

THERMODYNAMIC PROPERTIES OF THE SYSTEM METHANE + CARBON MONOXIDE AT 90·67° K

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An apparatus is described for measuring the following properties of mixtures of condensed gases: (i) the total vapour pressure, (ii) the condensation (i.e. dew-point) pressure, (iii) the volume change on mixing, (iv) the virial coefficients of the gases at the temperature of the other measurements. Such measurements have been made for the system carbon monoxide + methane at 90·67° K, the triple-point of methane. This system was chosen as being a particularly suitable one with which to test the predictions of the cell theory of solutions developed by Prigogine and co-workers. As predicted by this theory, the system does in fact show a *positive* excess free energy together with a *negative* excess volume, i.e. there is a *contraction* in volume on mixing. The quantitative agreement between the observed and calculated values of these two excess functions is very satisfactory.

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One of the recent theories of liquid mixtures is the so-called cell theory developed by Prigogine and co-workers.^{1, 2, 3} This was first applied to binary mixtures of molecules 1 and 2 satisfying the following conditions: (i) the energy of a pair of molecules depends only on the distance between their centres; (ii) the distance r^* for which this energy is a minimum is the same for the pairs 1—1, 2—2 and 1—2; (iii) the minimum energy ϵ_{12}^* for a pair of unlike molecules is the geometric mean of ϵ_{11}^* and ϵ_{22}^* , the corresponding quantities for the two pairs of like molecules. If these conditions are fulfilled, the cell theory predicts that the system will show *positive* deviations from Raoult's law, (i.e. that the excess free energy of mixing G^E is positive), but that the two liquids will mix with a contraction in volume (i.e. that the volume change on mixing V^E is negative). Other theories, by contrast, require that G^E and V^E should have the same sign.^{4, 5}

A positive excess free energy associated with a volume decrease on mixing has, in fact, been reported⁶ for the systems *neopentane* + carbon tetrachloride, *neopentane* + cyclohexane, and *neopentane* + benzene. These systems, however, are not very suitable for testing the cell theory, since the molecules concerned are of such complexity that the intermolecular forces cannot be isotropic. It is obviously desirable to have reliable experimental data on carefully selected binary systems, the molecules of which, if not monatomic, are at least very small.⁷ The object of the work described in this paper was to obtain such data for the system carbon monoxide + methane. This system was chosen primarily because it satisfies reasonably well the three conditions stated above. With regard to (i), the molecules are small, and the two pure substances conform closely to the law of corresponding states.⁸ As for (ii), the values of r^* for methane and carbon monoxide agree to within a few per cent. Finally, in connection with (iii), it is important that the intermolecular forces involved are essentially dispersion forces only.⁹ (Admittedly, carbon monoxide has a dipole moment, but this is small. The inability of the dipole to exert any marked orientational influence is shown by the residual entropy of solid carbon monoxide at the absolute zero.¹⁰) Furthermore, the system fulfils two essential experimental requirements, the first that the interactions between the two pairs of like molecules are sufficiently different for the departures from ideal behaviour to be large enough to be accurately measurable, and the second that measurements can be made over the whole liquid range. Admittedly, carbon monoxide is considerably more volatile than methane, and at the lowest temperature at which the whole liquid range can be covered, namely, the triple-point of methane, 90.67° K, the vapour pressure of carbon monoxide is rather high (about 2.5 atm), which has made the experiments somewhat more difficult.

The results of the following measurements (all at 90.67° K) are reported in this paper: (i) the total vapour pressure of liquid mixtures of known composition, (ii) the densities of such mixtures, (iii) the so-called dew-point or condensation pressures of gaseous mixtures of known composition, (iv) the second virial coefficient of pure carbon monoxide. To complete the investigation of this system it will also be necessary to measure the heat of mixing, and it is hoped to report on this in a later paper.

EXPERIMENTAL

THE PREPARATION OF MIXTURES OF KNOWN COMPOSITION.—This was an essential preliminary to the vapour-pressure, density, and dew-point pressure measurements. Mixtures were made up in the water-jacketed gas burette D (fig. 1). Mercury could be admitted into D when required from the steel reservoir M via the tap 10. The internal volume of D between tap 8 (excluding the tap barrel) and the mark V at the bottom was accurately known (539.24 cm³). To make a mixture, the vessel D (with a little mercury at the bottom) and the line connecting it with the manometer K were evacuated. The first gas was then admitted into D, the mercury adjusted to mark V, the temperature of the water-bath surrounding D taken, and the pressure of the gas measured on the manometer K. (Three

readings of every pressure were taken.) The line between tap 8 and the manometer was again evacuated, the mercury in D withdrawn until its surface was almost at the bottom of the small splash-trap below mark V, and the second gas then allowed to bubble up into D via tap 9 and the tube *e*. (This tube *e* was purposely made very long so that in the operations to be described later, when D was used as a compressor, it also served as a simple manometer reading up to 3.5 atm.) The gas mixture in D was then left overnight to ensure that it was homogeneous, and then, with the mercury once more on mark V, the pressure was again measured on manometer K, and the temperature of D and that of the room recorded. This pressure measurement was made with taps 6 and 7 closed, and with mercury filling the capillary above tap 19 as far as mark VI and the vessels C as far as mark I. To calculate the total quantity of the mixture and its composition, it was necessary to know the volume of the dead-space. This information was also required to make allowance for the amount of the mixture in the gaseous phase in the vapour-pressure measurements. The dead-space was made as small as was practicable by constructing the parts of the line concerned of capillary tubing of 1 to 2 mm. Its volume was determined by measuring the change in pressure on the addition to it of one or more of the calibrated bulbs C. These bulbs, of volumes approximately 1, 3 and 5 cm³, were water-jacketed, and were connected to the mercury reservoir M via tap 11. Provision was made in the same way for varying the amount of mercury in the manometer, and readings were taken with the mercury meniscus in the limb joined to the capillary in

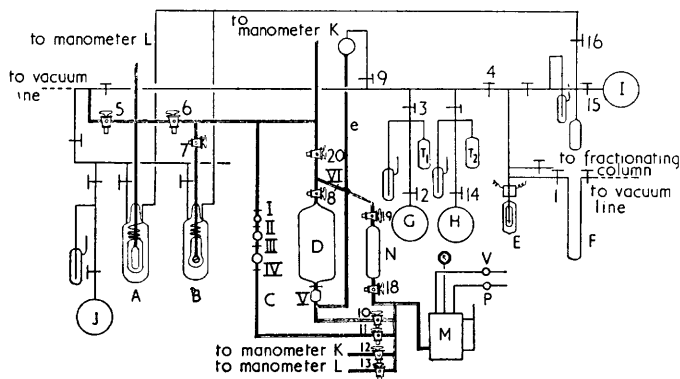


FIG. 1.—General diagram of the apparatus.

such a position as to minimize the volume of gas in this limb. When making a pressure measurement, the distance between the meniscus and a reference mark on the adjacent capillary tubing was measured, the internal volume of the manometer limb having previously been determined for various values of this distance.

THE LOW-TEMPERATURE THERMOSTAT.—When carrying out measurements of vapour pressure, density, and dew-point pressure, the vessel containing the mixture (or one of the two pure components) was surrounded by pure methane at its triple-point. Advantage was taken of the fact that the normal b.p. of oxygen, 90.2° K,¹¹ is only slightly below the methane triple-point, so that the oxygen b.p. can be raised to one or two tenths of a degree above the methane triple-point by arranging for the oxygen to boil under an overpressure of a few cm of mercury. Thus, while the vapour pressure of a mixture was being measured, this mixture was contained in the innermost bulb of vessel B (fig. 1). This bulb was embedded in methane which had just started to melt. The space around the vessel containing the methane was evacuated, and the whole vessel B was immersed in liquid oxygen contained in an enclosed Dewar vessel, and boiling under such an overpressure that its temperature (measured on a vapour pressure thermometer filled with pure oxygen) was slightly above 90.67°. (As the oxygen was not stirred, its temperature near the surface was a little below that of the main bulk.) Under these conditions the methane melted very slowly, and the temperature of the innermost vessel remained constant for several hours. A sensitive criterion of the constancy and reproducibility of the temperature afforded by this simple arrangement was the consistency of the values for the vapour pressure of carbon monoxide (1895.9 mm). These values were always within a range of 0.2 mm, corresponding to a temperature constant to $\pm 0.0007^\circ$.

If the methane was frozen from the bottom upwards by controlled cooling with liquid air, it crystallized into a transparent, glassy-looking mass. If it was frozen from the surface downwards by evaporation, the curious "snake formation" recently reported by Verschigel and Schiff¹² was observed. When the solid methane was warmed, the onset of melting was betrayed by the appearance of cracks in the transparent mass.

VAPOUR PRESSURE MEASUREMENTS.—The liquid was contained in the innermost bulb of vessel B. This bulb had a capacity of ~ 0.8 cm³ and contained a small iron-in-glass stirrer operated by an external electromagnet. The manometer K with which the vapour pressures were measured had to deal with pressures up to 189.59 cm of mercury, and it was therefore constructed as two single U-type manometers connected in series, each being about 1 m high.¹³ For pressures less than 1 m one section of the manometer only was used, the space common to the two sections being evacuated. For pressures above 1 m, this space was put in connection with a large water-jacketed globe containing air at a suitable pressure.

In these measurements it was essential that the gas mixture in the dead-space was homogeneous and in true equilibrium with the liquid in the vessel B. A special technique had to be adopted to achieve this, primarily because the length and narrow bore of the tubes forming the dead-space made diffusion therein slow. This technique was as follows. A known amount of a mixture of known composition was condensed into the innermost bulb of vessel B, tap 7 closed, and the dead-space evacuated. Some of the liquid was then allowed to evaporate into a volume made exactly double what the dead-space volume would be when the actual vapour-pressure measurements were made. The vapour was isolated from the liquid and made homogeneous by expansion into a large volume. Half of it was then compressed back into the liquid, the dead-space being reduced until it had reached the final desired volume, and the pressure then measured. This technique was justified by the following calculation. A known amount of a mixture of known composition was imagined to be condensed into B. Assuming that the system was ideal, the pressure p' which would be established at the end of the sequence of operations just described was calculated. This was compared with the calculated value of the true equilibrium vapour pressure p'' , i.e. the pressure which would be set up on direct evaporation of some of the liquid into the same final dead-space, assuming that the vapour was throughout homogeneous and in equilibrium with the liquid. Calculations were performed for mixtures initially containing carbon monoxide at mole fractions of 0.5 and 0.1. For neither of these did p' and p'' differ by more than 0.1 mm. The smaller the carbon monoxide content of a mixture, the greater is the difference between the compositions of the liquid and vapour phases (for the range of mixtures covered in this work), and the more serious will be the error involved in the technique we have adopted. No mixtures studied, however, contained carbon monoxide at a mole fraction less than 0.1. We may therefore conclude that our vapour pressure values represent true equilibrium values to within the limits of accuracy of measurement (0.1 mm).

After a mixture of known composition had been made up in D, and the quantity of it determined as already described, sufficient was condensed into the innermost bulb of B to fill the bulb to about two-thirds of its capacity. Tap 7 was closed, and with the mercury in vessel C at mark I, the amount of gas remaining in D and in the dead-space was determined. Tap 8 was then shut, the line evacuated, and the mercury withdrawn below mark I until the dead-space volume was double that at which the final pressure reading would be taken. The capillary tube extending upwards from tap 19 contained mercury as far as mark VI. With the mixture in B surrounded by methane which was just starting to melt, vapour was allowed to pass slowly through tap 7 until evaporation ceased. During this operation, which lasted about 15 min, the mixture was continually stirred. Tap 7 was closed, the mercury withdrawn from vessel N, and the gas in the dead-space admitted suddenly via taps 20 and 19 into N (capacity ~ 300 cm³). The gas was then re-compressed and expanded several times. After this, N was filled with mercury, and the meniscus brought to mark VI. Finally, tap 7 was opened, and the mercury level in C very slowly adjusted to mark I. The pressure then remained constant until the methane surrounding the innermost bulb of B had melted.

LIQUID-DENSITY MEASUREMENTS.—These were carried out on the two pure gases and on twelve mixtures of known composition by finding the number of moles required to fill the innermost bulb of B to a mark on the capillary leading into it. The volume of this bulb was determined at room temperature by finding the weight of mercury required to fill it to this mark, and its volume at 90–67° K calculated from this using the coefficient of expansion data of Buffington and Latimer.¹⁴ A slight error in this volume, while

affecting the absolute values of the liquid densities, has a negligible effect on the excess volume V^E . The densities of the two pure liquids were measured several times at suitable intervals, but there was no detectable alteration with time in the volume of the bulb. To make it unnecessary to bring the meniscus exactly to the mark on the capillary, the internal cross-section of this capillary had been determined, and the distance between the meniscus and the mark was measured with a low-power microscope through an unsilvered strip on the Dewar vessel containing the liquid oxygen.

With the innermost bulb of B surrounded by a mixture of about equal amounts of solid and liquid methane, gas was condensed into it until it was full of liquid. The methane was then completely frozen, and the outer jacket of B was evacuated. With B surrounded by liquid oxygen boiling under an overpressure, a series of readings of the position of the meniscus in the capillary in relation to the mark was taken after the methane had started to melt. In working out the liquid densities, allowance was made for the small amount of gas between tap 7 and the meniscus.

THE MEASUREMENT OF CONDENSATION PRESSURES AND SECOND VIRIAL COEFFICIENTS.—To determine the pressure at which, at 90.67° K, a gaseous mixture of known composition began to liquefy, the vessel A was used. This was similar to B, except that the innermost vessel of A was cylindrical and considerably larger than that of B, having a volume of $\sim 8 \text{ cm}^3$. With this vessel surrounded by melting methane, known quantities of a mixture were compressed into it in stages, and the pressure set up at each stage measured.¹⁵ If this pressure is p when the innermost vessel of A contains n moles of mixture, then a plot of p against n is almost linear so long as the mixture remains gaseous, but shows a kink at the pressure at which condensation begins. The kink actually appears more sharply in a plot of p/n against p .

At the beginning of an experiment, the innermost vessel of A was evacuated, and a known amount of gas of known composition was contained in the section bounded by taps 6, 7 and 8, by mercury at marks IV and VI, and by the meniscus in manometer K. Tap 6 was opened, and the resulting pressure measured on K, the mercury in manometer L being held at a mark on the capillary joined to this manometer.¹⁶ Further readings at higher values of p and n could then be taken by raising the mercury in C successively to the marks III, II and I. With pure carbon monoxide and with mixtures rich in this gas, the measurement of still higher values of p was carried out with the manometer L, which had the same range as K.

Ideally, the excess free energy GE would be evaluated by using both the total vapour-pressure and the dew-point curves. However, owing to the very considerable difference in the vapour pressures of the two pure components, the part of the dew-point curve which is important in this calculation is extremely steep, and is therefore much more susceptible to experimental error than the total vapour-pressure curve. Moreover, accurate determination of the condensation pressure is made difficult by the fact that in the plots of p/n against p , the angle of intersection of the two lines for the homogeneous and heterogeneous regions is not much less than 180°. For these reasons, we have preferred to work out GE not by combining two sets of results one of which is much more accurate than the other, but rather by using only the more accurate, namely, the total vapour-pressure data. We shall, however, make use of the condensation pressure results to check the thermodynamic consistency of the two sets of measurements. We may add that although it has been said¹⁷ that measurements of condensation pressures by the technique we have used can be complicated by the tendency of the vapour to become supersaturated, there was no evidence that this happened in our experiments.

The evaluation of GE requires a knowledge of the second virial coefficients B_{11} and B_{22} of the two pure gases and of the corresponding quantity B_{12} for interactions between pairs of unlike molecules. In principle, the value of B , the second virial coefficient for a mixture, can be derived from the slope of the line obtained by plotting p/n against p for values of p below the condensation pressure, since

$$\frac{p}{n} = \frac{RT}{V}(1 + B'p), \quad (1)$$

where $B' = B/RT$. Owing, however, to the very rapid decrease in the condensation pressure with increasing methane content, it was only possible to obtain accurate virial coefficients for pure carbon monoxide and for mixtures rich in this gas. Hence only the value of B_{11} (for pure carbon monoxide) was determined by experiment. (In this paper, a subscript 1 refers to carbon monoxide, a subscript 2 to methane). The values of B_{12} and B_{22} were calculated, as will be described later. But since for all mixtures

studied the vapour phase in equilibrium with a liquid consists very largely of carbon monoxide, the correction for non-ideality of the vapour is determined primarily by B_{11} rather than by B_{12} and B_{22} .

PREPARATION OF METHANE AND CARBON MONOXIDE.—Methane was prepared by the action of water on methyl magnesium iodide. It was purified by fractionation at the b.p. of oxygen in a column of the type described by Clusius and Riccoboni.¹⁸ Carbon monoxide obtained from the reaction between formic and sulphuric acids was passed successively through 50 % NaOH solution, concentrated H_2SO_4 , and a trap cooled in liquid oxygen, and finally fractionated in the same column at the b.p. of liquid air. The purity of both gases was repeatedly tested by measuring the constancy of the triple-point pressure during melting. For these measurements the apparatus described by Clusius and Staveley¹⁹ was used with a manometer similar to that described by Lambert and Phillips,²⁰ with which pressures could be read to 0.01 mm. With neither substance was there any significant trend in the triple-point pressure as a crystalline sample melted. The mean value obtained for the triple-point pressure of methane was 87.85 ± 0.05 mm (cf. 87.4 ± 0.1 , Clusius and Weigand,²¹ 87.75 ± 0.04 , Staveley and Gupta²²), and for carbon monoxide 115.44 ± 0.05 mm (cf. 115.376 ± 0.0095 , Clusius and Staveley;¹⁹ 115.30 ± 0.05 , Clayton and Giauque¹⁰). With carbon monoxide, the vapour pressure at the transition temperature (61.55° K) was also measured, and found to be 28.23 ± 0.05 mm (cf. 28.11 mm, Clayton and Giauque¹⁰).

All pressures recorded in this paper are expressed in international mm or cm of mercury. Kistemaker's results were used to correct manometer readings for capillary depression.²³

SCALE OF THE APPARATUS.—As explained, the measurements of vapour pressures and of the densities of liquid mixtures were carried out using quite small quantities of liquid ($< 1 \text{ cm}^3$). While an increase in the size of the bulbs in A and B should have given greater precision, it would have had certain disadvantages. Inconveniently large quantities of pure methane for the cryostats would have been required, and it would have been necessary to construct the combined burette and compressor D out of metal. (This vessel had to bear in any case a considerable weight of mercury.) Owing to the small size of the bulbs A and B, thermal equilibrium was always rapidly established, and although several litres of each pure gas were used, the quantities required were not so large as to prohibit the use of the apparatus to investigate a system involving more costly gases.

RESULTS

In estimating the quantity of a pure gas or a gaseous mixture condensed into B (or transferred to the vessel A), an accuracy of at least 1 in 2000 was aimed at, and it was therefore necessary to allow for the imperfection of the gases at or near room temperature. The second virial coefficient B for a mixture of gases 1 and 2 at mole fractions of y_1 and y_2 respectively is given by the equation

$$B = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}. \quad (2)$$

B_{11} , B_{12} and B_{22} were estimated by the procedure described by Guggenheim and McGlashan,²⁴ using the curves given in their paper and the critical constants for methane and carbon monoxide quoted by them. In assessing a quantity of gas, allowance was made for the fact that different parts of the apparatus containing the gas were at different temperatures. The part containing most of the gas, however, was either the vessel D or the system of bulbs C, and as these were surrounded by running tap-water they were usually below room temperature. For a temperature of 280° K, for example, use of the method of Guggenheim and McGlashan gave the following values of the second virial coefficients: $B_{11} = -14.6$; $B_{12} = -29.9$; $B_{22} = -50.8 \text{ cm}^3/\text{mole}$, where 1 denotes carbon monoxide, and 2 methane.

TOTAL VAPOUR PRESSURES.—For every measurement of the total vapour pressure of a mixture it was necessary to calculate the composition of the liquid in equilibrium with the vapour. In such an experiment, a known total amount of the mixture, n moles, containing carbon monoxide at a known mole fraction of x_{01} is condensed into the bulb in B. As already explained, some of this is allowed to evaporate and equilibrium is established between the liquid and vapour, when n_v moles are present as vapour containing carbon monoxide at a mole fraction of y_1 , and $(n - n_v)$ moles as liquid containing carbon

monoxide at a mole fraction of x_1 . By the so-called "lever rule",²⁵ the following relation holds:

$$\frac{n_v}{n - n_v} = \frac{x_{01} - x_1}{y_1 - x_{01}} \quad (3)$$

In order to calculate x_1 , allowance must be made for the non-ideality of the system (including the imperfection of the vapour), but it is sufficiently accurate to allow for departures from Raoult's law by writing

$$\ln f_1 = \alpha x_2^2, \quad (4)$$

where f_1 is the activity coefficient of component 1 and α is a constant, and to assume that

$$2B_{12} = B_{11} + B_{22}. \quad (5)$$

It then follows, from (3), (4), (5) and the later eqn. (13), that x_1 is a root of the equation

$$\begin{aligned} & x_1^2(p_{01}\beta_1 - p_{02}\beta_2) \left(\frac{pf(V/T)}{nR} - 1 \right) \\ & + x_1 \left\{ p_{01}\beta_1 \left[\frac{2f(V/T)}{nR} (p_{02}\beta_2 - p) + 1 \right] + x_{01}(p_{01}\beta_1 - p_{02}\beta_2) \right\} \\ & - p_{01}\beta_1 \left[\frac{f(V/T)}{nR} (p_{02}\beta_2 - p) + x_{01} \right] = 0. \end{aligned} \quad (6)$$

In eqn. (6), p_{01} is the vapour pressure of component 1 at the temperature of the mixture ($= 90.67^\circ \text{K}$), p is the measured vapour pressure, and β_1 is given by the equation

$$\beta_1 = \exp [(V_1 - B_{11})(p - p_{01})/RT], \quad (7)$$

in which B_{11} is the second virial coefficient of component 1 at 90.67°K , and V_1 its molar volume as liquid. The parameters with subscript 2 are the corresponding quantities for component 2. The function $f(V/T)$ is given by the equation

$$f(V/T) = \frac{v_r}{T_r} \left(1 - \frac{B_r p}{RT_r} \right) + \frac{v_T}{T} \left(1 - \frac{B_T p}{RT} \right) + \frac{v_{gr}}{T_r - T} \ln \frac{T_r}{T}. \quad (8)$$

v_r is the volume of vapour at room temperature T_r , v_T the volume of the vapour at $T = 90.67^\circ \text{K}$, and v_{gr} the volume of the vapour in the capillary connecting the bulb B with tap 7, between which there is a temperature gradient. The form taken by the term involving v_{gr} arises because it was assumed that this temperature gradient was linear—an assumption which cannot give rise to any serious error, since the amount of gas in the capillary was very small, so that imperfection can be neglected. B_r and B_T in eqn. (8) are the second virial coefficients of the mixture (as defined by eqn. (1)) at room temperature and at 90.67°K respectively. The calculation of the composition of the liquid phase (i.e. of x_1) therefore requires a knowledge of B_{11} , B_{12} and B_{22} at 90.67°K . For B_{11} (for pure carbon monoxide) our own value was used. B_{12} and B_{22} were estimated as will be described later in connection with the evaluation of the excess free energy.

The total vapour pressure results are given in table 1, and are plotted in fig. 2.

EXCESS VOLUME.—The observed values of the liquid molar volume V are given in table 2, together with the values of VE , the volume change on mixing, calculated from the equation

$$VE = V - x_1 V_1 - x_2 V_2, \quad (9)$$

where V_1 and V_2 are the molar volumes of liquid carbon monoxide and liquid methane respectively. VE is plotted against the mole fraction of carbon monoxide in fig. 3. The full curve has been drawn from the equation

$$VE = -x_1 x_2 [a - b(1 - 2x_1)], \quad (10)$$

where x_1 is the mole fraction of carbon monoxide;

$$a = 1.299 \pm 0.036 \text{ cm}^3/\text{mole}, \text{ and } b = 0.407 \pm 0.075 \text{ cm}^3/\text{mole}.$$

a and b were evaluated by applying the least squares method to the experimental data, weighting each point according to the constancy of the several readings which were taken in any one experiment of the position of the meniscus with respect to the mark just above the inner bulb of vessel B.

TABLE 1.—VAPOUR PRESSURE p IN INT. CM OF MERCURY OF A LIQUID MIXTURE OF CARBON MONOXIDE AND METHANE AT 90.67°K CONTAINING CARBON MONOXIDE AT A MOLE FRACTION OF x_1

x_1	p
1	189.590
0.83165	161.32
0.73895	147.09
0.60145	127.58
0.50655	114.28
0.45725	106.19
0.45095	105.315
0.33195	85.75
0.23260	67.02
0.11440	41.055
0	8.785

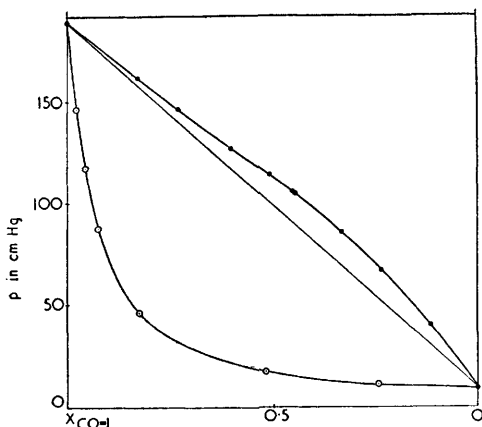


FIG. 2.—Plot of the total vapour pressure (full circles) and condensation pressure (open circles), both in int. cm of mercury, against the mole fraction of carbon monoxide.

TABLE 2.—MOLAR VOLUME V AND THE EXCESS MOLAR VOLUME VE (BOTH IN cm^3/MOLE) FOR LIQUID MIXTURES OF CARBON MONOXIDE AND METHANE AT 90.67°K CONTAINING CARBON MONOXIDE AT A MOLE FRACTION OF x_1

x_1	V	VE
0	35.5285	0
0.1228	35.655	-0.090
0.2447	35.765	-0.195
0.3451	35.850	-0.285
0.4699	35.975	-0.385
0.4732	36.085	-0.280
0.5210	36.075	-0.375
0.6145	36.310	-0.305
0.6553	36.370	-0.315
0.7474	36.555	-0.290
0.7831	36.630	-0.280
0.8370	36.775	-0.230
0.9242	37.060	-0.100
1.0	37.2928	0

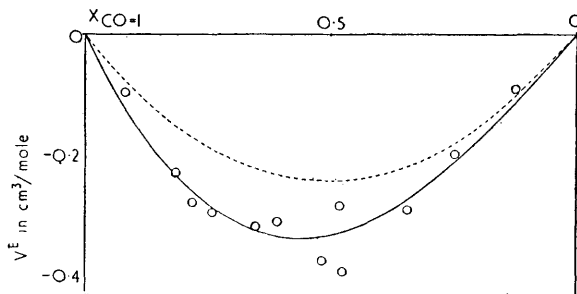


FIG. 3.—Plot of the excess volume VE in cm^3/mole , against the mole fraction of carbon monoxide. The full curve has been drawn through the experimental points according to eqn. (10). The dotted line is the theoretical curve, calculated from eqn. (23).

CONDENSATION PRESSURES.—These are given in table 3, and are plotted in fig. 2.

VIRIAL COEFFICIENT.—The value found for carbon monoxide at 90.67° K was $-233 \pm 5 \text{ cm}^3/\text{mole}$.

TABLE 3.—CONDENSATION PRESSURE p , IN INT. CM OF MERCURY, OF A GASEOUS MIXTURE AT 90.67° K CONTAINING CARBON MONOXIDE AT A MOLE FRACTION OF y_1 . THE QUANTITY δp IS DEFINED BY EQN. (21)

y_1	p	δp
0.24465	11.6	—
0.5210	17.8	—
0.8370	47.4	+ 0.25
0.9242	89.2	+ 2.7
0.9508	116.9	+ 3.6
0.9769	147.6	- 3.0

DISCUSSION

EVALUATION OF THE EXCESS FREE ENERGY, G^E

The activity coefficients f_1 and f_2 of the two components of a liquid mixture were assumed to be given by Duhem-Margules series expansions taken to two terms:

$$\begin{aligned}\ln f_1 &= Ax_2^2 + Bx_2^2(4x_1 - 1), \\ \ln f_2 &= Ax_1^2 + Bx_1^2(1 - 4x_2).\end{aligned}\quad (11)$$

When the constants A and B have been evaluated, G^E can readily be calculated, since

$$G^E = RTx_1x_2[A + B(1 - 2x_2)]. \quad (12)$$

Allowance for the non-ideality of the vapour phase was made by expressing the partial pressures p_1 and p_2 as follows:²⁶

$$\begin{aligned}p_1 &= p_{01}x_1f_1 \exp [(V_1 - B_{11})(p - p_{01})/RT - py_2^2\delta_{12}/RT], \\ p_2 &= p_{02}x_2f_2 \exp [(V_2 - B_{22})(p - p_{02})/RT - py_1^2\delta_{12}/RT].\end{aligned}\quad (13)$$

In these equations,

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}, \quad (14)$$

and the significance of the other symbols is the same as in eqn. (7).

A and B were evaluated by Barker's method,²⁷ in which they are adjusted to minimize the sum of the squares of the pressure residuals R , where R is the amount by which an observed pressure exceeds a calculated pressure. Whereas Barker assumed, however, that the pressure p is the only quantity liable to error, we have considered it necessary, owing to the steepness of the vapour pressure curve, to take into account possible errors in the composition of the liquid phase as well. To do this, we have modified Barker's method using the procedure described by Deming,²⁸ which involves weighting each point (p, x_1) by a factor $1/L$, where

$$L = (F_{x_1}F_{x_1}/w_{x_1}) + (F_pF_p/w_p). \quad (15)$$

In eqn. (15), F_{x_1} and F_p are the derivatives with respect to x and p of the function F , where

$$F = p - p_{01}x_1f_1\beta_1' - p_{02}x_2f_2\beta_2', \quad (16)$$

$$\text{with } \beta_1' = \exp [(V_1 - B_{11})(p - p_{01})/RT - py_2^2\delta_{12}/RT]. \quad (17)$$

$1/w_{x_1}$ and $1/w_p$ are respectively the squares of the absolute errors on x_1 and p , which were estimated as 0.0001 and 0.2 mm.

The evaluation of A and B requires a knowledge of B_{11} , B_{12} , and B_{22} at 90.67° K.

This temperature is, of course, far below the critical temperature of both gases, and the absence of reliable data for simple substances in this region precludes the use of the method of Guggenheim and McGlashan which was employed to estimate virial coefficients near room temperature. We have therefore made use of the table given by Lunbeck and Ten Seldam²⁹ of the values of the quantity $B/N\sigma^3$ for various values of the quantity kT/ϵ^* , where N is Avogadro's number, and $r^* = 2\frac{1}{2}\sigma$. This table was derived on the assumption that the Lennard-Jones 6:12 potential is valid. The values taken for ϵ_{22}^* and r^* for methane were those which we shall employ in the discussion in the theoretical evaluation of G^E and V^E . To calculate B_{12} it was assumed that ϵ_{12}^* is the geometric mean of ϵ_{11}^* and ϵ_{22}^* , and r^* was taken as 4.23 Å. The values obtained for B_{12} and B_{22} were -280 and -408 cm³/mole respectively. For B_{11} we have used our experimental value of -233 cm³/mole.

A and B were calculated by successive approximation, starting with the value $A = 0.6224$, $B = 0.0153$. These were obtained by applying Barker's treatment

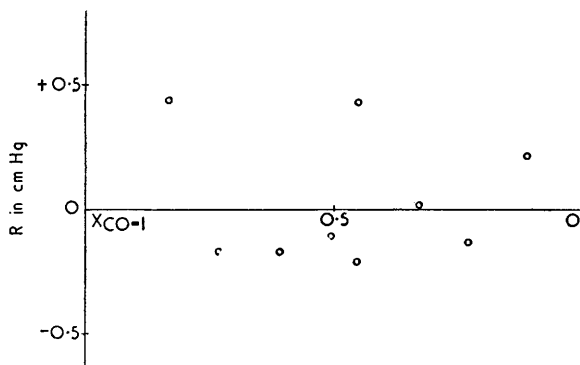


FIG. 4.—Plot of the pressure residuals R against the mole fraction of carbon monoxide in the liquid. R is the amount by which an observed vapour pressure, in cm of mercury, exceeds the corresponding value calculated using the final values of A and B given in the text.

without modification, using the experimental dew-point curve of fig. 2 to get y_1 and y_2 , the mole fractions for the vapour phase.

The final values for A and B were $A = 0.6217 \pm 0.0032$, $B = 0.0221 \pm 0.0043$. The satisfactory representation of the experimental results which is given by eqn. (11) and (13) with these values of A and B is shown by fig. 4, in which the pressure residuals R are plotted against composition (errors in p and x_1 being represented here as if they were in p only). The errors given for A and B are probable errors calculated from the formula given by Deming (ref. (28), p. 167) and by Musil *et al.*³⁰ The excess free energy G^E evaluated from eqn. (12) is plotted in fig. 5. The error in G^E should not exceed $\sim 1\%$.

The condensation pressure results in table 3 were used to check this curve for G^E . It was first necessary to find for each gaseous mixture the composition of the liquid in equilibrium with it. This involves interpolation from the curves of fig. 2, which is done most accurately by using eqn. (11) and (13) together with the values of A and B given above to provide the best smoothed curve through the experimental points in the plot of total vapour pressure against composition. Eqn. (11) and (13) were therefore solved for x_1 by successive approximation for each set of values of p and y_1 , p being, of course, the sum of the partial pressures p_1 and p_2 . This was done for all the mixtures of table 3 except the first two, for which the composition of the liquid is too close to pure methane for the results

to have any value here. Finally, for each set of values of p , x_1 , and y_1 , the activity coefficients were evaluated from the equations given by Scatchard and Raymond:²⁶

$$RT \ln f_1 = RT \ln (py_1/p_{01}x_1) + (V_1 - B_{11})(p_{01} - p) + \delta_{12}py_2^2, \quad (18)$$

$$RT \ln f_2 = RT \ln (py_2/p_{02}x_2) + (V_2 - B_{22})(p_{02} - p) + \delta_{12}py_1^2. \quad (19)$$

G^E was then calculated from the equation

$$G^E = RT(x_1 \ln f_1 + x_2 \ln f_2). \quad (20)$$

Values of G^E obtained in this way are plotted in fig. 5. While they do not deviate systematically from the full curve, they show a considerable scatter, and it is clear that, for reasons already given, the accuracy of the condensation pressure measurements was inferior to that of the total vapour pressure measurements. If δG^E is

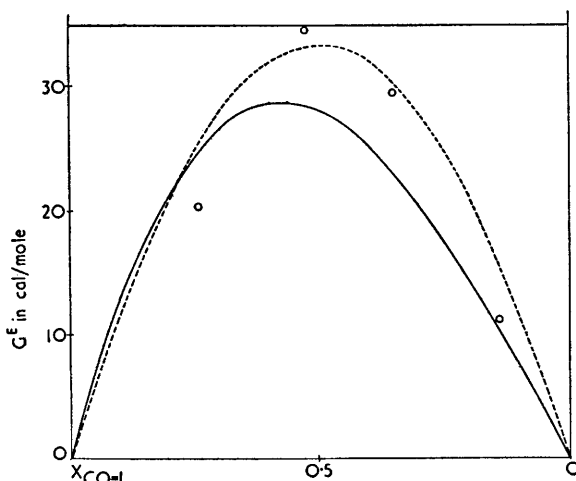


FIG. 5.—Plot of the excess free energy G^E , in cal/mole, against the mole fraction of carbon monoxide. The full curve is the experimental curve plotted from eqn. (12). The dotted curve is the theoretical curve calculated from eqn. (22). The circles are the values derived from the experimental dew-point curve.

the amount by which a point in fig. 5 lies above the full curve, the amount δp by which the observed condensation pressure must be reduced to cause the point to fall on the full curve can be calculated from the approximate relation

$$\delta p \approx \delta G^E p / RT, \quad (21)$$

which follows from eqn. (18), (19) and (20). The values of δp are given in table 3.

COMPARISON OF THEORY AND EXPERIMENT

This system shows the rather unusual combination of a positive excess free energy with a negative excess volume. This result is therefore in qualitative agreement with the predictions of the cell theory of Prigogine and co-workers,¹ but at variance with the theory of conformal solutions,^{4, 6a} according to which G^E and V^E should have the same sign.

To test the cell theory quantitatively, G^E and V^E are calculated from the following equations:

$$G^E/RT = x_1x_2 (0.179A_{11}/kT + 8.0kT/A_{11})\delta^2, \quad (22)$$

$$V^E/V_r = -1.52(kT/A_{11})x_1x_2\delta^2. \quad (23)$$

The quantities A_{11} , δ and V_r are defined by the following equations:

$$A_{11} = z |\epsilon_{11}^*|, \quad (24)$$

$$\delta = (\epsilon_{22}^* - \epsilon_{11}^*)/\epsilon_{11}^*, \quad (25)$$

$$V_r = 2^{-1}r^*3. \quad (26)$$

In (24), z is the number of nearest neighbours of a molecule in the liquid, which we shall take to be twelve. The quantities ϵ_{11}^* , ϵ_{22}^* and r^* were defined in the introduction. These equations for G^E and V^E follow from eqn. (6.9) and (6.11) of the paper by Prigogine and Mathot^{1b} by replacing the quantity θ used by these authors by $-\delta^2/8$. This corresponds to the assumption that ϵ_{12}^* is the geometric mean of ϵ_{11}^* and ϵ_{22}^* . Revised values for certain of the numerical coefficients have been given by Bellemans,³¹ and these have been used here.

To evaluate G^E and V^E we have used the values of ϵ^* and r^* given by Corner.³² For methane, ϵ_{22}^*/k is 148° , and $r^* = 4.25 \text{ \AA}$. For carbon monoxide, ϵ_{11}^*/k is 98° , and r^* is between 4.04 and 4.38 \AA , the latitude in r^* arising because the virial coefficient data can be analysed either assuming that each molecule is a single force centre, or alternatively that the forces operate from more than one force centre, in which case an average over all possible mutual orientations is taken. For our calculations, we have adopted the mean of 4.04 and 4.38 \AA . It is evident that, in any case, the requirement of the cell theory that r^* should be the same for the two different molecules is very closely approached in this system.

The calculated values of V^E and G^E are shown as dotted lines in fig. 3 and 5. For both quantities the agreement with experiment is very satisfactory, and lends strong support to the cell theory. A more detailed comparison of theory and experiment will be deferred pending the publication of a more accurate cell theory treatment based on the theory of corresponding states.³ In any case, a complete test of the theory must await the determination of the heat of mixing, a quantity much more sensitive to the value chosen for ϵ_{12}^* than is the excess volume.[†]

An extension by Balescu³³ of the cell theory of solutions to mixtures containing slightly polar molecules has shown that the contributions to the excess properties arising from the small dipole moment of the carbon monoxide molecule are quite negligible, and are actually positive for V^E as well as for G^E .

Finally, G^E can be calculated from Hildebrand's regular solution theory. The value so obtained is in surprisingly good agreement with experiment. According to eqn. (3) and (26) of chap. 8 of Hildebrand and Scott's book,⁵

$$G^E = V_m(\delta_1 - \delta_2)^2\phi_1\phi_2, \quad (27)$$

where ϕ_1 and ϕ_2 are the volume fractions of the two components, V_m is the molar volume of the mixture, and δ_1 and δ_2 are solubility parameters such that $\delta_1 = (-E_1/V_1)^{1/2}$, where $-E_1$ is the energy of vaporization of component 1, and V_1 its molar volume as liquid. δ_1 and δ_2 were evaluated from the heats of vaporization of the two gases, which from data for methane³⁴ and carbon monoxide¹⁰ have been estimated to be 2078 and 1346 cal/mole respectively at 90.67° K . Application of eqn. (27) to an equimolar mixture then gives $G^E = 26.9 \text{ cal/mole}$, as compared with the experimental value of 28.0 cal/mole . As for V^E , an extension of Hildebrand's theory such as that given by Scatchard³⁵ would predict that this quantity should also be positive.

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