

A CALORIMETER FOR MEASURING THE HEAT OF MIXING OF LIQUEFIED GASES

THE HEAT AND EXCESS ENTROPY OF MIXING OF LIQUID METHANE AND CARBON MONOXIDE

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A calorimeter is described for the measurement of the heat of mixing of two liquefied gases. It has been used to measure the heat of mixing of liquid carbon monoxide and liquid methane at 91.5°K over a considerable range of composition. In the absence of data on similar systems with which comparison could be made, the reliability of the calorimeter has been partially tested by using it to measure the energies of vaporization of carbon monoxide and oxygen and the heat of fusion of methane.

The heat of mixing results have been combined with previous estimates of G^E , the excess free energy of mixing, to obtain S^E , the excess entropy of mixing. S^E is negative in carbon monoxide-rich mixtures and positive in methane-rich mixtures. This behaviour, which is not predicted by existing theories of binary mixtures, is qualitatively explained on the basis that the carbon monoxide molecules do not freely rotate in the pure liquid, but that they gain in rotational freedom on increasing dilution with methane. The experimental values of G^E , S^E , the heat of mixing, and the volume change on mixing are compared with the values calculated from recent statistical theories.

This paper describes measurements of the heat of mixing of liquid carbon monoxide and liquid methane at $91.5 \pm 0.2^\circ \text{K}$. Values of the total vapour pressure for this system and of the volume change on mixing V^E , both at 90.67°K , have already been reported.¹ As was first predicted by the cell theory of Prigogine and co-workers^{2,3} for two substances such as this, which have small molecules of nearly the same size, the excess free energy of mixing G^E is positive, while V^E is negative. With the measurements reported here the comparison with experiment of this and other theories can be extended to the heat of mixing H^E and to the excess entropy of mixing S^E .

The determination of H^E has required the construction of a new kind of calorimeter, since as far as we are aware experiments on the heat of mixing of liquefied gases have been confined to one determination⁴ of the heat of mixing of He^3 and He^4 and to a demonstration⁵ that ordinary liquid hydrogen and liquid para-hydrogen mix without detectable heat change. It has therefore not been possible to test the calorimeter by repetition of any previous mixing experiments. The heat-of-mixing determinations, however, involve an evaporation correction which is largely determined by the energy of evaporation of carbon monoxide, and for this reason (and also to check the reliability of the electrical system associated with the calorimeter), we have used the apparatus to measure this energy of evaporation. As a further test we have also determined the energy of evaporation of oxygen and the heat of fusion of methane. Although the calorimeter is not ideally suited to the measurement of heats of phase changes, all the results obtained agree satisfactorily with the best values available.

EXPERIMENTAL

In designing the calorimeter shown in fig. 1 and 2, the chief problems were those of (i) bringing together the two liquefied gases, previously separated from each other, and

(ii) that of stirring the mixture. The first was solved by using flexible metal bellows, the second by employing an electromagnetic stirrer. The calorimeter consisted essentially of two compartments, separated by a thin copper diaphragm. The lower of these, a cylindrical stout-walled copper vessel of ~ 2.6 ml capacity was fitted with a small metal

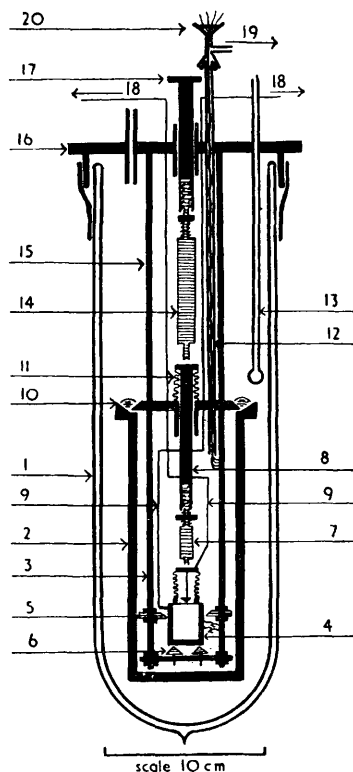


FIG. 1.—General diagram of calorimeter. 1, Dewar vessel; 2, cylindrical brass vessel; 3, one of three brass rods; 4, calorimeter, shown in detail in fig. 2; 5, one of three plastic spacers; 6, one of three plastic supports; 7, plastic rod; 8, metal plunger; 9, German silver tubes; 10, low-melting bismuth solder; 11, bellows; 12, tube bearing cable of leads; 13, oxygen vapour-pressure thermometer; 14, plastic rod; 15, one of three steel supporting tubes; 16, rigidly mounted brass plate; 17, metal plunger; 18, German silver tubes leading to three-way capillary taps; 19, to vacuum pumps; 20, lead seal.

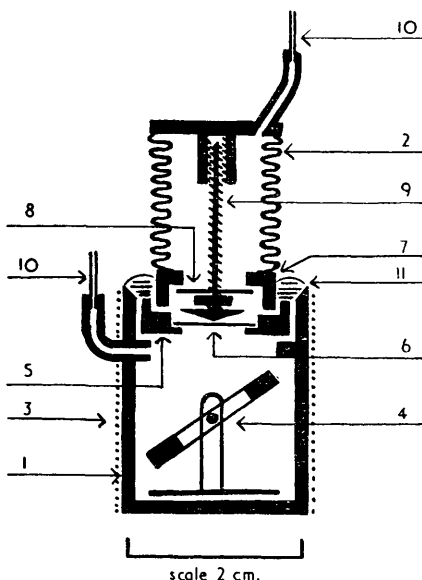


FIG. 2.—1, Lower compartment; 2, bellows forming upper compartment; 3, heater and resistance thermometer; 4, stirrer; 5, copper disc supporting diaphragm; 6, thin copper diaphragm; 7, perforated annulus; 8, one of three projecting rods; 9, adjustable threaded plunger; 10, German silver inlet tubes; 11, low-melting bismuth solder.

stirrer operated by an external electromagnet, and it contained at the start of the experiment a known amount of liquid methane. The upper compartment was made from a metal bellows with a capacity of about 1.7 ml, and contained a known amount of liquid carbon monoxide. From the roof of this compartment a metal plunger projected downwards, the pointed end of which was just above the diaphragm. The bellows could be compressed by the downward stroke of a plastic rod, with a concave end to minimize the area of contact with the calorimeter roof. This rod was situated inside the vacuum

jacket surrounding the calorimeter and was joined to another bellows in the roof of this jacket. On depressing this bellows by an external plunger, the plastic rod communicated the thrust to the bellows of the upper compartment, thereby puncturing the copper diaphragm. The higher vapour pressure of the carbon monoxide forced it into the lower compartment where it was mixed with the methane by means of the electromagnetic stirrer. Since in all experiments mixing was accompanied by absorption of heat, the calorimeter tended to cool, and a known amount of energy was therefore supplied to it via a coil wound on the outside of the lower compartment to compensate as nearly as possible for the heat absorption.

Most experiments were carried out by mixing the two pure components, but the values of the heat of mixing for the three mixtures richest in carbon monoxide were obtained by mixing pure carbon monoxide with a carbon monoxide + methane mixture.

The lower compartment had initially to contain a vapour phase of volume sufficient to accommodate the liquid carbon monoxide, while after mixing the upper compartment was left empty of liquid. Consequently only about half of the total internal volume of the calorimeter was occupied by liquid. While there is an obvious advantage in designing a heat-of-mixing calorimeter to avoid the vapour phase altogether, there is nothing in principle against having to make quite large allowances for evaporation effects so long as they can be accurately evaluated. This requires precise knowledge of (i) the heats of vaporization, (ii) the composition of the vapour phase before and after mixing, (iii) the volume of the vapour phase. With regard to (i), the molar heats of vaporization of methane and carbon monoxide have been accurately determined by Frank and Clusius⁶ and by Clayton and Giauque⁷ respectively, and we have moreover carried out check determinations in the heat-of-mixing calorimeter itself. The composition of the vapour phase and the total vapour pressure as functions of the composition of the liquid are known from the previous work on this system in this laboratory.¹ We have assumed that after mixing equilibrium was reached between the vapour and liquid phases, but if equilibrium was not completely established owing, for example, to slowness in diffusion through the hole in the punctured diaphragm, the error involved cannot be large because over almost all the range of composition studied the vapour phase consisted of more than 90 % carbon monoxide. The volumes of the two compartments could be determined sufficiently accurately (i.e. to within ± 0.003 ml) by simple gas-volumetric methods. This had to be done for each experiment and admittedly added considerably to the time of the whole investigation. Allowance was made for the volumes occupied by the liquid phases using the figures previously obtained for the molar volumes of the pure components and the mixtures. Finally, although carbon monoxide has a vapour pressure of about 3 atm at the temperatures of the experiments, the vaporization correction is not in general large, since the admission of the carbon monoxide to a larger vapour space on mixing is largely compensated by the corresponding drop in its partial vapour pressure. For one particular mixture, for which the mole fraction of carbon monoxide was ~ 0.4 , the vaporization correction vanished.

The calorimeter is shown in detail in fig. 2. It rested on three pointed, plastic supports, and was centred by three plastic spacers. The inlet tubes were of German silver, int. diam. 1 mm. Temperature changes were followed with a copper resistance thermometer (47 s.w.g.), with a resistance of ~ 20 ohms at 90° K, wound on the outside of the lower compartment, and provided with manganin leads. Changes in resistance were measured using the circuit described by Pitzer.⁸ Although owing to the small thermal capacity of the calorimeter the thermometer current had to be comparatively small (~ 1 mA), temperature changes of 5×10^{-4} deg. could be detected. To obtain the absolute temperature of the calorimeter (which had to be known both in making the evaporation corrections and in the determination of the internal volumes of the calorimeter), the thermometer was calibrated *in situ* by making vapour pressure measurements on methane, oxygen, or carbon monoxide condensed in the lower compartment. The methane triple-point also provided a fixed point. The heater wound on the lower compartment was of 40 s.w.g. manganin with copper leads (~ 50 ohms at 90° K). Heating periods were timed to 0.02 sec with an electrically operated stop-watch. The cable of leads to the heater and thermometer passed down tube 12 (fig. 1), and each wire was separately wound round one of the brass rods, 3, before reaching the calorimeter.

The moving part of the stirrer consisted of a bar made of soft iron at one end and brass at the other which was made to swing twice a second about a horizontal axis by the operation of an electromagnet situated outside the Dewar vessel 1. Although both heater and thermometer were non-inductively wound, there was sufficient disturbance from the

field of the electromagnet to prevent the resistance of the thermometer being measured with the desired precision. Accordingly, provision was made for automatically running the electromagnet at regular intervals for a period of 35 sec in each minute, and shunting the galvanometer in the thermometer circuit while the electromagnet was in use. Thermometer resistance measurements were made during the off-periods of the stirrer.

The diaphragm separating the upper and lower compartments was of annealed copper, all diaphragms being cut from the same piece of foil of thickness 0.002 in. It was pierced by a brass plunger which was threaded to enable its position relative to the diaphragm to be adjusted. With the head of the plunger shaped as shown in fig. 2, no guide for the plunger was necessary, and there was no danger of over-compressing the bellows. In any one heat-of-mixing experiment, it was necessary to ensure that the volume of the upper compartment remained constant both before and after mixing, regardless of the value of the prevailing internal pressure, and to achieve this three small projecting rods were fixed to the plunger so that they pressed against a fixed, perforated annulus, keeping the bellows always in a state of slight compression. In assembling the calorimeter, the diaphragm was first soft-soldered to the disc 5 (fig. 2). Care was taken to keep the centre of the diaphragm free of solder. The disc was then soldered to both upper and lower compartments using a low-melting bismuth solder.

Since the triple-point of methane lies above the normal b.p. of oxygen, it was essential to have the liquid oxygen surrounding the outer vessel 2 (fig. 1) boiling under an over-pressure of about 20 cm of mercury, and the apparatus was therefore provided with a Leiden cap. The temperature of the refrigerant was measured with an oxygen vapour-pressure thermometer. The two German silver tubes 18 were waxed just above the Leiden cap into the limbs of three-way capillary taps. In order to make allowance for evaporation effects in a heat-of-mixing experiment, it was necessary to determine the volume of each compartment, including the associated German silver tube, and glass capillary up to the tap, and also, for each of these volumes, to divide it into two parts, a major part which could be regarded as being at the low temperature of the calorimeter, and a minor part at the air-temperature prevailing just above the Leiden cap. The determination of these two component parts of each dead-space was made by measuring the number of moles of hydrogen required to fill the dead-space (i) when the whole apparatus was at room-temperature, (ii) when the calorimeter assembly was immersed in liquid oxygen to the same depth as in an actual mixing experiment, the precise temperature of the calorimeter being determined by the copper resistance thermometer. Never less than four measurements of each dead-space were made after assembly of the calorimeter, and the mean value used.

Methane and carbon monoxide were prepared by fractionating cylinder gases in a column of the type described by Clusius and Riccoboni.⁹ The constancy of the triple-point pressures of the middle fractions used showed that their purity was not inferior to that of the samples employed in the earlier work, which were prepared in the laboratory. The oxygen used was prepared by the thermal decomposition of potassium permanganate and fractionated. The apparatus used for measuring a known quantity of a gas and compressing it into the calorimeter was that already described.¹

The sequence of operations in a determination of a heat of mixing was as follows. With a small pressure of hydrogen inside the vessel 2 (fig. 1) and with liquid air as the refrigerant, a known amount of carbon monoxide was condensed into the upper compartment. The liquid air was replaced by liquid oxygen, and the temperature of this allowed to rise to $\sim 90.7^\circ \text{K}$ by suitable adjustment of the over-pressure. A known amount of methane (m.p. 90.67°K) was then condensed into the lower compartment, whereupon the temperature of the calorimeter rose somewhat. It was allowed to fall to $\sim 90.7^\circ \text{K}$, when the vessel 2 was evacuated, and the over-pressure increased until the liquid-oxygen temperature was $\sim 92.5^\circ \text{K}$. About 1 hour later, a steady state was reached both in respect of the temperature of the liquid oxygen and the degree of evacuation of the vessel 2, and moreover any liquid methane or carbon monoxide originally in the inlet tubes would have distilled into the compartments of the calorimeter. The electromagnetic stirrer was started, and the resistance of the copper thermometer measured at 1-min intervals for the next hour. Then the diaphragm was broken, and electrical energy supplied to the calorimeter in bursts of about 25 sec each to compensate the observed cooling. Heat was only supplied during the off-periods of the stirrer, and three to nine heating bursts were required, depending on the relative amounts of the two liquids. The cycle of events here was stirring—resistance readings taken—stirring—heat supplied—stirring, etc. Mixing was complete about 20 min after the breaking of the diaphragm.

Resistance thermometer readings were taken for about another hour. In this way a temperature against time curve for the whole operation, such as the curve *a* of fig. 3, was obtained. The calorimeter was then cooled about 1°, and its thermal capacity measured by supplying a known amount of electrical energy and following the change in resistance. This energy was supplied in some experiments continuously (curve *b*) or in a number of short periods, as in a mixing experiment (curve *c*), and there were no systematic discrepancies in the values of the effective heat capacity of the calorimeter arrived at in the two ways. Heating current was supplied by a battery of accumulators

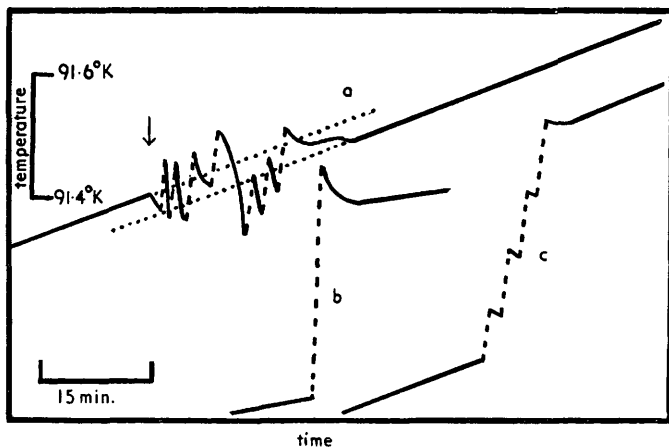


FIG. 3.—Temperature against time curves obtained in a typical heat-of-mixing experiment. *a* represents the actual mixing experiment. The arrow indicates the time at which the diaphragm was broken, and the dotted lines are the extrapolated fore- and after-drifts. *b* and *c* represent heating experiments to determine the quantity *A* (see text). In all three curves, the almost vertical dashed lines indicate periods of electrical heating.

discharging continuously through a resistance much larger than the calorimeter heater resistance. The voltage tapped from a portion of this resistance was applied to another large resistance in series with either a stabilizing resistance equal to that of the calorimeter heater, or in the heating periods to the latter itself. In this way, even though each heating period was short, the heating current could be readily held constant at a pre-determined figure. In those heat-of-mixing experiments where it was known that particularly rapid cooling would follow rupture of the diaphragm, some heat was supplied just before the diaphragm was broken.

In evaluating a heat of mixing a number of factors have to be considered, since temperature changes are produced not only by the mixing itself but by evaporation effects and also by changes in pressure. (Pure carbon monoxide has a vapour pressure of ~ 3 atm at the temperature in question and departs considerably from ideal behaviour.) The evaluation of heats of mixing and of heats of evaporation was based on the equation

$$\Delta E_{el} + q_r = Q_m(N_{1b} + N_{2b}) + A\Delta T + Q - \delta_1\Delta E_{1v} - \delta_2\Delta E_{2v} + (\delta_1c_{1g} + \delta_2c_{2g} - \delta_1\bar{c}_{1l} - \delta_2\bar{c}_{2l})\Delta T. \quad (1)$$

The quantity sought in a heat-of-mixing experiment is Q_m , which is the heat absorbed per mole of mixture under the conditions of the experiment, i.e. the liquids being under their saturation vapour pressures before mixing, and the mixture under its own vapour pressure after mixing. ΔE_{el} is the heat supplied electrically. q_r is the heat evolved on rupture of the diaphragm. δ_1 and δ_2 are defined by the equations:

$$\begin{aligned} \delta_1 &= n_{1b} - n_{1a}, \\ \delta_2 &= n_{2b} - n_{2a}. \end{aligned} \quad (2)$$

Each of the quantities N_{1b} , N_{2b} , n_{1b} , n_{2b} , n_{1a} , n_{2a} is the number of moles of component 1 (carbon monoxide) or 2 (methane). The capital refers to the liquid phase, the small letter to the gaseous phase, and suffixes *b* and *a* to before and after mixing respectively. ΔT is the observed increase in temperature of the calorimeter consequent on the heating

and mixing, and is given by the temperature difference of the extrapolated fore- and after-drifts at the mid-time of the "reaction period". A is the heat capacity of the calorimeter and contents, after mixing, excluding evaporation effects. Q embraces four small correction terms, and is given by the equation

$$Q = q_1 + q_2 + q_3 + q_4, \quad (3)$$

where q_1 is the heat absorbed due to the Joule effect, q_2 is the heat absorbed consequent on work being done to compress gas into the lower inlet tube when the diaphragm is ruptured, and q_3 the corresponding quantity for the upper tube. (q_3 was usually opposite in sign to q_2 , and the two quantities nearly cancelled.) q_4 is a small correction (evaluated graphically from the temperature against time curve during the reaction period) to allow for the departures during this period from the extrapolated fore- and after-drifts. ΔE_{1v} and ΔE_{2v} are the molar energies of evaporation of components 1 and 2 at the temperature at the moment of mixing. Finally, the quantities c_{1g} , c_{2g} , \bar{c}_{1l} , \bar{c}_{2l} are the molar or partial molar heat capacities, subscripts g and l denoting gaseous and liquid phases respectively.

The terms in eqn. (1) differ considerably in importance, the largest being ΔE_{el} and $Q_m(N_{1b} + N_{2b})$, which were each between 1 and 2 cal. In an ideal experiment, ΔT would be zero, and the terms involving this quantity would vanish. In fact, in most runs $A\Delta T$ amounted to about 10 % of ΔE_{el} . q_r and Q were each about 1 % of ΔE_{el} , but while the contribution from $\delta_2\Delta E_{2v}$ was almost negligible, that from $\delta_1\Delta E_{1v}$ varied from 0 to 30 % of ΔE_{el} , depending on the composition of the mixed liquid. The last term in eqn. (1) was negligible in all heat-of-mixing experiments. Eqn. (1) was also applied to the evaporation experiments to evaluate ΔE_{1v} , the energy of evaporation of carbon monoxide (and also of oxygen), when Q_m and also all terms with suffix 2 vanished. In determining an energy of evaporation, the upper compartment contained some liquid, and the lower was evacuated. On breaking the diaphragm, there was a very rapid drop in temperature and thermal equilibrium was very quickly re-established. For this reason, the procedure followed was simply to measure ΔT on rupture of the diaphragm, and then, after a steady after-drift had been set up, to apply electrical heating until the temperature was nearly restored to its original value. In the first part of such an experiment, therefore, ΔE_{el} vanished, and ΔT was considerably larger than in a heat of mixing experiment, and the last term in eqn. (1), which now reduced to $\delta_1\Delta T(c_g - c_l)$ could amount to 1 % of $A\Delta T$.

Several determinations of q_r were made. In some of these, the pressure on either side of the diaphragm was zero or very small. In others, the calorimeter contained hydrogen or carbon monoxide under conditions such that pressure changes occurred on breaking the diaphragm similar to those taking place in heat-of-mixing or evaporation experiments. When appropriate corrections had been applied, reproducible values of q_r were obtained, the mean figure being 0.017 ± 0.003 cal.

The required values of N_{1b} , N_{2b} , n_{1a} , n_{2a} , n_{1b} , n_{2b} were obtained from (i) the total amounts of the components 1 and 2, (ii) the measured volumes of the two compartments of the calorimeter, (iii) the densities of the pure liquids and mixtures, (iv) the virial coefficients of the pure and mixed vapours, (v) the vapour-liquid equilibrium diagram. (iii), (iv) and (v) were taken from the earlier work. Knowledge of (v) is necessary to calculate the composition and pressure of the vapour in equilibrium with the mixture. As the equilibrium had been studied at 90.67° K the results were corrected to be applicable to the slightly different temperatures prevailing in these experiments.

The quantity A was evaluated from experiments such as those represented by curves b and c in fig. 3. The value of the temperature coefficient of the second virial coefficient of carbon monoxide needed to estimate q_1 was obtained by combining the value¹ of the virial coefficient at 90.67° K with those given by Deming and Sharpe¹⁰ for higher temperatures. q_4 was negligible except in those experiments in which carbon monoxide was mixed, not with pure methane, but with a methane + carbon monoxide mixture. For ΔE_{1v} we used our measured value, which, as will be shown, was in reasonably satisfactory agreement with the value derived from published data. Finally, c_l for carbon monoxide was taken from the paper of Clayton and Giauque.⁷

Four determinations of the heat of fusion of methane were made. In these, the lower compartment was almost full of methane (~ 0.07 mole), the surroundings were kept at $\sim 92^\circ$ K, and the calorimeter was heated from ~ 88.5 to $\sim 91.5^\circ$ K. The heat capacity of the empty calorimeter had to be determined over the same range, while the necessary values of the heat capacities of solid and liquid methane near the m.p. were taken from the paper by Clusius.¹¹

RESULTS

The mean value obtained for the heat of fusion of methane was 221 ± 2.5 cal/mole (1 cal = 4.1840 abs. joules). This agrees satisfactorily with Clusius's value¹¹ of 224 ± 2 cal/mole. From three experiments on carbon monoxide, a mean value of 1205 ± 12 cal/mole was obtained for ΔE_{1v} at 91.4° K. For oxygen at 90.56° K (when ΔT on evaporation was much smaller), one experiment gave 1490 cal/mole. These compare with values estimated from data in the literature of 1163 cal/mole for carbon monoxide and 1455 cal/mole for oxygen^{6, 12}. This last value should be very accurate. The figure of 1163 cal/mole derives from the heat of evaporation at the normal b.p. determined by Clayton and Giauque.⁷ This should be reliable, but the evaluation of ΔE_{1v} at 91.4° from ΔH_{vap} at 81.61° K requires a knowledge of the equation of state of the gas over this range of temperature. We have used the Berthelot equation, and thereby an uncertainty of perhaps 1 % has been introduced into the derived value of ΔE_{1v} . There is a discrepancy of about 3 % between the two sets of ΔE_{1v} . But since the term $\delta_1 \Delta E_{1v}$ of eqn. (1) never exceeded 30 % of ΔE_{el} , the uncertainty in the final value of Q_m due to evaporation effects should never have exceeded ~ 1 %.

The values of the molar heat of mixing Q_m are given in table 1.

TABLE 1.—EXPERIMENTAL VALUES OF Q_m AT $91.5 \pm 0.2^\circ$ K. Q_m = HEAT ABSORBED IN CAL (1 CAL = 4.1840 ABS. JOULES), WHEN x_1 MOLES OF CARBON MONOXIDE AT THE VAPOUR PRESSURE OF THIS LIQUID AND $(1 - x_1)$ MOLES OF METHANE AT ITS VAPOUR PRESSURE ARE MIXED TO GIVE 1 MOLE OF MIXTURE AT THE VAPOUR PRESSURE OF THE MIXTURE AT THE SAME TEMPERATURE

x_1	Q_m	x_1	Q_m
0.193	18.9	0.506	25.3
0.242	23.5	0.550	25.8
0.292	24.2	0.588	22.5
0.350	28.3	0.694	21.5
0.394	27.8	0.733	17.5
0.442	25.0	0.795	15.2
0.470	24.5		

DISCUSSION

Q_m does not refer to mixing carried out at constant pressure, whereas in work on systems at ordinary temperatures the heat of mixing H^E is usually measured under a constant pressure of ~ 1 atm, while the theories with which comparison will be made give expressions for H^E at zero pressure. Q_m can be corrected to give values of H^E valid at zero pressure using the equation

$$(\partial H / \partial p)_T = V - T(\partial V / \partial T)_p, \quad (4)$$

and so the correction strictly requires a knowledge not only of the molar volumes of the pure and mixed liquids but also of their temperature coefficients. $(\partial V / \partial T)_p$ for the mixtures has not been measured, so we have assumed that it is a linear function of mole fraction. The difference between Q_m and H^E at zero pressure is quite small, being ~ 0.22 cal/mole for the equimolar mixture.

The experimental values of Q_m , in cal/mole, can be represented by the equation

$$Q_m/x_1(1 - x_1) = A + B(2x_1 - 1), \quad (5)$$

where x_1 = the mole fraction of carbon monoxide, $A = 105.3 \pm 1.3$ and $B = -32.6 \pm 3.6$. The derived values of H^E at zero pressure are given by the equation

$$H^E/x_1(1 - x_1) = 104.3 - 33(2x_1 - 1). \quad (6)$$

The unsymmetrical nature of the relation between Q_m and x_1 , apparent in fig. 4, persists almost unchanged in the relation between H^E and x_1 . The probable errors given above in A and B of eqn. (5) correspond to a probable error of $\sim \pm 0.3$ cal/mole in Q_m for the equimolar mixture.

The experimental values of Q_m are plotted against x_1 in fig. 4, together with smoothed values of the excess free energy G^E (taken from eqn. (12), ref. (1)), and the derived values of TS^E , where S^E is the excess entropy of mixing. Statistical theories of solutions from which quantitative predictions can be made about the excess thermodynamic functions all predict that these functions, S^E included, will be symmetrical, parabolic functions of x , the mole fraction of one component, any asymmetry being a second-order effect. In this system, by contrast, S^E is positive at high methane concentrations, and negative at high carbon monoxide concentrations. A dependence of S^E of this kind on concentration is not, of

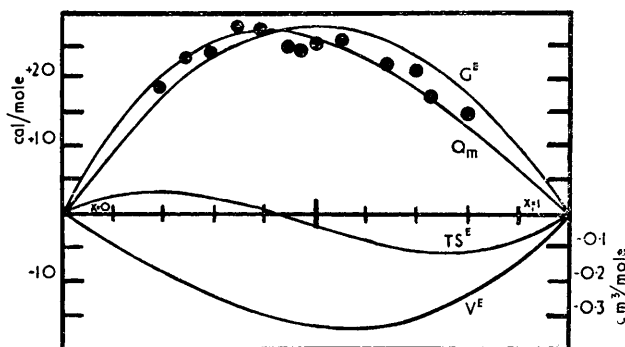


FIG. 4.—Plots of the excess thermodynamic functions G^E , V^E , and TS^E for the system carbon monoxide + methane at 90.67° K, against x_1 , the mole fraction of carbon monoxide. The units of V^E are cm^3/mole , and of G^E and TS^E cal/mole (1 cal = 4.1840 abs. joules). The points are the experimental values of Q_m in cal/mole , and the smooth curve through them has been plotted from eqn. (5).

course, unknown. It is found, for example, in systems of ethanol with a non-polar liquid.¹³ For the system carbon monoxide + methane, all the theories which we shall test correctly predict that V^E is negative, and they also predict that S^E is negative. The discrepancy between experiment and theory with S^E most probably arises because the assumption made in these theories that the rotational partition function for either species is the same in the pure liquids as in the mixtures is not valid. The assumption is more likely to hold for methane than for carbon monoxide. For methane there is evidence that the molecules are actually capable of free rotation in the solid,¹⁴ a situation now known to be much less common than was once supposed. For carbon monoxide, however, there is evidence that rotational movement in the pure liquid is restricted. Thus, the entropy of vaporization is appreciably higher than that of methane when compared on the basis of the Hildebrand rule.¹⁵ (It is unlikely that an important contribution to the hindrance to rotation comes from the dipole moment of carbon monoxide, since this is so small. The entropy of vaporization of carbon monoxide is, in fact, almost the same as that of liquefied gases with non-polar diatomic molecules such as nitrogen, oxygen, and chlorine.) We should expect that the carbon monoxide molecules should gain in freedom of rotational movement the more they are diluted with the more symmetrical methane molecules. (Compare, for example, the effect of krypton in solid solutions of krypton and methane in depressing the λ -point in methane,¹⁶ above which the molecules probably rotate in the lattice.) This gain in freedom of rotation will make a *positive* contribution to S^E . Meanwhile there should be the *negative* contribution predicted by theory and associated with the volume contraction on mixing. Unfortunately, estimates of the positive contribution cannot as yet be made, though Pople¹⁷ has considered in a general way the effect of directional intermolecular force fields on the thermodynamic properties.

The predictions of five recent statistical theories about the excess thermodynamic properties of the system carbon monoxide + methane are compared with experiment in table 2. (The experimental values of V^E and G^E refer to

TABLE 2.—COMPARISON OF OBSERVED AND CALCULATED VALUES OF THE EXCESS THERMODYNAMIC FUNCTIONS OF EQUIMOLAR MIXTURES IN THE SYSTEM CARBON MONOXIDE + METHANE AT 90.67° K (FOR V^E AND G^E), AND AT 91.5° K FOR H^E . V^E IS IN CM³/MOLE, G^E , H^E AND TSE IN CAL/MOLE.

(1 CAL = 4.1840 ABS. JOULES)

authors	basis of calculation	V^E	G^E	H^E	TSE
(i) Prigogine and Mathot ³	(a) $\delta = 0.51$	- 0.25	35.5	21.5	- 14
	(b) $\delta = 0.44$	- 0.15	26.5	16	- 10.5
(ii) Prigogine, Bellemans and Englert-Chwoles ²⁰	(a) CO as ref., $\delta = 0.44$	- 1.1	35	25	- 10
	CH ₄ as ref., $\delta = -0.305$	- 0.19	18	14.5	- 3.5
	(b) CO as ref., $\delta = 0.44$, $\rho = 0$	- 0.75	30	24.5	- 5.5
	CH ₄ as ref., $\delta = -0.305$, $\rho = 0$	- 0.13	16	13	- 3
	CO as ref., $\delta = 0.44$, $\rho = 0.032$	- 0.67	37	29.5	- 7.5
	CH ₄ as ref., $\delta = -0.305$, $\rho = -0.032$	- 0.07	20	18.5	- 1.5
(iii) Scott ²³	(a) CO as ref.	- 0.35	28	26	- 2
	(b) CH ₄ as ref.	- 0.003	32.5	31.5	- 1
(iv) Byers Brown	(a) CO as ref.	- 0.44	29.5	25	- 4.5
	(b) CH ₄ as ref.	- 0.37	25	17.5	- 7.5
(v) Salsburg and Kirkwood ²⁴	see text	- 0.30	32	20	- 12
experimental values		- 0.325	26.9	26.0	- 0.9

90–67° K, the triple-point of methane, those of H^E to 91.5° K. The small temperature difference cannot have a significant effect on the excess functions.) The following points should be noted.

(i) The values predicted by the cell theory of Prigogine and Mathot³ have been calculated from eqn. (6.9) to (6.12) of their paper. This theory assumes that the molecules have the same size, i.e. that the distances r_{11}^* and r_{22}^* at which the intermolecular potential energies for the pairs 1—1 and 2—2 have their minimum values are equal. The excess functions then depend on the parameter δ , where

$$\delta = (|\epsilon_{22}^*| - |\epsilon_{11}^*|) / |\epsilon_{11}^*| \quad (7)$$

and $|\epsilon_{11}^*|$, $|\epsilon_{22}^*|$ are the minimum potential energies of the pairs 1—1 and 2—2. Use of the values $|\epsilon_{11}^*|/k = 98^\circ$ and $|\epsilon_{22}^*|/k = 148^\circ$ for carbon monoxide and methane respectively derived from second virial coefficient data¹⁸ gives $\delta = 0.51$. The values in the row designated (a) have been calculated with this value of δ . Alternatively, estimates of $|\epsilon_{11}^*|$ and $|\epsilon_{22}^*|$ can be made from critical constant and viscosity data. Use of these¹⁹ gives rather different values for δ , and a figure of $\delta = 0.44$ might be taken as an overall mean, which then leads to the figures in the row (b). Since the excess functions depend on the square of δ , there is a considerable difference between the two sets of calculated values.

(ii) The theory of Prigogine, Bellemans and Englert-Chwoles²⁰ is essentially a "corresponding states" treatment in which the excess functions are expressed in terms of certain thermodynamic properties of one of the two components and of the parameters δ and ρ , where ρ is effectively a measure of the difference in molecular size defined by the equation

$$\rho = (r_{22}^* - r_{11}^*)/r_{11}^* \quad (8)$$

The authors give a set of equations (a) for the special case of $\rho = 0$, and (b) a more general set valid for systems where $\rho \neq 0$. The two sets of equations do not become identical when, for the second set, ρ is put equal to zero. Estimates of r_{11}^* and r_{22}^* from second virial coefficient data are the same within their limits of uncertainty, corresponding to $\rho = 0$. On the other hand, use of the relation $r^* \propto V_c$, where V_c is the critical volume, gives $\rho = 0.032$, there being a difference of 10 % in the critical volumes of carbon monoxide and methane. We therefore give, in table 2, values of the excess functions (a) for the equations valid when $\rho = 0$, (b) from the more general equations for the two cases $\rho = 0$ and $\rho = 0.032$. As Prigogine and his co-workers themselves remark, the values obtained for the excess functions differ according to whether carbon monoxide or methane is chosen as the reference substance. This difference arises because the value of δ is relatively large, and the limitation to a few terms only of the series expansions involved in the evaluation of the excess functions is not really valid. The excess functions have accordingly been calculated using both carbon monoxide and methane as the reference substance. It must be stressed that to perform this calculation accurately it is necessary to have accurate values for $\partial V/\partial T$, $\partial^2 V/\partial T^2$, c_p and $\partial c_p/\partial T$ for the reference liquid, V and c_p being the molar volume and heat capacity of this liquid respectively. Unfortunately, data of the required reliability are not available for carbon monoxide and methane, values of $\partial^2 V/\partial T^2$ being particularly uncertain. The precision with which V^E can be evaluated suffers considerably from this, since for $\rho = 0$,

$$V^E/x_1x_2 = \delta^2 \left(-\frac{1}{2} T \partial V/\partial T - \frac{3}{8} T^2 \partial^2 V/\partial T^2 \right), \quad (9)$$

and the second term could be numerically larger than the first. The figures of table 2 have been derived assuming that for carbon monoxide²¹ $\partial V/\partial T = 0.21$, $\partial^2 V/\partial T^2 = 0.002$, while for methane²² we have taken $\partial V/\partial T = 0.12$ and $\partial^2 V/\partial T^2 = 0$. The other data required have been taken from table 2 of the paper by Prigogine *et al.*²⁰

(iii) Independently of Prigogine, Bellemans and Englert-Chwoles, Scott²³ has presented a very similar theory which also gives expressions for the excess functions with a crucial dependence on the first and second temperature coefficients of the volume and energy of the reference liquid. The values given in table 2 have been calculated from the equations derived for what Scott calls the two-liquid solution, assuming that his parameter ψ and ρ (not to be confused with the ρ of Prigogine and co-workers) are both zero, that is, that the following relations hold:

$$r_{12}^* = \frac{1}{2}(r_{11}^* + r_{22}^*), \quad (10)$$

$$\epsilon_{12}^* = (\epsilon_{11}^* \epsilon_{22}^*)^{\frac{1}{2}}. \quad (11)$$

Here also, the excess functions have been evaluated for each component as reference substance.

(iv) Dr. W. Byers Brown has kindly communicated to us privately the excess functions for this system which he has calculated from a theoretical treatment to be published shortly, also based on the principle of corresponding states. Here the effect of the choice of reference substance on the calculated values of the excess functions appears to be smaller than for the theories considered under (ii) and (iii).

(v) The values given by the free-volume theory of Salsburg and Kirkwood²⁴ have been calculated using the values of ϵ_{11}^* and ϵ_{22}^* given above in paragraph (i), while the values of the distance parameter a used by these authors have been calculated from the critical constants and their eqn. (21).

It is, of course, impossible to draw fair conclusions about the relative merits of these theories by a comparison with experiment for one system only for which none of the theories in its present form can account for the excess entropy of mixing. It is at least satisfactory, however, that all predict a negative V^E , and a heat of mixing of approximately the observed magnitude.

With molecules of the rare gases, the question of molecular rotation does not arise, and probably with highly symmetrical, compact molecules with only slightly polar bonds, such as methane and silane, freedom of rotation is largely independent of environment. But as our work has indicated that the change with the composition of a mixture of the freedom of molecular rotation of a diatomic component can have important effects on the thermodynamic properties and since diatomic molecules must inevitably frequently constitute one if not both components of a binary mixture of small molecules, it would seem that the chief need on the theoretical side is for further consideration to be given to the effect of directional forces. On the experimental side, almost all the systems suitable for study should be investigated, since their number is very limited. Those consisting of mixtures of diatomic molecules may be particularly interesting, since if the molecules have approximately the same size molecular rotation (or torsional oscillation) in the mixture may be much the same as in the pure liquids, so that the excess thermodynamic functions may be quite accurately predicted by current theories. For testing theories with a corresponding states basis which give expressions for the excess functions deriving from limited series expansions, it is clearly desirable to have information on systems where the difference in the intermolecular potential energy curves is less than it is for carbon monoxide and methane. This will mean a smaller value of δ , and since the excess functions depend on the square of δ it will be necessary to attempt the measurement with reasonable accuracy of departures from ideality considerably smaller than those shown by the present system. Finally, it will be essential to have more accurate and comprehensive data on the pure substances themselves, and particularly on the variation with temperature of the density and heat capacity.

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- ¹ Mathot, Staveley, Young and Parsonage, *Trans. Faraday Soc.*, 1956, **52**, 1488.
- ² Prigogine and Garikian, *Physica*, 1950, **16**, 239.
- ³ Prigogine and Mathot, *J. Chem. Physics*, 1952, **20**, 49.
- ⁴ Sommers, Keller and Dash, *Physic. Rev.*, 1953, **92**, 1345.
- ⁵ Swenson, *J. Chem. Physics*, 1950, **18**, 520.
- ⁶ Frank and Clusius, *Z. physik. Chem. B*, 1939, **42**, 395.
- ⁷ Clayton and Giauque, *J. Amer. Chem. Soc.*, 1932, **54**, 2610.
- ⁸ Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.
- ⁹ Clusius and Riccoboni, *Z. physik. Chem. B*, 1937, **38**, 81.
- ¹⁰ Deming and Sharpe, *Physic. Rev.*, 1931, **38**, 2245.
- ¹¹ Clusius, *Z. physik. Chem. B*, 1929, **3**, 41.
- ¹² Giauque and Johnston, *J. Amer. Chem. Soc.*, 1929, **51**, 2300.
- ¹³ Brown, Fock and Smith, *Austral. J. Chem.*, 1956, **9**, 364. Barker, Brown and Smith, *Faraday Soc. Discussions*, 1953, **15**, 142.
- ¹⁴ Staveley, *Quart. Rev.*, 1949, **3**, 65.
- ¹⁵ Staveley and Tupman, *J. Chem. Soc.*, 1950, 3597.
- ¹⁶ Eucken and Veith, *Z. physik. Chem. B*, 1936, **34**, 275.
- ¹⁷ Pople, *Proc. Roy. Soc. A*, 1954, **221**, 498, 508.
- ¹⁸ Corner, *Proc. Roy. Soc. A*, 1948, **192**, 275.
- ¹⁹ Hirschfelder, Curtiss and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, New York, 1954), pp. 245, 1111.
- ²⁰ Prigogine, Bellemans and Englert-Chwoles, *J. Chem. Physics*, 1956, **24**, 518.
- ²¹ Baly and Donnan, *J. Chem. Soc.*, 1902, **81**, 914.
- ²² Keyes, Taylor and Smith, *J. Math. Physic. Mass. Inst. Tech.*, 1922, **1**, 211.
- ²³ Scott, *J. Chem. Physics*, 1956, **25**, 193.
- ²⁴ Salsburg and Kirkwood, *J. Chem. Physics*, 1953, **21**, 2169.