 147.0 | .926 | 1.248 | 1.47 | 8.43 | 5.04 | 2.03 |

TABLE II. (*Continued*).

| 1 $p$ atm. | 2 $v$ cc/mole | 3 $\rho$ g/cc | 4 $f$ atm. | 5 $-\frac{p}{v}\left(\frac{dv}{dp}\right)_T$ | 6 $\frac{T}{v}\left(\frac{dv}{dT}\right)_p$ | 7 $\Delta C_p$ calories/mole degree | 8 $C_p$ | 9 $C_v$ | 10 $\Delta$ cc/mole |
|---|---|---|---|---|---|---|---|---|---|
| 200 | 127.6 | .2195 | 197.5 | .851 | 1.229 | 1.72 | 8.68 | 5.08 | 5.51 |
| 300 | 92.40 | .3031 | 306.2 | .724 | 1.116 | 1.93 | 8.89 | 5.02 | 12.30 |
| 400 | 76.25 | .3673 | 430.8 | .612 | .984 | 1.95 | 8.91 | 4.99 | 18.82 |
| 500 | 67.04 | .4177 | 576.4 | .540 | .869 | 1.93 | 8.89 | 5.08 | 24.82 |
| 600 | 60.94 | .4596 | 748.1 | .488 | .772 | 1.89 | 8.84 | 5.22 | 30.13 |
| 800 | 53.55 | .5230 | 1191 | .417 | .644 | 1.80 | 8.76 | 5.30 | 40.24 |
| 1000 | 48.97 | .5719 | 1808 | .387 | .555 | 1.73 | 8.69 | 5.52 | 49.06 |
| 1100 | 47.22 | .5930 | 2201 | .373 | .522 | 1.71 | 8.66 | 5.59 | 53.05 |
| 1200 | 45.77 | .6119 | 2661 | .348 | .493 | 1.67 | 8.63 | 5.52 | 56.97 |
| $t=50°$ $C_p^*=6.965$, $C_v^*=4.979$ cal./mole deg. | | | | | | | | | |
| 25 | 1059 | .02645 | 24.94 | 1.000 | 1.058 | .23 | 7.19 | 4.98 | −1.90 |
| 50 | 529.8 | .05286 | 49.82 | .995 | 1.109 | .46 | 7.42 | 4.97 | −.45 |
| 75 | 354.5 | .07899 | 74.74 | .985 | 1.149 | .68 | 7.64 | 4.97 | 1.01 |
| 100 | 267.7 | .1046 | 99.81 | .969 | 1.176 | .88 | 7.85 | 4.99 | 2.53 |
| 150 | 182.2 | .1537 | 150.8 | .925 | 1.193 | 1.21 | 8.17 | 5.03 | 5.58 |
| 200 | 140.6 | .1992 | 203.7 | .871 | 1.177 | 1.42 | 8.39 | 5.04 | 8.54 |
| 300 | 101.0 | .2773 | 317.8 | .755 | 1.097 | 1.62 | 8.59 | 4.97 | 14.43 |
| 400 | 82.47 | .3396 | 447.5 | .650 | .984 | 1.68 | 8.65 | 4.97 | 20.14 |
| 500 | 71.87 | .3896 | 597.7 | .580 | .883 | 1.68 | 8.64 | 5.02 | 25.54 |
| 600 | 64.92 | .4314 | 772.9 | .527 | .796 | 1.65 | 8.61 | 5.11 | 30.45 |
| 800 | 56.53 | .4955 | 1218 | .454 | .673 | 1.58 | 8.54 | 5.16 | 39.88 |
| 1000 | 51.27 | .5462 | 1826 | .418 | .580 | 1.50 | 8.46 | 5.37 | 47.88 |
| 1100 | 49.28 | .5684 | 2207 | .402 | .551 | 1.46 | 8.42 | 5.36 | 51.46 |
| 1200 | 47.65 | .5877 | 2649 | .376 | .518 | 1.42 | 8.38 | 5.33 | 55.11 |
| $t=100°$ $C_p^*=6.987$, $C_v^*=5.001$ cal./mole deg. | | | | | | | | | |
| 25 | 1231 | .02276 | 25.11 | .994 | 1.037 | .17 | 7.16 | 5.00 | 5.94 |
| 50 | 619.3 | .04522 | 50.48 | .986 | 1.069 | .34 | 7.33 | 5.00 | 7.03 |
| 75 | 416.2 | .06730 | 76.18 | .974 | 1.092 | .50 | 7.49 | 5.00 | 8.07 |
| 100 | 315.1 | .08889 | 102.3 | .959 | 1.108 | .64 | 7.63 | 5.01 | 9.16 |
| 150 | 215.0 | .1303 | 155.9 | .924 | 1.119 | .87 | 7.86 | 5.02 | 11.43 |
| 200 | 165.7 | .1690 | 211.9 | .881 | 1.112 | 1.04 | 8.02 | 5.01 | 13.67 |
| 300 | 117.9 | .2375 | 333.1 | .792 | 1.064 | 1.24 | 8.22 | 4.94 | 18.34 |
| 400 | 95.04 | .2947 | 469.8 | .705 | .980 | 1.32 | 8.31 | 4.95 | 22.96 |
| 500 | 81.70 | .3428 | 625.9 | .643 | .898 | 1.34 | 8.33 | 5.00 | 27.31 |
| 600 | 73.04 | .3835 | 805.1 | .588 | .831 | 1.33 | 8.32 | 4.98 | 31.50 |
| 800 | 62.44 | .4485 | 1249 | .514 | .715 | 1.27 | 8.26 | 5.04 | 39.43 |
| 1000 | 55.91 | .5009 | 1835 | .470 | .635 | 1.21 | 8.20 | 5.08 | 46.20 |
| 1100 | 53.54 | .5231 | 2194 | .453 | .600 | 1.18 | 8.16 | 5.13 | 49.44 |
| 1200 | 51.56 | .5431 | 2604 | .428 | .569 | 1.15 | 8.14 | 5.10 | 52.65 |
| $t=150°$ $C_p^*=7.024$, $C_v^*=5.038$ cal./mole deg. | | | | | | | | | |
| 25 | 1401 | .02000 | 25.21 | .991 | 1.024 | .13 | 7.16 | 5.04 | 11.96 |
| 50 | 707.0 | .03961 | 50.86 | .980 | 1.044 | .26 | 7.28 | 5.04 | 12.88 |
| 75 | 476.2 | .05881 | 77.00 | .968 | 1.058 | .38 | 7.41 | 5.04 | 13.67 |
| 100 | 361.1 | .07755 | 103.7 | .954 | 1.067 | .49 | 7.52 | 5.05 | 14.52 |
| 150 | 246.8 | .1146 | 158.8 | .923 | 1.074 | .67 | 7.70 | 5.05 | 16.31 |
| 200 | 190.1 | .1473 | 216.6 | .888 | 1.070 | .81 | 7.84 | 5.03 | 18.10 |
| 300 | 134.5 | .2082 | 341.9 | .814 | 1.037 | 1.01 | 8.03 | 4.98 | 21.87 |
| 400 | 107.4 | .2607 | 482.5 | .741 | .971 | 1.11 | 8.13 | 5.01 | 25.54 |
| 500 | 91.60 | .3057 | 641.5 | .685 | .906 | 1.15 | 8.17 | 5.03 | 29.24 |
| 600 | 81.19 | .3449 | 821.9 | .634 | .848 | 1.16 | 8.19 | 5.03 | 32.72 |
| 800 | 68.42 | .4093 | 1260 | .562 | .743 | 1.16 | 8.18 | 5.10 | 39.45 |
| 1000 | 60.72 | .4612 | 1825 | .514 | .668 | 1.13 | 8.15 | 5.13 | 45.48 |
| 1100 | 57.86 | .4840 | 2164 | .495 | .638 | 1.12 | 8.14 | 5.14 | 48.21 |
| 1200 | 55.50 | .5046 | 2548 | .473 | .606 | 1.11 | 8.13 | 5.17 | 50.97 |
| $t=200°$ $C_p^*=7.076$, $C_v^*=5.090$ cal./mole deg. | | | | | | | | | |
| 25 | 1569 | .01784 | 25.26 | .989 | 1.015 | .11 | 7.18 | 5.09 | 16.76 |
| 50 | 793.5 | .03529 | 51.08 | .977 | 1.028 | .21 | 7.28 | 5.09 | 17.47 |
| 75 | 535.2 | .05233 | 77.48 | .964 | 1.035 | .31 | 7.38 | 5.10 | 18.21 |
| 100 | 406.3 | .06893 | 104.5 | .951 | 1.040 | .39 | 7.47 | 5.10 | 18.93 |
| 150 | 277.7 | .1008 | 160.5 | .923 | 1.045 | .54 | 7.62 | 5.09 | 20.32 |
| 200 | 213.9 | .1309 | 219.4 | .892 | 1.038 | .66 | 7.74 | 5.09 | 21.82 |
| 300 | 150.7 | .1858 | 347.1 | .830 | 1.014 | .84 | 7.91 | 5.04 | 24.82 |
| 400 | 119.7 | .2340 | 489.8 | .769 | .962 | .94 | 8.02 | 5.07 | 27.91 |
| 500 | 101.4 | .2763 | 649.9 | .718 | .908 | .99 | 8.07 | 5.09 | 30.96 |
| 600 | 89.28 | .3137 | 830.1 | .671 | .859 | 1.03 | 8.10 | 5.09 | 33.91 |
| 800 | 73.39 | .3765 | 1261 | .600 | .767 | 1.06 | 8.14 | 5.15 | 39.65 |
| 1000 | 65.50 | .4276 | 1805 | .550 | .692 | 1.08 | 8.15 | 5.24 | 45.01 |
| 1100 | 62.22 | .4501 | 2128 | .531 | .664 | 1.08 | 8.16 | 5.25 | 47.47 |
| 1200 | 59.51 | .4706 | 2488 | .510 | .632 | 1.08 | 8.16 | 5.30 | 49.96 |

TABLE II.—(*Continued*)

| 1<br>$p$<br>atm. | 2<br>$v$<br>cc/mole | 3<br>$\rho$<br>g/cc | 4<br>$f$<br>atm. | 5<br>$\frac{p}{v}\left(\frac{dv}{dp}\right)_T$ | 6<br>$\frac{T}{v}\left(\frac{dv}{dT}\right)_p$ | 7<br>$\Delta C_p$<br>calories/mole degree | 8<br>$C_p$ | 9<br>$C_v$ | 10<br>$\Delta$<br>cc/mole |
|---|---|---|---|---|---|---|---|---|---|
| | | | $t=300°$ | $C_p^*=7.218,$ | $C_v^*=5.232$ | cal./mole deg. | | | |
| 25 | 1905 | .01470 | 25.31 | .988 | 1.006 | .07 | 7.29 | 5.23 | 23.86 |
| 50 | 964.3 | .02905 | 51.27 | .975 | 1.009 | .14 | 7.36 | 5.23 | 24.35 |
| 75 | 651.0 | .04302 | 77.88 | .962 | 1.010 | .20 | 7.42 | 5.24 | 24.89 |
| 100 | 494.5 | .05664 | 105.2 | .950 | 1.010 | .26 | 7.48 | 5.24 | 25.45 |
| 150 | 338.0 | .08285 | 161.9 | .924 | 1.010 | .36 | 7.58 | 5.21 | 26.46 |
| 200 | 257.8 | .1086 | 221.6 | .900 | 1.000 | .45 | 7.66 | 5.22 | 27.56 |
| 300 | 182.2 | .1537 | 350.8 | .850 | .976 | .58 | 7.80 | 5.21 | 29.60 |
| 400 | 143.6 | .1951 | 494.1 | .803 | .946 | .68 | 7.90 | 5.20 | 31.77 |
| 500 | 120.6 | .2322 | 653.2 | .763 | .904 | .76 | 7.98 | 5.25 | 34.03 |
| 600 | 105.3 | .2659 | 829.7 | .722 | .864 | .82 | 8.04 | 5.28 | 36.20 |
| 800 | 86.42 | .3241 | 1243 | .655 | .792 | .92 | 8.14 | 5.34 | 40.64 |
| 1000 | 75.02 | .3733 | 1749 | .606 | .721 | .99 | 8.21 | 5.49 | 44.67 |
| 1100 | 70.87 | .3952 | 2042 | .586 | .698 | 1.01 | 8.23 | 5.49 | 46.62 |
| 1200 | 67.40 | .4155 | 2372 | .567 | .670 | 1.03 | 8.25 | 5.54 | 48.53 |
| | | | $t=400°$ | $C_p^*=7.386,$ | $C_v^*=5.400$ | cal./mole deg. | | | |
| 25 | 2238 | .01252 | 25.32 | .987 | 1.000 | .05 | 7.44 | 5.40 | 28.90 |
| 50 | 1133 | .02472 | 51.31 | .975 | .999 | .10 | 7.49 | 5.40 | 29.26 |
| 75 | 765.0 | .03661 | 77.96 | .962 | .997 | .15 | 7.54 | 5.41 | 29.68 |
| 100 | 581.0 | .04821 | 105.3 | .950 | .996 | .19 | 7.58 | 5.40 | 30.16 |
| 150 | 396.9 | .07057 | 162.1 | .927 | .987 | .26 | 7.65 | 5.40 | 30.92 |
| 200 | 304.9 | .09186 | 221.8 | .905 | .978 | .33 | 7.71 | 5.40 | 31.70 |
| 300 | 212.9 | .1316 | 350.6 | .864 | .954 | .44 | 7.82 | 5.40 | 33.27 |
| 400 | 166.9 | .1678 | 492.4 | .823 | .931 | .53 | 7.92 | 5.39 | 34.86 |
| 500 | 139.4 | .2009 | 648.6 | .790 | .897 | .62 | 8.00 | 5.45 | 36.52 |
| 600 | 121.0 | .2314 | 820.3 | .758 | .861 | .69 | 8.08 | 5.52 | 38.11 |
| 800 | 98.18 | .2852 | 1215 | .696 | .793 | .83 | 8.21 | 5.66 | 41.45 |
| 1000 | 84.41 | .3318 | 1688 | .649 | .733 | .93 | 8.32 | 5.81 | 44.61 |
| 1100 | 79.42 | .3527 | 1958 | .626 | .716 | .97 | 8.35 | 5.78 | 46.20 |
| 1200 | 75.25 | .3722 | 2252 | .605 | .696 | 1.00 | 8.38 | 5.78 | 47.79 |

$\Delta \equiv v(pv/RT-1)$ in cc/mole extrapolated to zero pressure

| $t$°C | $\Delta$ | $t$°C | $\Delta$ |
|---|---|---|---|
| −70 | −39.65 | 100 | 4.84 |
| −50 | −30.89 | 150 | 11.09 |
| −25 | −21.96 | 200 | 16.09 |
| 0 | −14.63 | 300 | 23.37 |
| 25 | −8.51 | 400 | 28.50 |
| 50 | −3.38 | | |

larger scale chart for that purpose. It is planned to publish large size plots of $\Delta$ vs. $\rho$ isotherms and isobars for the gases nitrogen, carbon monoxide, hydrogen, 3:1 hydrogen nitrogen mixture, methane, and helium, as a U. S. Department of Agriculture publication.

### Fugacity $f$, column 4.

Fugacities are computed from the equation

$$f = p \exp\left(-\,1/RT\right) \int_0^p \alpha dp. \tag{28}$$

The integral was evaluated by mechanical integration of the $\alpha$ vs. $p$ isotherms of Fig. 11.

### Expansion coefficients $-(p/v)(dv/dp)_T$ and $(T/v)(dv/dT)_p$, columns 5 and 6.

The $\Delta$ vs. $p$, $\alpha$ vs. $p$, and $\Delta$ vs. $\rho$ isotherms and the $\Delta$ vs. $T^{-1}$, $\alpha$ vs. $T^{-1}$, and $\Delta$ vs. $\rho$ isobars are now used to get derivatives. The slopes of these curves can be determined at any point by the graphical method described in the paper on nitrogen.[5] This method consists of estimating the slope of an $\alpha$ or $\Delta$ curve by mechanical means, and then using this slope as a correction term to find the corresponding derivative of $v$, by Eqs. (3) *et seq.* The three determinations of $-(p/v)\,(dv/dp)_T$ obtained through Eqs. (6), (7), (8) at each point were plotted in isotherms against pressure and in isobars against temperature, and

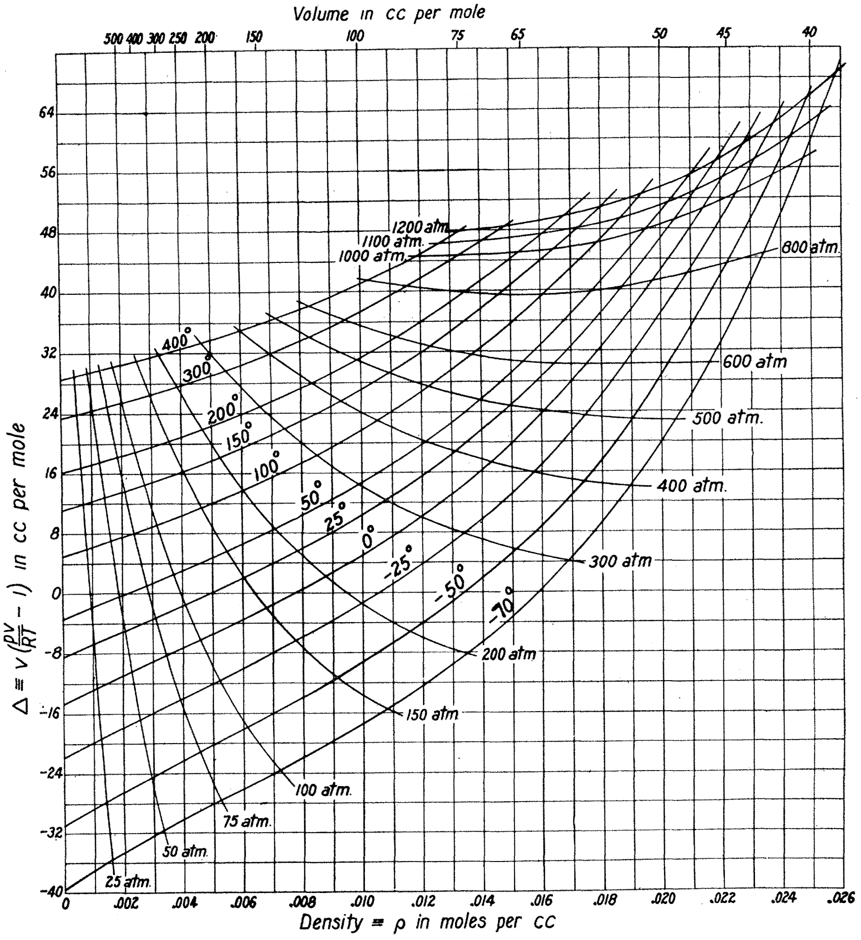

Fig. 12. $\Delta$ vs. $\rho$ isotherms and isobars for carbon monoxide. By means of this graph one can readily interpolate the $p-v-T$ data. Thus, for $\rho=0.010$ moles per cc and $t=0°$C, the pressure can be roughly estimated as 240 atm. By reading off $\Delta=5.0$ cc per mole at this point and using $v=1/\rho=100$ cc per mole, $T=273.18°$, $R=82.049$ cc atm./mole deg., the equation $\Delta=v(pv/RT-1)$ gives $p=235.3$ atm.

were adjusted by placing smooth curves that have the same ordinate on both plots at any pressure and temperature, just as the $\Delta$ and $\alpha$ curves were smoothed. The ordinates read from either plot are given in column 5.

Likewise there are three determinations of $(T/v)(dv/dT)_p$ at each point, through Eqs. (15), (16), (17). They were adjusted by plotting $pv(dv/dT)_p$ vs.

$T$ isobars at 25, 50, 75, 100 atm.; these isobars turn out to be straight lines. At higher pressures the adjustment was made by drawing smooth curves to $pv(dv/dT)_p$ vs. $T$ and $(dv/dT)_p$ vs. $T^{-1}$ isobars and $(T/v)\ (dv/dT)_p$ vs. $p$ isotherms, and taking the average of $(T/v)\ (dv/dT)_p$ obtained from the three ordinates at a given temperature and pressure.

It should be noted that, at every point, the determinations of an expansion coefficient obtained through the different equations agreed very closely and consequently little smoothing was necessary. Agreement to three figures in all three determinations was not unusual.

### $\Delta C_p$, and the heat capacity $C_p$, columns 7 and 8 and Fig. 14.

$\Delta C_p$ is the change in $C_p$ caused by a change in pressure at constant temperature. It is obtained through the thermodynamic equation

$$(dC_p/dp)_T = -\ T(d^2v/dT^2)_p, \tag{11}$$

which when integrated between 0 and $p$ along an isotherm gives

$$C_p = C_p{}^* + \Delta C_p = C_p{}^* + \int_0^p -\ T(d^2v/dT^2)_p dp. \tag{12}$$

$C_p{}^*$ is the heat capacity at zero pressure, and it is necessary to assume some value for it at each temperature in order to complete the calculations.

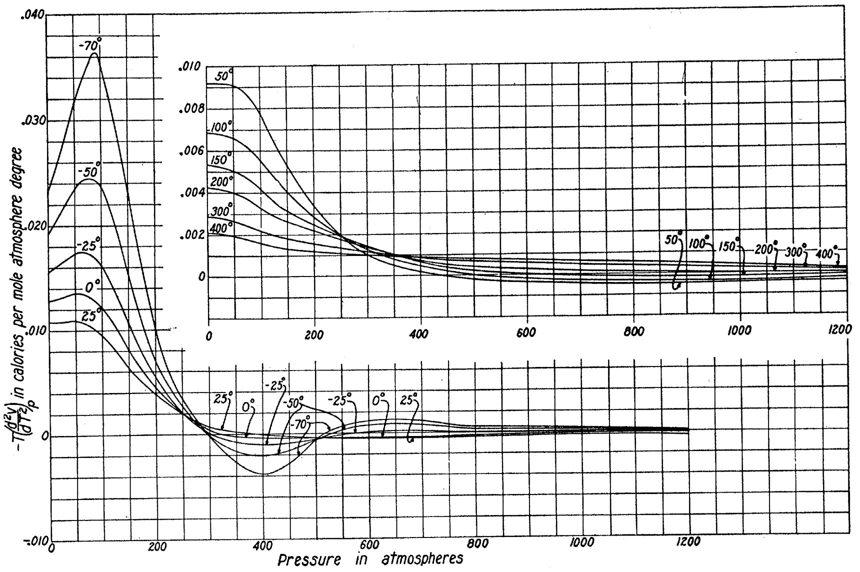

Fig. 13. $-T(d^2v/dT^2)_p = (dC_p/dp)_T$ vs. $p$ isotherms. The area under a curve between any two pressures is the change in heat capacity (at constant pressure) in cal./mole degree between these two pressures, at that temperature.

There are some experimental determinations of $C_p$ at 1 atm., but they are scattered. When corrected to zero pressure by an equation of state they all agree pretty well with the quantum equation

$$C_p^* = 7R/2 + R(3090/T)^2 e^{3090/T}/(e^{3090/T} - 1)^2, \qquad (29)$$

which we have accordingly used for $C_p^*$. $C_v^* = C_p^* - R$. We have assumed that the rotational states remain fully excited down to $-70°$. We wish to thank Dr. W. M. D. Bryant of the Du Pont Ammonia Corporation for advice concerning the choice of a formula for $C_p^*$.

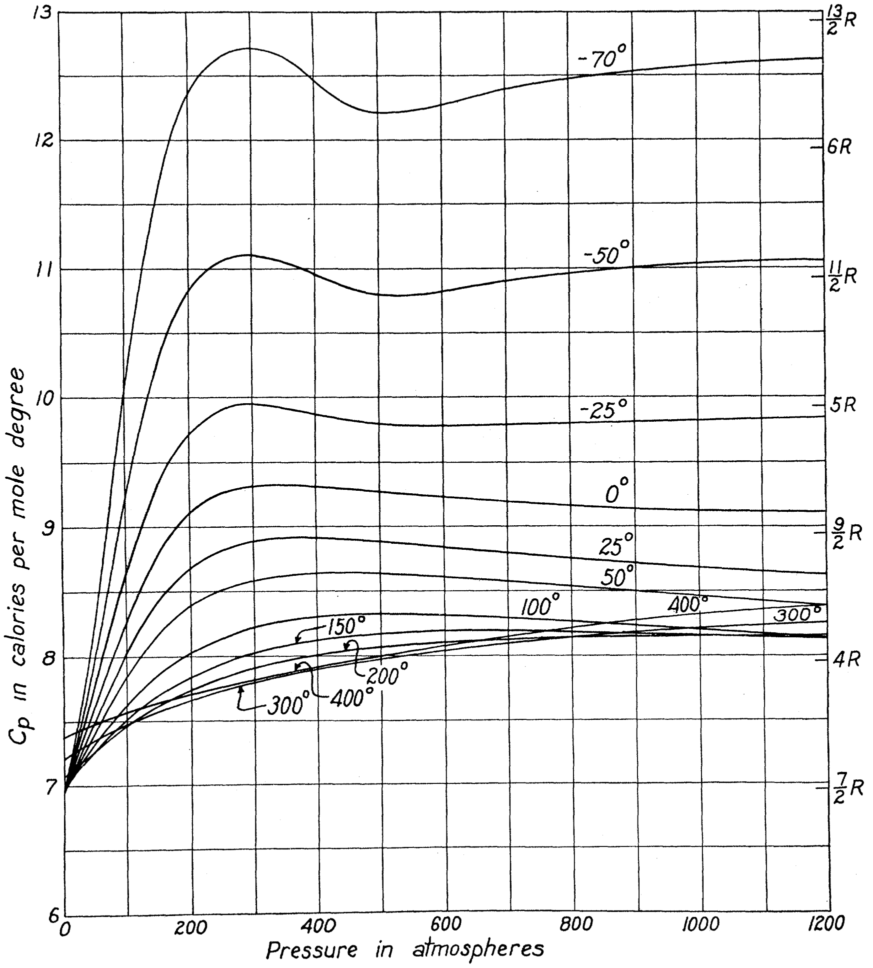

Fig. 14. Carbon monoxide. $C_p$ vs. $p$ isotherms.

The integral in Eq. (12) was evaluated by a mechanical integration under the $-T(d^2v/dT^2)_p$ vs. $p$ isotherms, which are shown in Fig. 13. For these curves at 25, 50, 75, 100 atm., the ordinate was obtained at any point through Eq. (18) from the slope and ordinate of the corresponding $pv(dv/dT)_p$ vs. $T$ isobar, which for the four low pressures was always a straight line, as was previously noted. There is little doubt that the values of $-T(d^2v/dT^2)_p$ therefrom obtained are very accurate, since the slopes and ordinates of straight lines can be definitely determined. This means that $C_p$ must be quite accurately calculated through these pressures.

Beyond 100 atm. the determination of the second derivative by means of the $pv(dv/dT)_p$ vs. $T$ isobars was supplemented at each point by taking the slopes of the $(dv/dT)_p$ vs. $T^{-1}$ isobars. The two determinations agreed well enough to lead one to expect $\Delta C_p$ to be correct to within a few hundredths cal./mole deg. throughout the whole range.

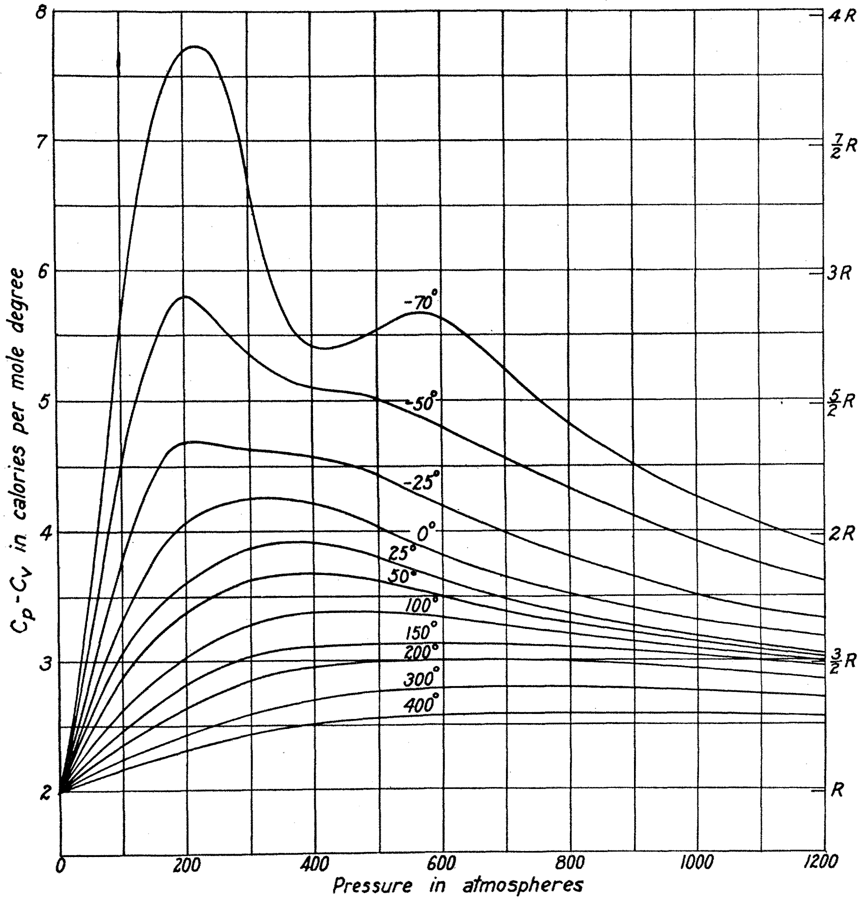

Fig. 15. Carbon monoxide. $C_p - C_v$ vs. $p$ isotherms.

Eq. (24) was used for the zero pressure intercept in Fig. 13. Some time ago the question was raised by the writers[16] whether $-T(d^2v/dT^2)_p$ or $(dC_p/dp)_T \rightarrow 0$ as $p \rightarrow 0$, as would happen if the behavior of the heat capacity of the actual gas approaches that of a perfect gas. As the gas expands, $pv \rightarrow RT$ and $C_p - Cv \rightarrow R$, but Eq. (22) shows that $-T(d^2v/dT^2)_p \rightarrow 2a/RT^2 \neq 0$, as $p \rightarrow 0$.

[16] W. Edwards Deming and Lola E. Shupe, Phys. Rev. **37**, 220 (1931).

Since $(dC_p/dp)_T \neq 0$ at very low pressures, the limiting heat capacity $C_p{}^*$ is not reached except at zero pressure. As the gas expands, there is no

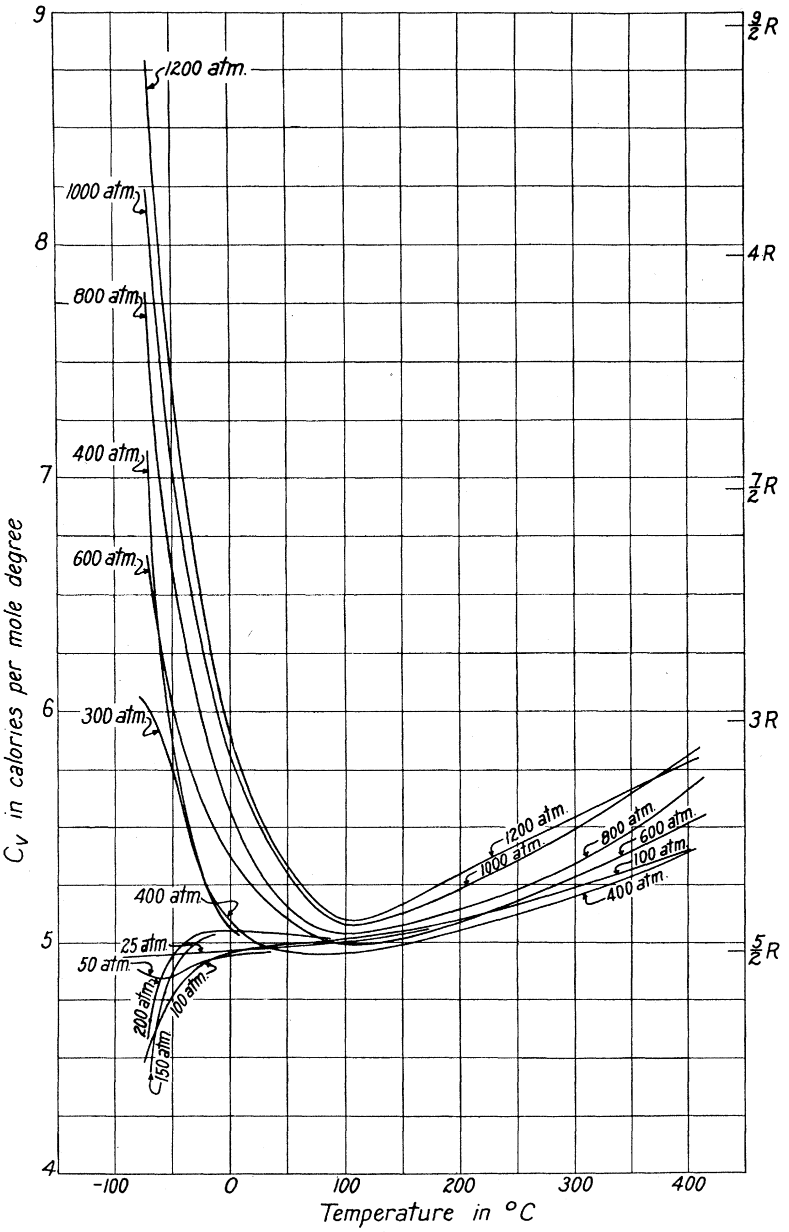

Fig. 16. Carbon monoxide. $C_v$ vs. $t$ isobars.

point reached beyond which further expansion is accompanied by changes in $C_p$ that are infinitesimal compared with the changes in $p$.

The curves in Fig. 13 show that at low temperatures $(dC_p/dp)_T$ varies considerably with pressure, the lower the temperature the greater the variation. At 25° and above, this derivative is nearly constant through 50 atm.

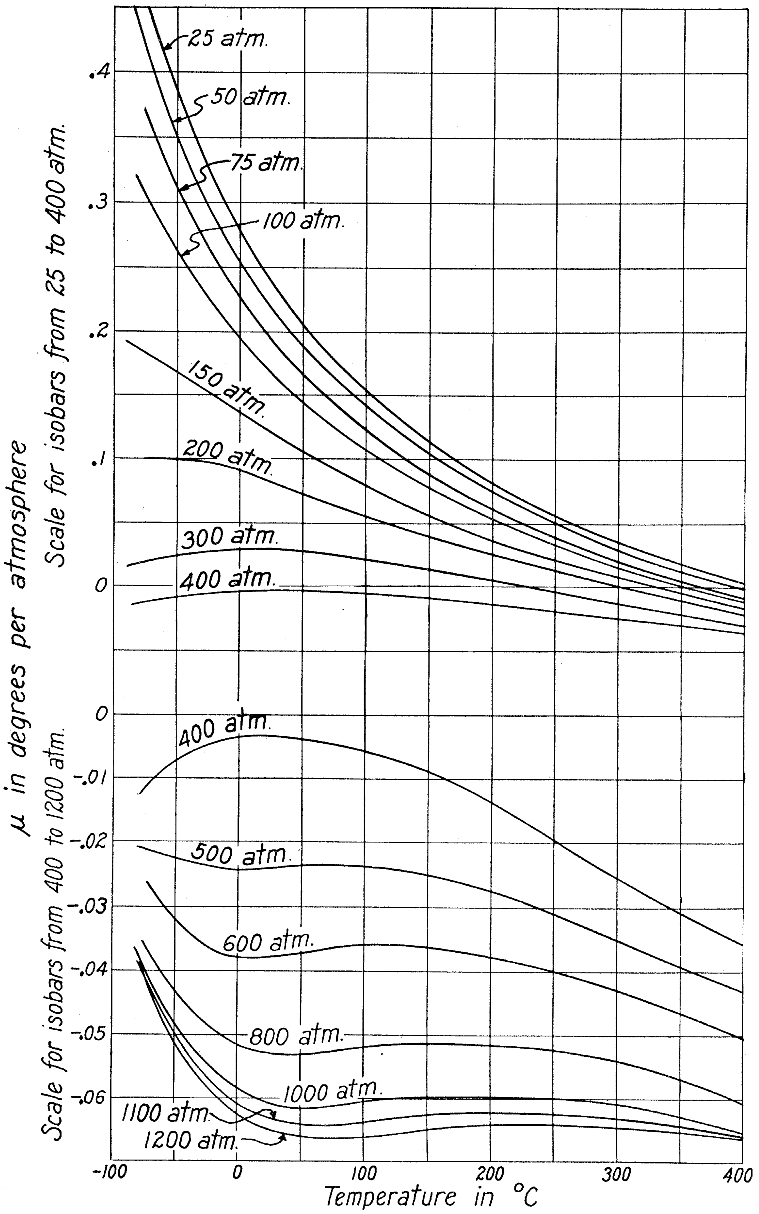

Fig. 17. Carbon monoxide. $\mu$ vs. $t$ isobars.

and then decreases with further increase in pressure. Beyond 500 atm. this derivative is small at all temperatures, so very little change in $C_p$ is produced at any of our temperatures by compression beyond 500 atm.

There are no experimental data available on carbon monoxide, but there are the authors'[5] calculations on nitrogen to compare with. Fig. 3 for nitrogen and Fig. 14 for carbon monoxide show that the $C_p$ curves are very similar. At $-50°$ and $-70°$, $C_p$ for carbon monoxide is slightly higher than it is for nitrogen, but at $-25°$ and above, the reverse is true. The difference is nowhere greater than some tenths cal./mole deg.

**The quantity $C_p - C_v$, Fig. 15; the heat capacity $C_v$, column 9 and Fig. 16.**

$$C_p - C_v = -T(dv/dT)_p^2/(dv/dp)_T \tag{13}$$

The derivatives in this equation are simply related to the expansion coefficients in columns 5 and 6, so $C_p - C_v$ can be calculated for each pressure and temperature. The results are shown in Fig. 15. According to Eq. (22), $C_p - C_v \to R$ as $p \to 0$, at all temperatures.

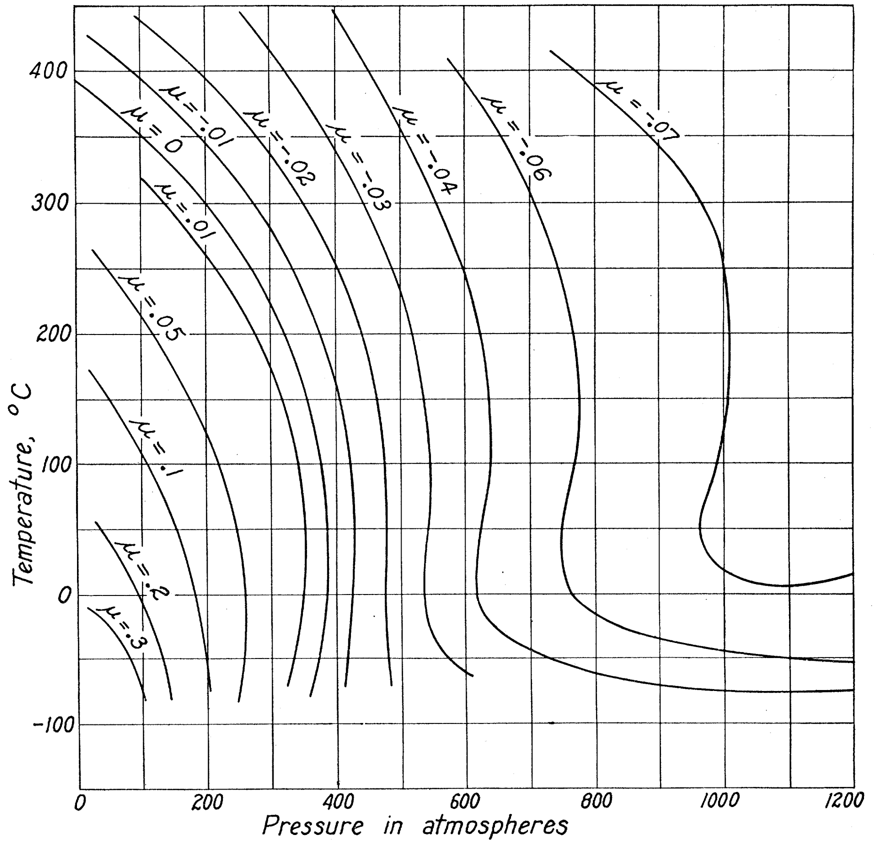

Fig. 18. Carbon monoxide. $t$ vs. $p$ $\mu$ = constant curves. $\mu$ is given in °C per atm. $\mu > 0$ means that the gas is heated by an adiabatic compression.

$C_v$ is calculated by subtracting $C_p - C_v$ from $C_p$. Some of the $C_v$ vs. $t$ isobars are shown in Fig. 16. More of them could not be drawn without causing confusion. Above 50°, isobars for $p=0$, 25, . . . , 400 almost coincide. At higher pressures $C_v$ is higher. Below 50°, $C_v$ at 25 atm. falls a few hundredths cal./mole deg. under $C_v$*. Below 50°, $C_v$ at 50, 75, 100, 150, 200 atm. deviates considerably from $C_v$*. The isobars for 100, 150, 200 atm. take peculiar quick descents as the temperature drops below $-25°$; this is most pronounced for 150 atm. The isobars for 300, 400, . . . , 1200 atm. have a minimum at about 100°. On the low temperature side of this minimum the curves are very steep. The graph for nitrogen in Fig. 5 shows the same characteristics.

**Joule-Thomson coefficient $\mu$, Figs. 17 and 18.**

The Joule-Thomson coefficient can be calculated from the equation

$$\mu\rho C_p = (T/v)(dv/dT)_p - 1. \qquad (14)$$

The values of $\mu$ can be read from the curves of Figs. 17 or 18. The latter is a family of $\mu$ curves obtained from the $\mu$ vs. $t$ isobars (Fig. 17) and $\mu$ vs. $p$ isotherms (not shown). The $\mu=0$ curve in Fig. 18 is the inversion curve.

The ultimate accuracy of calculations made by the present method is the accuracy of the $p$-$v$-$T$ relations. Data from the various laboratories that have undertaken compressibility work agree very closely, and thus give assurance that calculations made from them should be reliable provided the derivatives can be accurately evaluated. Compressibility data over a wide range of temperature and pressure for a number of gases are now available, and the present method is a quick and accurate means for the determination of a number of physical properties. Calculations for other gases are in progress.