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A Thermodynamical Investigation of the System Benzene-Diphenyl. Parts I-IV

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A THERMODYNAMICAL INVESTIGATION OF THE SYSTEM BENZENE-DIPHENYL

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CONTENTS

The partial molar heat content, entropy and free energy of benzene in solutions of diphenyl in benzene have been determined by measurement of the partial pressures of benzene over the solutions. The whole composition range has been covered (as far as the solubility of diphenyl will allow), at temperatures from 30 to 80° C. A check on the accuracy of the experimental method has been made by measuring the vapour pressure of pure benzene over this temperature range, and good agreement has been found with recent values reported in the literature.

The calculation of the thermodynamic functions from the vapour pressures requires a knowledge of the compressibility of benzene vapour. An experimental method has been devised for determining the gas imperfections of vapours, and using this the second and third virial coefficients of benzene vapour at various temperatures have been obtained.

The variation of the thermodynamic functions of benzene with the composition of the solutions has been compared with that to be expected on the basis of recent statistical theories. It is found that whereas the non-ideal partial molar free energy can be accounted for almost exactly by the theoretical expression, the separate heat contents and entropies show some deviations. It is suggested that these deviations arise from slight changes in molecular packing as the composition is varied.

The activities of benzene and diphenyl in saturated solutions at 30 to 60° C have been obtained from the vapour pressures of saturated solutions at these temperatures. These lead to values for the latent heat of fusion of diphenyl in agreement with the calorimetric value.

The vapour pressure of saturated solutions is discussed.

GENERAL INTRODUCTION

The recent development of the statistical thermodynamics of solutions of molecules of unequal size has met with a certain amount of success in explaining the non-ideality of solutions of long-chain molecules. However, for solutions of smaller molecules a detailed comparison of the theoretical expressions with experimental observations has not yet been made. In this case the deviations from ideality due to the unequal size of the solute and solvent molecules is small, and hence much more accurate observations are required than is the case with polymer solutions. Moreover, to make a useful comparison with the theory, the system must be chosen to fulfil as far as possible the assumptions made in its development. The basic assumption is that the liquid structure has sufficient regularity for the solute and solvent molecules to be considered as occupying one or more sites in a uniform solid lattice. The assumed interchangeability of solute and solvent units on the lattice points requires that the units should not differ too much in size, although a certain difference may be permissible without producing much deviation from the theoretical expressions (Fowler & Guggenheim 1939). Implicit in the lattice model is the assumption that mixing of solute and solvent is not accompanied by a volume change. In the earlier developments of the theory it had also been assumed that the non-random distribution of the molecules is unaffected by a small heat of solution, that is, that the non-ideal entropy arises only from the differences in the number of units in the solute and solvent molecules. However, recent treatments by Orr (1944) and Guggenheim (1945) have been more rigorous and general.

Together with these restrictions laid down by the model, the system must be such that the thermodynamic properties such as relative partial molar free energies and heat contents can be determined to the accuracy required to test the theoretical formulae. Of the methods available for the determination of these quantities, the measurement of the vapour pressure of the solutions has advantages over others such as osmotic pressure, elevation of boiling-point and depression of freezing-point, in being accurate and experimentally convenient over wide ranges of the temperature and composition of the system. The main source of error in using this method for a study of this kind on two component systems in general is in the determination of the composition of the vapour phase, but this can be avoided by the choice of a particular system in which the solute has a negligible vapour pressure over the temperatures used.

The system benzene-diphenyl, which was chosen for the present study, is one in which the solute molecule diphenyl consists of two units of the solvent molecule benzene, and appears to be suitable for a test of the theoretical formulae. However, it is not entirely satisfactory, since the theory would apply exactly only if the molar volume of diphenyl were twice that of benzene. It is, in fact, less than this by about 15 %. Moreover, the units, in this case phenyl groups, are not spherical. From the experimental aspect the system is easy to handle; diphenyl has a conveniently low vapour pressure, and both components can be obtained pure without much difficulty.

This system has been examined previously by Washburn & Read (1915, 1919), Warner, Scheib & Svirbely (1934) and Gilman & Gross (1938), but the precision and extent of the work was not such as to allow the necessary calculations to be made with the required accuracy. More recently, Tompa (1948) has measured the vapour pressures of solutions of diphenyl in benzene at 25° C up to the saturation point, and using these in conjunction with a calorimetric determination of the heat of mixing he has compared the experimental and theoretical vapour pressures. However, this comparison has the disadvantage that the heat of mixing was determined at one composition only, and theoretical formulae were then used to calculate it at other compositions. In the present study we have measured the vapour pressures of the benzene used and those of solutions of diphenyl in benzene up to saturation, from 30 to 80° C at intervals of 10° C. We have thus obtained the relative partial molar thermodynamic quantities of benzene and diphenyl over the whole range of composition.

We have also determined the second and third virial coefficients of benzene over this temperature range at pressures from 60 to 515 mm.

I. EXPERIMENTAL METHOD AND THE VAPOUR PRESSURE OF PURE BENZENE

By J. H. Baxendale, B. V. Enüstün and J. Stern

In this first section we shall be concerned with a description of the apparatus used in the vapour-pressure measurements, its application to the determination of the vapour pressure of pure benzene, and a discussion of the accuracy of the method.

The determination of the vapour pressure of benzene independently has certain experimental advantages in addition to providing a check on the purity of the benzene used and the accuracy of the technique. These are discussed below.

Apparatus

The apparatus used is shown in figure 1. It differs from that used in the differential method of measuring the lowering of vapour pressure, which is frequently employed in a study of this kind, in that absolute pressures are measured. The reasons for this choice were twofold.

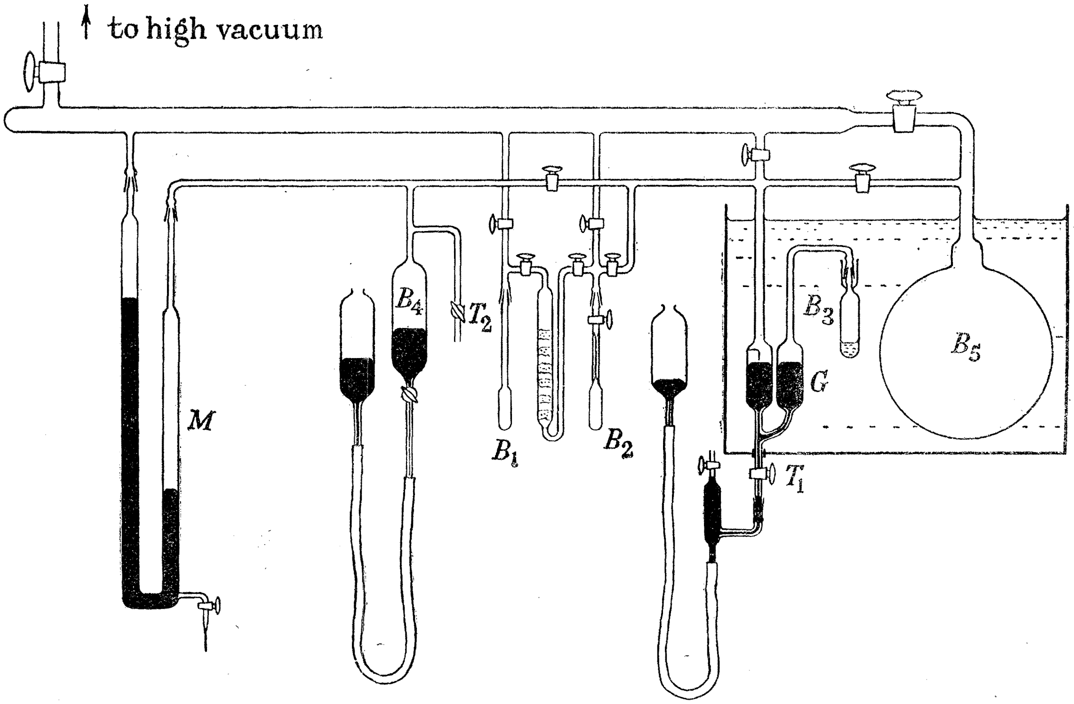

Figure 1. Apparatus for the measurement of vapour pressures.

In the differential method it is usual to distil over a certain amount of the solvent on to a weighed amount of solute, and the difference in pressure between the solution and remaining solvent is then measured. Unless the solvent is extremely pure, this introduces the possibility of a more volatile fraction of the solvent being distilled on to the solute, thus giving a high value for the vapour pressure of the resulting solution. Secondly, in the differential technique it is necessary to keep the tubes connecting the liquids to the manometer at or above the temperature of the liquids to avoid condensation of solvent. This means that either the liquid in a large thermostat (in which the whole apparatus is immersed) must be kept accurately temperature-controlled at all points, which, to the degree necessary for precision measurements is rather difficult, or alternatively subsidiary heating of the tubes by means of heating coils must be employed. The latter method is the one usually adopted. However, Meyer & Lühdermann (1935) found that with their apparatus if the temperature of the vapour over the solution was 10° C higher than that of the liquid, the measured vapour pressure showed an increase of as much as 1 %. The reason for this is somewhat obscure, but in the absence of any further investigation of the phenomenon it was considered desirable to avoid the conditions leading to it. One further advantage of measuring absolute vapour pressures by the present method is that the actual pressure is measured on a manometer which is not in direct contact with the solution being examined. This makes it possible to have manometer tubing wide enough to eliminate meniscus errors.

In outline the *modus operandi* was as follows:

(*a*) After thoroughly heating and pumping down to 10^{-5} mm. as much of the apparatus as possible, a sample of benzene was put into bulb B_1 whose capacity was 10 ml. (see figure 1), thoroughly degassed by freezing and pumping, and distilled to bulb B_2 and back several times through a column of phosphorus pentoxide. After the final transfer it was weighed in B_2.

(*b*) With the mercury in tubes G lowered, the benzene was distilled completely into bulb B_3.

(*c*) With B_3 immersed in liquid air the mercury in gauge G was raised until the glass point in the left-hand limb just touched the mercury surface. Tap T_1 was then closed, and the temperature of the mercury at which the point had been set was noted.

(*d*) The thermostat was then filled and brought to the required temperature.

(*e*) By leading dry nitrogen via T_2 and making fine adjustments by means of the mercury in B_4, the mercury in G was again brought to the glass point.

(*f*) The pressure required for this is the vapour pressure of the benzene in B_3 and was measured on the manometer M by a cathetometer. This procedure was repeated at 10° intervals from 30 to 80° C. We will now deal in more detail with the above operations and the apparatus concerned.

(*a*) In the drying procedure, the first two distillations to and from B_1 were made using liquid air, and care was taken never to have the benzene present as a liquid. This was necessary because hard rubber grease was used for joint and tap lubrication, and to prevent absorption of benzene the vapour pressure of benzene must be kept as low as possible. The final distillation was made with B_2 immersed in a solid carbon dioxide-acetone mixture, and before removal for weighing, B_2 was pumped out for 2 min. while immersed to about 1 in. of the 1 mm. capillary in this freezing mixture. The aim of this last operation was to remove carbon dioxide or gases of similar volatility from the benzene, and it was repeatedly observed that the measured vapour pressures were irreproducible unless it was carried out.

(*b*) The same precautions about keeping the benzene solid were observed in the distillation from B_2 to B_3, and that this was effective in preventing absorption of benzene by the tap grease was shown by independent checks that a quantitative transfer of benzene from B_2 to B_3 was obtained. Bulb B_3 was made detachable in order that diphenyl could be introduced into it for the subsequent examination of solutions. It was fitted with a cone very carefully ground to its socket. A column of mercury in the cup around this cone and socket gave a greaseless joint from which there was no evidence of leaking throughout the whole of the work.

(*c*) After the transfer of the benzene to B_3, the mercury in G was raised three times while evacuating before finally raising and adjusting to the glass point. This removes any air trapped in the mercury. The setting to the point was facilitated by having a background of illuminated opal glass upon which there was a black vertical line 1 mm. thick. The reflexion of this line in the mercury surface was adjusted so that the glass point touched the surface at the reflected edge. The appearance of this edge was very sensitive to the distance of the point from the mercury surface, and the position chosen for a 'set' was that of minimum distortion of the reflexion. The irreproducibility involved in this operation was found to be less than the minimum observable difference on the cathetometer, i.e. 0·01 mm.

(*d*) The thermostat was a tank of about 200 l. capacity lagged with cotton-wool except for a plate-glass window 6 in. wide. The tubes G were set about 10 cm. behind this window and the glass point observed through a lens. The thermostat water was efficiently stirred by two paddles, and temperature control was obtained by a regulator constructed of copper tubing 3 cm. in diameter, containing about 200 ml. of toluene. This provided the make and break in an electronic circuit controlling a 250 W heating lamp immersed in the bath. At the higher temperatures a layer of oil on the surface of the water prevented undue evaporation. The variation in temperature of the bath in the region of the bulb B_3 was followed by observing a thermometer graduated in 0·01° C through the cathetometer telescope. By this method it was possible to read to 0·001° C, and it was found that the variation was ±0·002° C over a period of several hours. This fluctuation was decreased by surrounding B_3 with a beaker, and observations of the temperature inside the beaker showed variations smaller than ±0·001° C over a period of several hours. During the 'setting' of the glass point the stirring motors were switched off to prevent vibration of the mercury, and it was established that no temperature changes occurred in the beaker during the time required for the setting. The thermometers used covered 10° intervals in 0·01° and had N.P.L. certificates, with calibrations to ±0·005° C.

(*e*) The nitrogen let into the apparatus through T_2, to balance the vapour pressure, was contained mainly in the buffer bulb B_5. This had a capacity of 3 l. and was immersed in the thermostat to prevent fluctuations in pressure of the gas due to changes in room temperature.

(*f*) The manometer M on which the vapour pressure was measured consisted of two lengths of 'Veridia' uniform bore tubing of diameter 22 mm. Within the accuracy obtained in this work no meniscus corrections are necessary with this diameter of tubing. The manometer was mounted on a stout frame, and the mercury levels were illuminated diffusely from behind. The temperature of the manometer mercury was taken to be that of mercury in a similar tube mounted on the frame between the manometer limbs, and was kept constant to ±0·1° C during measurements by a thermostatic control of the room temperature. The cathetometer was mounted on a concrete block about 90 cm. from the manometer. It was fitted with a vernier and could be read to 0·01 mm. A calibration of the scale was made every 20 mm. against a standard Invar scale of the Societé Génèvoise, kindly lent by Professor Whytlaw-Gray.

The measurement of the vapour pressure at each temperature was made at least twice, once when the temperature was raised in 10° intervals from 30 to 80° C and again when it was dropped over the same range. On each occasion the glass point was first 'set' and the manometer pressure measured, then deliberately 'off-set' and 'reset', and the pressure measured again.

Purification of benzene

A.R. grade benzene was fractionally distilled and then recrystallized five times. Of 2 l. 300 ml. remained after the final crystallization, and this was stored over sodium wire. A determination of the freezing-point gave 5·51° C. Values recorded in the literature vary between 5·49 and 5·56° C.

Corrections to be applied to the observed pressures

Apart from the reduction of the measured pressures to the standard conditions of temperature and gravity, another correction is necessitated by the nature of the apparatus. Thus when the mercury in G is set to the glass point with the benzene in B_3 immersed in liquid air (operation (*c*) above), the mercury is at room temperature. At the higher temperatures used in the vapour-pressure measurements this mercury expands, and as a result a higher applied pressure than the vapour pressure is required to set the point. In addition, the vapour pressure of mercury is not negligible, being 0·09 mm. at 80° C. The corrections required were obtained as follows by direct measurement. The procedure described for vapour-pressure measurements was carried out with no benzene in bulb B_3, in which case the pressures required to set the point at the various temperatures arise from the above circumstances. The value of this 'blank' pressure at the appropriate temperature was subtracted from the measured vapour pressure.

No great care was taken to adjust the temperature of the thermostat exactly to a specified temperature, and usually these differed by a few hundredths of a degree. For later calculations, however, it was desirable to have the vapour pressures at specified temperatures, and the observed values were adjusted using the temperature coefficient of the vapour pressure. Since the extrapolation was never over more than a few hundredths of a degree, negligible errors result from this procedure. The 'blank' pressure corrections referred to above are not so sensitive to temperature as to require this correction.

An example of the application of the various corrections to a measurement at 70° C is given below. All pressures are in mm. of mercury:

temperature of benzene (° C)	observed pressure	blank pressure at 70° C	correction to Hg at 0° C	gravity correction	reduction to 70·000° C	total correction	corrected pressure at 70·000° C
69·994	554·32	−1·50	−2·37	+0·39	+0·11	−3·37	550·95

Reproducibility of measurements

An idea of the experimental reproducibility at various temperatures is given in table 1. These observations were made with the same sample of benzene in the apparatus. Measurements on three different samples of the stock benzene were made at 25° C and showed average deviations of ±0·01 mm. This indicates that the transfer and drying processes are reproducible.

TABLE 1. REPRODUCIBILITY OF VAPOUR PRESSURE MEASUREMENTS

temperature (°C)	no. of observations	average deviation from mean		maximum deviation from mean	
		(±mm. Hg)	(±%)	(±mm. Hg)	(±%)
30	8	0·02	0·017	0·03	0·025
40	4	0·01	0·006	0·01	0·006
50	4	0·02	0·007	0·03	0·011
60	4	0·02	0·005	0·03	0·008
70	9	0·08	0·015	0·18	0·033
80	3	0·10	0·013	0·14	0·018

RESULTS

The results of the present investigation are compared in table 2 with those of Scatchard, Wood & Mochel (1939) and Smith (1941). It can be seen that except at 30° C the values differ by 0·08 mm. or less from those of Scatchard *et al.* and except at 40° C by 0·06 mm. or less from those of Smith.

TABLE 2. VAPOUR PRESSURES OF BENZENE IN MM. HG

temperature (°C)	present investigation	Scatchard *et al.*	Smith*
25·000	95·27	—	95·27
30·000	119·40	118·75	119·44
40·000	182·69	182·61	182·91
50·000	271·40	271·41	271·42
60·000	391·62	391·7	391·61
70·000	551·00	550·96	550·94
80·000	757·68	757·65	757·71

* Calculated from empirical formula of Smith (1941).

Discussion of errors

In the later stages of this work we shall be concerned with the deviations of solutions of diphenyl in benzene from ideality. These deviations are small, amounting at the most to a difference of about 10 mm. in the vapour pressure. Since non-ideal relative partial molar entropies and heat contents are derived from these deviations, it is important to consider the accuracy of the determinations in order that the limits of accuracy of the thermodynamic functions can be assessed.

The factors determining the accuracy can be divided into those arising from the irreproducibility of conditions, e.g. fluctuations in thermostat temperature, and those which determine the absolute accuracy, e.g. the limits of accuracy of the thermometers. In the former are (*a*) errors in manometry, (*b*) those due to temperature fluctuations in the thermostat and (*c*) those arising from setting the glass point to the mercury surface. We will consider these in turn.

(*a*) In the measurement of mercury heights, independent observations showed that the maximum irreproducibility of the cathetometer readings was ±0·01 mm. for a series of ten settings to a fixed line. Since two settings are involved in the measurement of a pressure the maximum possible error is ±0·02 mm. If we allow a possible fluctuation of ±0·1° C in the temperature of the mercury manometer column, which is well outside the variation observed during measurements, this would lead to a further possible error of ±0·01 and ±0·02 mm. at 30 and 80° C. respectively. The total maximum possible error in manometry is therefore ±0·03 mm. or 0·025 % at 30° C and ±0·04 mm. or 0·005 % at 80° C.

(*b*) The maximum fluctuation in the temperature of the thermostat water in the vessel surrounding the benzene was observed to be less than ±0·001° C. This would mean a maximum variation in vapour pressure from this source of about 0·005 % at 30 and 80° C.

(*c*) As stated previously it was found that the glass point could be set to an accuracy of at least that involved in reading the cathetometer, i.e. ±0·01 mm. Hence arising from irreproducibilities the maximum possible errors in the vapour pressure are altogether ±0·038 % at 30° C and ±0·012 % at 80° C. This estimate is in fair agreement with the observed reproducibility given in table 1.

The absolute accuracy is determined by the limits of accuracy in (*d*) calibration of the thermometers, (*e*) calibration of the cathetometer scale, (*f*) setting the point for zero pressure, i.e. with the benzene in liquid air, (*g*) measurement of the 'blank' pressure. Again considering these in turn:

(*d*) The thermometers had recent N.P.L. certificates quoting temperatures ±0·005° C which corresponds to about ±0·015 % possible error in the vapour pressures.

(*e*) Errors in the calibration of the cathetometer scale were those of setting as quoted in (*a*) above, i.e. ±0·02 mm.

(*f*) The maximum error possible introduced in setting the point for zero pressure is the same as in (*c*) above, i.e. ±0·01 mm.

(*g*) In the determination of the 'blank' pressure the errors given in (*a*), (*c*) and (*f*) might occur together giving a maximum possible error of ±0·074 % at 30° C and ±0·036 % at 80° C.

To these must be added those arising from irreproducibility to give a total maximum possible error of ±0·121 % or ±0·14 mm. at 30° C and ±0·049 % or ±0·37 mm. at 80° C.

In the determinations of deviations from ideality some of the above uncertainties, e.g. those arising from the limits of accuracy of the thermometers do not arise, and the accuracy of the deviations from ideality is better than would be indicated by the above estimates.

II. DEVIATIONS FROM IDEAL GAS BEHAVIOUR OF BENZENE VAPOUR

By J. H. Baxendale and B. V. Enüstün

In the calculation of activities from vapour-pressure measurements it is necessary to know the equation of state of the vapour concerned, in this case benzene. The gas imperfection coefficient α, given by the equation

$$V=\frac{\boldsymbol{R}T}{P}+\alpha, \tag{1}$$

has been determined directly by Eucken & Meyer (1929) for benzene at various temperatures above 60° C at a pressure of about 250 mm. Values of α at various temperatures can also be obtained indirectly from the variation of the vapour pressure of pure benzene with temperature, and the calorimetric latent heat of vaporization. Comparing the results it was found that the former method gave appreciably smaller values of α than the latter. Now α obtained from vapour pressures and heat of vaporization is that corresponding to the saturation pressure of benzene at the temperature concerned, and in all cases this pressure was higher than that used by Eucken & Meyer. It would appear then that α is appreciably pressure-dependent, and calculation shows that neglect of this would introduce significant errors into calculations of the activities of benzene from the vapour pressures of solutions. It was therefore decided to investigate the pressure dependence of α in more detail.

METHOD

Eucken & Meyer determined α by measuring the pressure given by a known weight of benzene in a known volume. This method has certain experimental difficulties which might give rise to errors much greater than can be allowed if α as a function of P is to be determined with the required accuracy.

In the present method benzene vapour was compressed at constant temperature from one volume to another, the pressure being measured before and after the compression. Applying equation (1) to the two volumes and pressures

$$\frac{V_1}{V_2}=\frac{\boldsymbol{R}T/P_1+\alpha_1}{\boldsymbol{R}T/P_2+\alpha_2}=r, \tag{2}$$

where α_1 and α_2 are the values of α at P_1 and P_2, and r is the experimentally determined volume ratio. For the first approximation we will assume that α can be represented as a function of pressure by

$$\alpha=B+CP, \tag{3}$$

where B and C are temperature dependent. From equation (2) we can obtain experimentally a 'mean' $\bar{\alpha}$ given by

$$\bar{\alpha}=\frac{r\alpha_2-\alpha_1}{r-1}=\frac{\boldsymbol{R}T}{r-1}\left(\frac{1}{P_1}-\frac{r}{P_2}\right). \tag{4}$$

From equation (3) $\bar{\alpha}$ is also given by

$$\bar{\alpha}=B+C\frac{rP_2-P_1}{r-1}.$$

Or defining a 'mean' pressure $\bar{P}$ by

$$\bar{P}=(rP_2-P_1)/(r-1),$$

we have

$$\bar{\alpha}=B+C\bar{P}. \tag{5}$$

Since $\bar{\alpha}$ is given by (4) and $\bar{P}$ is calculable, it is possible from (5) to determine B and C by measurement of $\bar{\alpha}$ at various measured pressures.

APPARATUS

The apparatus used is shown in figure 2. The bulbs F_1, F_2 and F_3 had capacities about 500, 300 and 250 ml. respectively, and the capillary junctions between the bulbs were inscribed with fine lines M_1 and M_2. The bulbs were placed in the thermostat and connected to the gauge G (figure 1) by the mercury sealed dry joint described previously. After thoroughly degassing and introducing mercury into F_1, an amount of benzene was transferred into B_3 sufficient to give a pressure just below the saturation pressure at the maximum compression. The thermostat was then brought to the required temperature, and by varying the applied pressures in F_1 and G, and the amount of mercury in G, the mercury was adjusted so that simultaneously (*a*) the levels in the two limbs of G were the same (observed through the cathetometer), (*b*) the level in the left limb was set to the glass point, and (*c*) the level in F_1 was at the mark M_1. Under these conditions the pressure on manometer M (figure 1) was measured. This gives P_1 (uncorrected). Next the mercury was raised into F_2 and by similar manipulations was adjusted to M_2 simultaneously with the condition (*b*) above. The pressure on M was again measured to give P_2 (uncorrected).

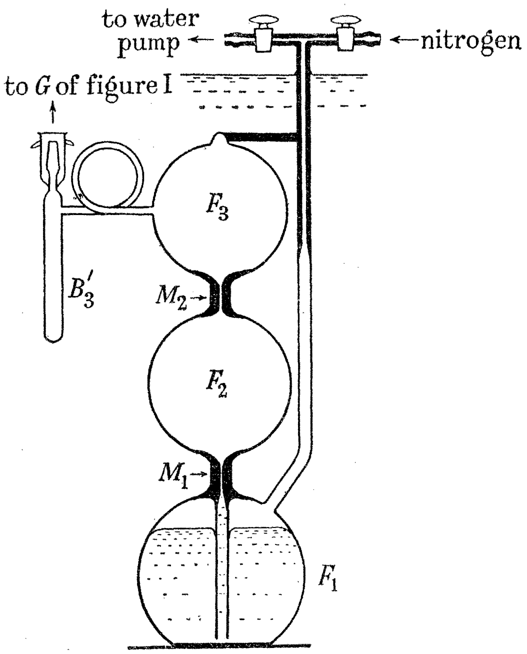

FIGURE 2. Apparatus for the measurement of benzene vapour compressibilities.

This procedure was repeated at 10° intervals from 30 to 80° C on the same sample of benzene vapour. For measurements of compressions at lower pressures, vapour was bubbled out through the mercury in F_1 until the required pressure was obtained approximately.

For the calculation of $\bar{\alpha}$ from these observations a value for the volume ratio r is required. This was obtained by compressing purified nitrogen from about 250 to about 500 mm. (in the manner described above for benzene vapour) at 25·00 and 50·00° C. Inserting the measured pressures into the equation of state for nitrogen gas obtained by Michels, Wouters & de Boer (1934) gave $r = 1{\cdot}8984 \pm 0{\cdot}0001$ at 25° C, and as expected an identical value and average deviation at 50° C. These were the means of nine and six readings respectively with maximum deviations of $\pm 0{\cdot}0002$ in each case.

RESULTS

The observed pressures of benzene vapour were corrected to mercury at 0° C and standard gravity. No 'blank' pressure correction was made in this case, since in the operation the volume of mercury in G is adjusted to be the same at all temperatures, but an additional correction due to the vapour pressure of mercury is necessary. Theoretical values of the irreproducibility to be expected in $\bar{\alpha}$ at various temperatures and pressures have been calculated using an error of ±0·01 on the pressure measurements. These errors, together with $\bar{\alpha}$ and the observed mean deviations, are given in table 3. It can be seen that the accuracy decreases as $\bar{P}$ decreases, and at about 170 mm. the error can be as large as ±5 %. Because of this no measurements were made below this pressure.

TABLE 3. COMPRESSIBILITIES OF BENZENE VAPOUR

temperature (°C)	$\bar{P}$ (mm.)	$-\bar{\alpha}$ ml./mole	no. of observations	mean deviation ±	theoretical maximum irreproducibility
80·00	779·8	1001	3	3	5
	688·7	1000	3	2	6
	543·3	1046	3	2	10
	356·8	1033	2	3	25
70·00	756·5	1085	3	0·3	5
	651·8	1083	3	1	7
	527·1	1114	3	7	11
	346·2	1163	2	2	25
60·00	578·8	1225	3	3	9
	496·1	1180	2	5	12
	408·3	1200	2	1	18
	332·9	1248	2	0	26
	250·2	1248	1	—	47
50·00	395·5	1326	3	6	18
	320·0	1329	2	12	28
	242·4	1411	2	10	49
	186·0	1426	2	6	83
40·00	255·4	1563	2	40	43
	180·7	1524	2	15	85
30·00	174·2	1881	2	40	88

According to equation (5) $\bar{\alpha}$ should be linear with $\bar{P}$. The plot in figure 3 shows that this holds over most of the pressure range at 70 and 80° C, but because of the bigger experimental errors at the lower pressures the linearity is not so well defined for temperatures below 70° C. It can also be seen from figure 3 that at 50, 60 and 70° C there are considerable deviations from linearity at pressures approaching the saturation vapour pressures. The deviations

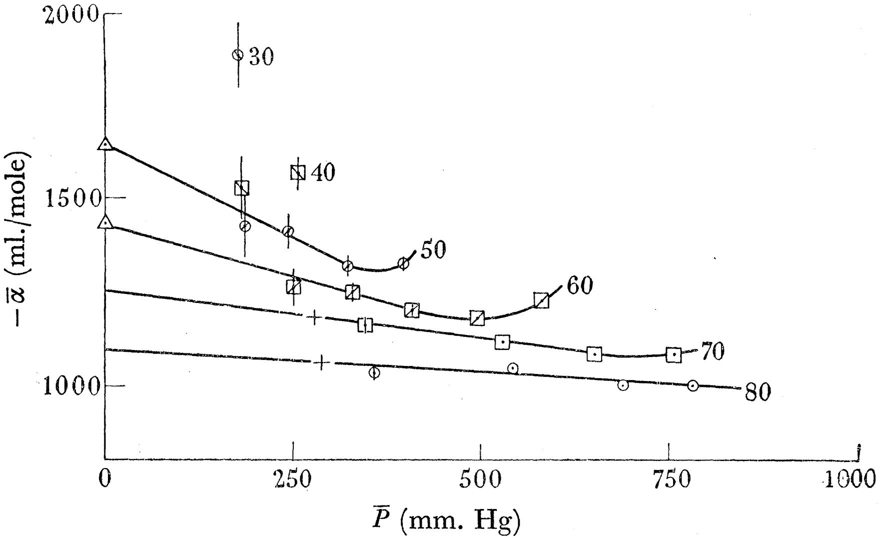

FIGURE 3. Variation of $-\bar{\alpha}$ with $\bar{P}$. ⦸, ⧅, ⊘, ⧄, ⊡, ⊙, observed in present investigation; +, values of Eucken & Meyer (1929); △, extrapolated by equation (8). The numbers on the curves give the values of the temperature (°C).

correspond to a higher compressibility in this region, and might indicate that virial coefficients higher than the second (B) and third (C) are required in equation (3) to describe the compressibility accurately over the entire pressure range. B and C can be obtained fairly accurately at 70° C and 80° C from figure 3 and equation (5). At lower temperatures the values are uncertain, but it is possible to approximate to them by extrapolation as follows.

Two equations have been proposed for the variation of the second virial coefficient with temperature. The Berthelot equation, which gives B in the form

$$B = a - \frac{b}{T^2}, \tag{6}$$

where a and b are functions of the critical properties of the substance, has been found to apply to many substances. Our results for benzene differ from those recently reported by Lambert, Roberts, Robinson & Wilkinson (1949), in that they do not fit (6) using the calculated values of a and b. We have therefore used (6) empirically and obtained

$$B = 1527 - \frac{3{\cdot}271 \times 10^8}{T^2} \text{ ml./mole.}$$

Eucken & Meyer (1929) used an equation due to Callendar of the form

$$B = c - \frac{d}{T^x}, \tag{7}$$

which they found could be applied to several vapours including benzene. Using the experimental values of B at 70 and 80° C we have extrapolated to the lower temperatures using these two formulae. In applying equation (7) we have taken the value of c found by Eucken & Meyer for benzene and calculated d and x from the experimental values of B at 70 and 80° C to give

$$B = 145 - 3{\cdot}44 \times 10^{13}/T^{4{\cdot}1} \text{ ml./mole.} \tag{8}$$

Within the limits of the experimental accuracy the extrapolated values of B at the lower temperatures are independent of which formula is used, and the points at $\overline{P} = 0$ in figure 3 were calculated from (8). Using these values of B at 50 and 60° C it is possible to draw in the linear portion of the curve of $\bar{\alpha}$ against $\overline{P}$ at these temperatures (as has been done in figure 3), so that from the slopes of these lines values of C, the third virial coefficient, can be obtained at four temperatures. These are tabulated together with the corresponding values of B in table 4.

TABLE 4. SECOND AND THIRD VIRIAL COEFFICIENTS OF BENZENE VAPOUR

temperature (° C)	$-B$ (ml./mole)	C (ml./mole mm. Hg)
30	[2170]	[3·09]
40	[1885]	[1·78]
50	1660	1·0
60	1430	0·6
70	1250	0·3
80	1095	0·1

Extrapolated values are given in brackets.

Discussion

The results show that the second and third virial coefficients are sufficient to describe the compressibility of benzene vapour, within the limits of accuracy of the present experiments, except in the region of the saturation pressure where the vapour shows an abnormal increase in compressibility. The values of the second virial coefficient (B) agree well with those obtained by Eucken & Meyer at 80 and 70° C and about 250 mm. There is a big discrepancy between both these sets of values and those of Lambert *et al.* (1949), who found B at 80° C to be 10 % lower and at 40° C 32 % lower than we have obtained.

Values of α, at the saturation vapour pressure P_s, i.e. $B+CP_s$, can also be obtained from the calorimetric latent heat of vaporization and the variation of the vapour pressure of benzene with temperature. Scott, Waddington, Smith & Hufmann (1947) have used this method for benzene, and repeating the calculations using our own vapour pressures of benzene given in part I, we have obtained the calorimetric values of α given in table 5. They are compared with the corresponding values from the present investigation. The latter have been obtained from equation (3) using the values of B and C given in table 4. This assumes that (3) holds up to the saturation pressure which is not strictly true, as has been mentioned above. It can be seen from table 5 that the agreement between the values is good. If we take into account the deviations from (3) in the region of saturation, it is found that $-\alpha$ is somewhat bigger. Thus we estimate that at 60° C the extrapolated value of 1210 is increased to 1270.

Table 5. Comparison with α obtained from calorimetric data

temperature (° C)	$-\alpha$, extrapolated	$-\alpha$, calorimetric
40	—	1430
50	1360	1320
60	1210	1160
70	1110	1070
80	1000	1000

This would seem to indicate that the deviations from (3), which lead to bigger discrepancies between the values of α determined by these two methods, do not arise from a higher compressibility of the vapour but from some other source. One possibility is that there is adsorption of the benzene on the walls of the vessel. Lambert *et al.* (1949) have reported that in their experiments the introduction of glass wood did not affect the results and presumed that adsorption could be neglected. However, the pressures were not stated exactly and may have been sufficiently low for the effect to be absent. Moreover, with the experimental accuracy quoted by these authors it would not be possible to detect the effect. On the other hand, Hirschfelder, McClure & Weeks (1942) state that this increase in compressibility is general for vapours below their critical temperatures. Further work would be necessary to establish this beyond doubt for benzene, but as far as the calculation of thermodynamic functions from the vapour pressures of benzene solutions is concerned, the effect is too small to introduce any appreciable inaccuracies. Because of this uncertainty we can only obtain a rough idea of the third virial coefficient at 30 and 40° C with the present technique, but it can be shown that a negligible error in the thermodynamic functions results at these temperatures.

III. VAPOUR PRESSURES OF BENZENE-DIPHENYL SOLUTIONS

By J. H. Baxendale and B. V. Enüstün

The apparatus described in part I, with a few operational modifications, was used to determine the vapour pressure of solutions of diphenyl in benzene over the temperature range 30 to 80° C. The solutions used covered the whole range of composition in mole fraction units of 0·1 as far as the solubility of diphenyl would allow.

Diphenyl purification

Commercial diphenyl was twice recrystallized from alcohol, pumped dry, and distilled at 9 mm. pressure. The middle 17 g. fraction of a total of 50 g. was retained for use in these experiments. To check the purity a cooling curve was obtained. Solidification began at 68·86° C, and the temperature was 68·81° C when more than one-half of the sample was frozen. By the usual method this gives a melting-point of $68{\cdot}885 \pm 0{\cdot}025^\circ$ C for pure diphenyl. Values from 68·3 to 69·1° C have been reported at various times. It also indicates an impurity of less than 0·1 molar % in the sample, assuming that no solid solutions are formed between diphenyl and the impurity. This was considered pure enough for the vapour-pressure measurements providing the impurity was not volatile, and this was established by the method described below.

In the preparation of a solution for vapour-pressure measurements a weighed amount of diphenyl was first introduced into the bulb B_3 (figure 1). This was roughly pumped out at room temperature and then taken to 10^{-5} mm. with the sample immersed in an acetone-solid carbon dioxide bath. With the gauge G full of mercury and the tube connecting it to B_3 heated electrically to prevent distillation, the sample was kept at 80° C for half an hour by immersion in hot water. The liquid diphenyl was stirred frequently during this time by magnetically operated rods in the bulb. After cooling, the bulb was pumped down to 10^{-5} mm. with the diphenyl immersed in the freezing bath. This operation, which is necessary to remove gases from the sample, was repeated, and then the glass point was 'set' as described previously, with the bulb in liquid air. To check that no volatile impurities remained after this treatment, the vapour pressure of the diphenyl at 80° C was measured. We found that a sample of 0·5655 g. had a vapour pressure of 1·24 mm. and one of 4·8110 g., 1·22 mm. at 80° C. These compare favourably with the 1·3 mm. quoted by Gilman & Gross (1938) and indicate the absence of volatile impurities.

After transferring a weighed amount of benzene on to the diphenyl in the manner described in part I, the vapour pressures of the solution were measured at 10° intervals from 30 to 80° C. After measuring, the composition of the solution was changed by distilling further quantities of benzene into the bulb. For mole fractions 0·1 and 0·2 of the solute 0·5655 g. of diphenyl were used and 4·8110 g. were used for the remainder of the composition range.

Composition of solutions

The amount of benzene in the liquid phase was appreciably less than that weighed out and distilled over, because of the fairly large volume of the vapour phase. This volume was determined by independent experiments using gas compressibility and found to be 53·0 ml. at 30° C. Slight differences which can be estimated arise at different temperatures because of the expansion of the mercury in the gauge G. The amount of benzene in the vapour phase was calculated using the equation of state for benzene vapour determined in part III.

The mole fractions of benzene in the solutions at different temperatures are given in table 6.

Table 6. Mole fractions of benzene in the solutions at various temperatures

T (°C)	1	2	3	4	5	6	7	8	9
30	0·7990	0·8995	—	—	—	—	—	0·6000	0·7000
40	0·7976	0·8991	—	—	—	—	0·5012	0·5996	0·6998
50	0·7957	0·8986	—	—	—	0·3963	0·5004	0·5990	0·6994
60	0·7932	0·8979	—	0·2019	0·2966	0·3951	0·4994	0·5983	0·6989
70	0·7899	0·8970	0·0966	0·2006	0·2952	0·3937	0·4982	0·5974	0·6984
80	0·7857	0·8959	0·0956	0·1990	0·2933	0·3919	0·4967	0·5962	0·6977

Partial pressures of benzene

As mentioned above the vapour pressure of diphenyl at 80° C is 1·3 mm. and hence, in addition to the various corrections to the observed pressures mentioned in part I, we must subtract the partial pressure of diphenyl to obtain those of benzene. The data quoted by Gilman & Gross (1938) were used for diphenyl vapour pressures, and they were extrapolated to temperatures below the melting-point. The partial pressures of diphenyl over the solutions were calculated assuming the solution to be ideal. Negligible error can arise in this procedure since the maximum calculated partial pressure, viz. that in a solution of 90 molar % diphenyl at 80° C, was 1·2 mm. The corrected partial pressures of benzene over the various mixtures are given in table 7, and the mean deviations in each case are shown in table 7*a*.

Table 7. Corrected partial pressures of benzene over the solutions at various temperatures in mm. Hg

The numbers of the mixtures correspond to those in table 6.

T (°C)	1	2	3	4	5	6	7	8	9
30	95·84	107·45	—	—	—	—	—	73·44	84·81
40	146·47	164·57	—	—	—	—	94·67	112·07	129·63
50	216·74	244·01	—	—	—	111·73	139·79	165·81	192·03
60	311·35	351·91	—	83·55	121·15	159·80	200·34	238·07	276·11
70	435·00	493·77	56·60	115·57	168·05	222·25	279·68	333·16	387·06
80	594·61	677·68	76·05	156·05	227·68	302·59	381·36	455·54	530·37

Table 7*a*. Mean deviations of $P(mm)$ for mixtures in table 6

The number of observations is given in brackets

T (°C)	1	2	3	4	5	6	7	8	9
30	0·03 (4)	0·02 (6)	—	—	—	—	—	0·01 (4)	0·01 (4)
40	0·02 (2)	0·01 (6)	—	—	—	—	0·01 (5)	0·02 (7)	0·02 (4)
50	0·03 (3)	0·03 (4)	—	—	—	0·01 (4)	0·01 (4)	0·01 (6)	0·01 (6)
60	0·02 (2)	0·01 (3)	—	0·01 (4)	0·01 (8)	0·01 (4)	0·01 (6)	0·02 (5)	0·01 (3)
70	0·01 (4)	0·06 (4)	0·01 (6)	0·02 (4)	0·01 (7)	0·01 (4)	0·02 (4)	0·01 (4)	0·01 (5)
80	0·10 (3)	0·04 (2)	0·01 (10)	0·02 (17)	0·01 (4)	0·03 (7)	0·03 (10)	0·02 (4)	0·02 (5)

Activity coefficients of benzene in the solutions

From these data we have obtained the relative partial molar thermodynamic functions of benzene and diphenyl in various mixtures.

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

The first step is the calculation of the activity coefficients of benzene in the solutions, at some standard pressure P^*. At the temperature T the activity coefficient γ, in a solution with a mole fraction of benzene X_B, is given by the equation

$$\log\gamma = \log\frac{P}{P_0} - \log X_B - \frac{B}{\boldsymbol{R}T}(P_0-P) - \frac{C(P_0^2-P^2)}{2\boldsymbol{R}T} + \frac{V_L^0(P_0-P)}{\boldsymbol{R}T} + \frac{(V_L^0-V_L)(P-P^*)}{\boldsymbol{R}T}, \tag{9}$$

where P = vapour pressure of benzene over the mixture,

P_0 = vapour pressure of pure benzene at the temperature T,

V_L^0 and V_L are the partial molar volumes of benzene in pure liquid benzene and the solution respectively, at the temperature T, and

B and C are the second and third virial coefficients for benzene vapour.

The only assumptions made in the derivation of equation (9) are that V_L^0 and V_L are independent of pressure and that virial coefficients higher than the third can be neglected. The latter assumption is justified by the results given in part II. Taking P^* as 1 atm. and using the densities of solutions of diphenyl in benzene obtained by Washburn & Read (1919) it is found that the last term in equation (9) is negligible.

It is interesting to compare the relative contributions of each of the terms in (9) to the total $\log_{10}\gamma$. Details are given in table 8 for mixture 7 where the mole fraction of diphenyl X_D is about 0·5. It can be seen that the term involving the second virial coefficient B can amount to about 50 % of the value of $\log_{10}\gamma$ at the higher temperatures, while the term in C contributes about 3 %. It is clear from this that accurate data on benzene compressibility are necessary for the calculation of the activity coefficients.

The values of $\log_{10}\gamma$ for all the solutions, corresponding to the compositions in table 6, are given in table 9. The deviations from ideal are everywhere positive.

TABLE 8. TERMS WHICH MAKE UP $\log_{10}\gamma$ FOR MIXTURE 7 ($X_B \sim 0{\cdot}5$)

temperature (°C)	$\log_{10} P/P_0X_B$	$\dfrac{-B(P_0-P)}{2{\cdot}303\boldsymbol{R}T}$	$\dfrac{C(P_0^2-P^2)}{4{\cdot}606\boldsymbol{R}T}$	$\dfrac{V_L^0(P^0-P)}{2{\cdot}303\boldsymbol{R}T}$
40	0·0145	0·0037	0·0005	0·0002
50	0·0125	0·0047	0·0006	0·0003
60	0·0105	0·0057	0·0007	0·0004
70	0·0081	0·0069	0·0006	0·0005
80	0·0058	0·0081	0·0005	0·0007

TABLE 9. $\text{Log}_{10}\gamma$ FOR THE MIXTURES IN TABLE 6

T (°C)	1 (±0·0002)	2 (±0·0002)	3 (±0·0010)	4 (±0·0008)	5 (±0·0007)	6 (±0·0005)	7 (±0·0004)	8 (±0·0003)	9 (±0·0002)
30	0·0041	0·0007	—	—	—	—	—	0·0129	0·0076
40	0·0036	0·0015	—	—	—	—	0·0179	0·0126	0·0080
50	0·0034	0·0011	—	—	—	0·0219	0·0169	0·0120	0·0076
60	0·0032	0·0014	—	0·0329	0·0260	0·0206	0·0159	0·0112	0·0070
70	0·0026	0·0010	0·0395	0·0305	0·0239	0·0189	0·0149	0·0108	0·0066
80	0·0030	0·0010	0·0365	0·0284	0·0223	0·0184	0·0141	0·0103	0·0064

Discussion of errors

The uncertainties in the values of $\log_{10}\gamma$ can be divided into three groups:

(i) Experimental irreproducibility in the determination of the vapour pressure of the solution, P (see table 7*a*) and possible errors in these due to the calibration of the cathetometer. These together produce uncertainties in $\log_{10}\gamma$ at any one T and X_D which are not connected with those at any other T and X_D. These amount to about $\pm 0{\cdot}0001$ in $\log_{10}\gamma$ at all T and X_D.

(ii) Errors at a particular T and various X_D. These arise from the possible errors in P_0 (all those discussed previously in part I except those due to thermometry), in P due to uncertainties in the blank pressures, and those arising from uncertainties in the virial coefficients of benzene vapour. If random errors from these sources were present they would affect the $\log_{10}\gamma$ at any one T in the same way (i.e. increase or decrease) for all X_D, and as pointed out below, the experimental results show no indication of this.

(iii) Errors at a particular X_D and various T. These arise from possible errors in X_D. Independent measurements on the transfer of benzene by the technique described above showed that for each transfer the maximum error incurred was 0·5 mg. in the weight of benzene. From this source, errors in $\log_{10}\gamma$ from $\pm 0{\cdot}0001$ to $\pm 0{\cdot}0009$ can arise from $X_D = 0{\cdot}1$ to $X_D = 0{\cdot}9$. These would affect $\log_{10}\gamma$ at any one X_D by the same amount at all temperatures. Errors due to setting the point for zero pressure at each X_D should also be included here but they are negligible.

The uncertainties in $\log_{10}\gamma$ given in table 9 have been calculated from (i) and (iii) above.

Relative partial molar heat contents, non-ideal entropies and free energies

The composition of a given mixture changes with temperature due to varying amounts of benzene in the vapour phase as is shown in table 6. In order to calculate the relative partial molar heat contents of benzene ΔH_B it is necessary to obtain $\log_{10}\gamma$ at the same values of the mole fractions at each temperature. This was done graphically for intervals of 0·1 in mole fraction, and the values plotted against $1/T$ for each composition as shown in figure 4. It

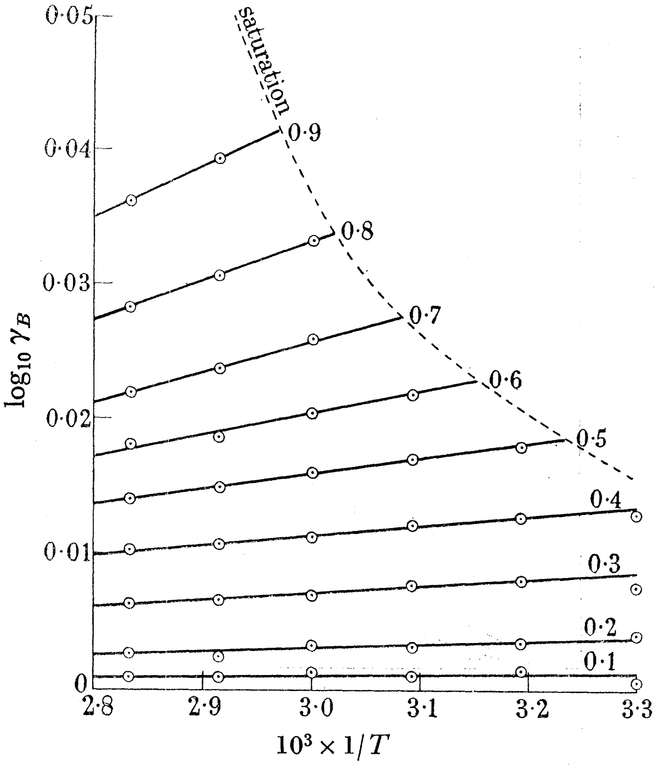

FIGURE 4. Variation of $\log_{10}\gamma_B$ with T at various concentrations.

can be seen from this that the variation of $\log_{10}\gamma$ with $1/T$ is linear. Since there is no systematic deviation of the points from these lines at any one temperature, it follows that no appreciable errors considered above in (ii) have been introduced at any one temperature. Also it is clear that errors in (iii) cannot affect the relative positions of the points at any one X_D. Hence we have taken the uncertainty in $\log_{10}\gamma$ in figure 4 as arising only from the considerations in (i) above, i.e. $\pm 0{\cdot}0001$.

Since $\log_{10}\gamma$ is linear with $1/T$ it follows that within the above uncertainty ΔH_B and the non-ideal relative partial molar entropy ΔS_B are independent of temperature. Values of ΔH_B calculated from the slopes of these lines, and ΔS_B obtained from $\log_{10}\gamma$ and ΔH_B, together with $\Delta\mu_B/T$ at 80° C and the probable errors in these quantities, are given in table 10. The corresponding values for diphenyl ΔH_D and ΔS_D, which are also given in table 10, have been

TABLE 10. RELATIVE PARTIAL MOLAR HEATS, NON-IDEAL ENTROPIES AND FREE ENERGIES OF BENZENE AND DIPHENYL

X_D	ΔH_B (cal.)	ΔS_B (cal./deg.)	ΔH_D (cal.)	ΔS_D (cal./deg.)	$\dfrac{\Delta\mu_B}{T}$ at 80° C (cal./deg.)
0·100	3·9 ± 2	0·007 ± 0·007	168	0·292	0·004 ± 0·001
0·200	11·8 ± 2	0·021 ± 0·007	127	0·220	0·012 ± 0·001
0·300	22·5 ± 2	0·036 ± 0·007	97	0·180	0·028 ± 0·001
0·400	33·2 ± 2	0·048 ± 0·007	73	0·148	0·046 ± 0·001
0·500	50·5 ± 2	0·079 ± 0·009	52	0·108	0·064 ± 0·002
0·600	75·0 ± 3	0·132 ± 0·011	34	0·070	0·080 ± 0·002
0·700	192·5 ± 5	0·190 ± 0·018	19	0·038	0·100 ± 0·003
0·800	132 ± 5	0·245 ± 0·019	9	0·016	0·129 ± 0·004
0·900	172 ± 11	0·321 ± 0·036	2	0·004	0·165 ± 0·005

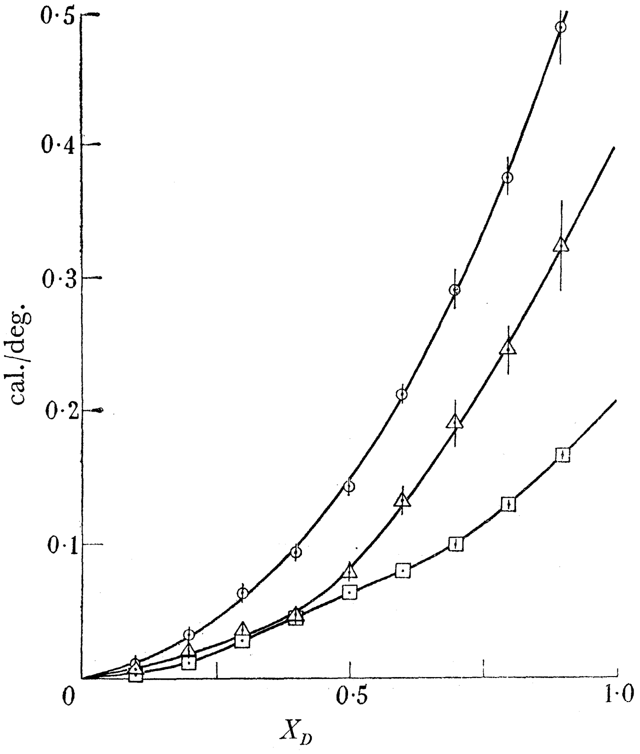

FIGURE 5. Contributions of heat and non-ideal entropy to non-ideal free energy of benzene at 80° C. ⊙, $\Delta H_B/T$; △, ΔS_B; □, $\Delta\mu_B/T$.

obtained in the usual way using the Gibbs-Duhem equation. The uncertainties in $\Delta\mu_B$ given here follow from those in $\log_{10}\gamma$ (table 9), and those in ΔH_B have been calculated from the uncertainties in the points of figure 4.

The contributions of the heat and non-ideal entropy to the non-ideal free energy at 80° C are shown in figure 5. It can be seen that over the whole composition range the heats and entropies to some extent compensate in the final free energy. Thus at a mole fraction of diphenyl $X_D = 0{\cdot}9$ the vapour pressure differs by only about 10 % from the ideal value, whereas if the deviation from ideality had been due to heat or entropy alone the difference would have been 28 and 18 % respectively at 80° C. It is interesting to note that the deviations from Raoult's law are less than 10 %. At 80° C with $X_D = 0{\cdot}9$ the positive deviation is only 5 % and decreases with X_D until at $X_D \sim 0{\cdot}2$ the law is obeyed. At concentrations below this the deviations from Raoult's law are negative and show a minimum at $X_D = 0{\cdot}15$. The reason for this is that the non-ideal behaviour of the solutions is offset by the non-ideality of benzene vapour.

Discussion

Relative partial molar heat contents

The most rigorous theoretical treatment of partial molar heat contents in solutions of molecules of unequal size is due to Orr (1944) and Guggenheim (1945). They treat the solution as a quasi-crystalline phase in which the solute and solvent molecules each occupy a number of sites arranged in the crystal lattice, and have derived an expression for the relative partial molar heat contents of the components of a binary mixture in which the solvent occupied one site and the solute more than one. For the solvent B this is

$$\Delta H_B = \frac{Nwz}{\beta}\, y_D^2\left(1+\frac{\beta-1}{\beta+1}\frac{y_B}{y_D}\right), \tag{10}$$

and for the solute D

$$\Delta H_D = \frac{Nwzq_D}{\beta}\, y_B^2\left(1+\frac{\beta-1}{\beta+1}\frac{y_D}{y_B}\right), \tag{11}$$

where

$$\beta = \sqrt{\left[1+4y_By_D\left\{\exp\left(\frac{2Nw}{RT}\right)-1\right\}\right]}, \tag{12}$$

$$\left.\begin{aligned} y_D = 1-y_B &= \frac{q_DX_D}{X_B+q_DX_D},\\ q_D &= (r_Dz-2r_D+2)/z. \end{aligned}\right\} \tag{13}$$

X_D is the mole fraction of D, r_D is the number of sites occupied by the molecule D in the lattice having co-ordination number z, and N is the Avogadro number. The term w is given by

$$w = w_{BD}-\tfrac{1}{2}w_{DD}-\tfrac{1}{2}w_{BB}, \tag{14}$$

where w_{DD}, w_{BB} and w_{BD} are the potential energies of two neighbouring sites occupied respectively by segments of different D molecules, two B molecules, and B with a segment of a D molecule. In a recent publication by Guggenheim (1948) the nature of w has been discussed in more detail, and this will be considered later.

It is easier to compare equation (10) with the experimental results if an expansion of (10) due to Orr (1944) is used. Taking only the first two terms this is

$$\Delta H_B = Nwzy_D^2\left[1+(1-y_D)\,(1-3y_D)\,\frac{2Nw}{RT}\right] = Nwz\,[f(y_D)]^2. \tag{15}$$

Since ΔH_B is small in the present case it can be shown that errors of less than 1 % are introduced by this approximation. For any z, w can be calculated from (15) using the experimental values of ΔH_B. If (15) is applicable to the experimental results there should be a reasonable value of z for which w is constant over the whole range of composition. We find that this is only true for $z = 2$, which would seem to have little physical significance. For higher values of z, w increases with X_D if X_D is greater than 0·5. This uncertainty in w, however, has a negligible effect on $f(y_D)$ at all values of z and we can therefore test (15) by plotting $\surd(\Delta H_B)$ against $f(y_D)$ for various z. This is shown in figure 6. The variation in w with X_D is obvious from this plot, since w at any value of X_D is determined by the slope of the line joining the origin and the corresponding point. It can also be seen that except at $z = 2$, even allowing for the experimental uncertainty it is not possible, with a constant value of w, to fit the results to (15) over the whole composition range. For instance, with $z = 6$ the experimental value of ΔH_B would have to be 102 cal. instead of the 172 cal. observed at $X_D = 0{\cdot}9$ which is a sixfold increase over the estimated experimental error. Moreover, the trend in the experimental values of ΔH_B would seem to argue against an error of this magnitude. However, up to $X_D = 0{\cdot}5$ they are consistent with (15), but the function is not sufficiently sensitive for z to be determined explicitly.

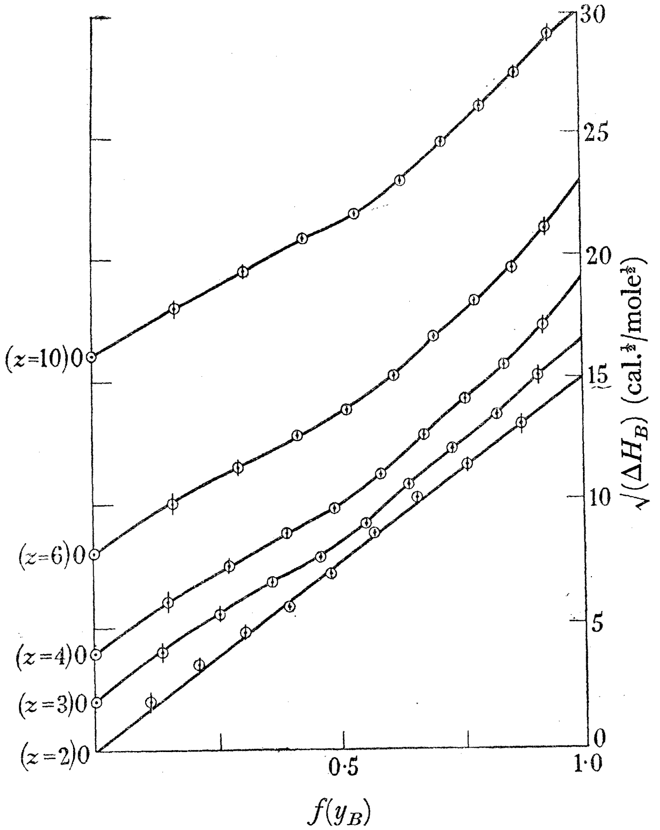

FIGURE 6. Comparison of theoretical and experimental partial molar heat contents of benzene.

As was mentioned previously the significance of w in the above formula has been examined in more detail by Guggenheim. His conclusion is that rather than regard w as a potential energy term, as had been done in the previous theoretical treatments, it should be considered as a free energy. If we denote this free energy by w' the relation to w is given by

$$w' = w + T\frac{dw'}{dT} \tag{16}$$

(w' and w correspond to Guggenheim's w and u respectively).

This results in changes in the formulae such that in (12) w is replaced by w'. The w in (10) remains.

It is desirable to know whether this new formulation will account for the lack of agreement of the experimental results with (10). At a constant temperature this modification would mean replacing w by w + a constant in $f(y_D)$. Now it can be seen by inspection of $f(y_D)$ that such a change will have less effect on $f(y_D)$ as $X_D \to 1$. However, the deviations from linearity in figure 6 increase as $X_D \to 1$, and hence it must be concluded that the new formulation of w cannot alone account for the discrepancies when $X_D > 0{\cdot}5$.

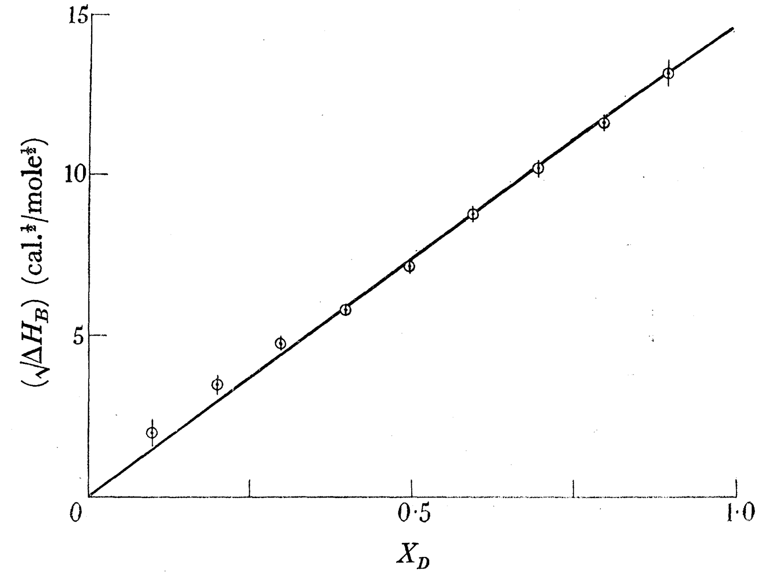

FIGURE 7. Variation of partial molar heat content of benzene with composition.

The fact that equation (10) holds with $z = 2$ is really a consequence of the fact that empirically we find that

$$\Delta H_B = 213X_D^2\,\text{cal./mole},$$

as shown in figure 7, since (10) reduces to this form when $\beta \div 1$ and $z = 2$. However, equation (10) gives ΔH_B as the same function of X_D either for $r_D = 2$ and $z = 2$ or for $r_D = 1$ with any value of z. The latter would mean that the system is strictly regular, and any non-ideal entropy of dilution could only arise as a result of the heat of mixing. However, in this case ΔS_B must always be negative at $X_D > \frac{1}{3}$, but as can be seen from the experimental results, it is everywhere positive in the present system. Moreover, it will be shown later that the magnitude of ΔS_B is in fair agreement with the assumption that solvent and solute molecules occupy one and two sites respectively. It is also clear from the difference in molar volumes of the pure components that the solutions cannot be strictly regular.

The conclusion from the above discussion on ΔH_B is that for reasonable values of z the theoretical expression only holds up to $X_D = 0{\cdot}5$. It is convenient at this stage to make a similar comparsion of experimental and theoretical entropies.

Non-ideal relative partial molar entropies

The theoretical expression for the non-ideal relative partial molar entropy ΔS_B, corresponding to equation (10) for ΔH_B is

$$\Delta S_B = \frac{Nwz}{\beta T} y_D^2 \left(1 + \frac{\beta - 1}{\beta + 1} \frac{y_B}{y_D}\right) - \frac{z\mathbf{R}}{2} \log \frac{\beta + y_B - y_D}{y_B(\beta + 1)} + \frac{z\mathbf{R}}{2} \log (X_B + q_D X_D) - \frac{(z-2)}{2} \mathbf{R} \log (X_B + r_D X_D), \qquad (17)$$

where the symbols are as defined previously.

Although there is some doubt about the value of w, it does in fact make little difference in (17), since w is in any case small and hence β is within a few per cent of unity. In these conditions ΔS_B reduces to the final two terms of (17), which give the non-ideal entropy for athermal dilution. To compare the experimental values of ΔS_B with (17) we have calculated

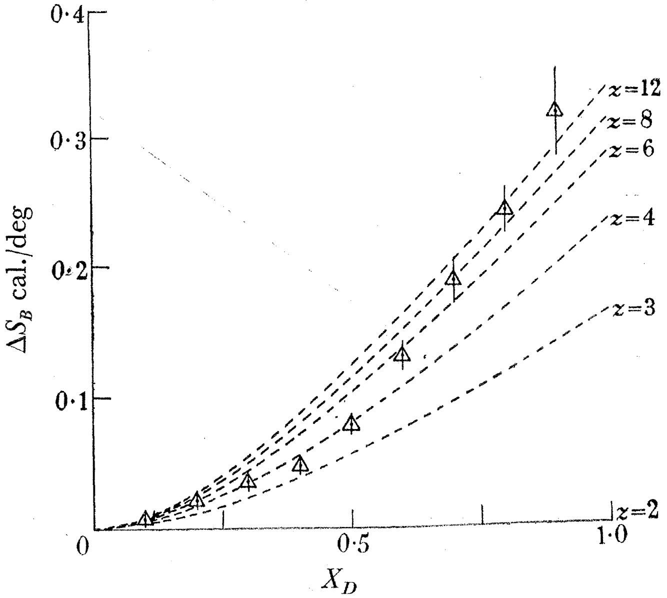

FIGURE 8. Comparison of theoretical and experimental non-ideal partial molar entropies of benzene.

ΔS_B at various X_D using different values of z with $r_D = 2$, and plotted these together with the observed ΔS_B in figure 8. It can be seen that the experimental values of ΔS_B are of the numerical order predicted by the theory over the whole concentration range. Further, up to $X_D = 0{\cdot}5$ the agreement with $z = 4$ is good, although beyond this deviations are apparent. These deviations from the theoretical values are in the same direction as those of ΔH_B, and it follows that the theoretical and experimental free energies should agree better than do ΔS_B and ΔH_B individually. That this is the case is shown in figure 9, where $\Delta \mu_B / T$ (calculated from equations (10) and (17) using the w for $z = 3$, 4 and 6 obtained at $X_D < 0{\cdot}5$ from figure 6) is compared with the experimental $\Delta \mu_B / T$, at 80° C. The agreement for $z = 4$ is seen to be good. It is interesting to note that a similar agreement on $\Delta \mu$ and discrepancy with ΔS and ΔH has been observed with the system rubber-benzene and discussed by Gee (1946, 1947). It has been suggested by Guggenheim (1948) that this behaviour is due to the neglect of $T(dw'/dT)$ in equation (16), but we have seen that for the present system equation (16) does not correct the deviations of ΔH_B from the theoretical formula, and by similar arguments it can be shown that deviations in ΔS_B cannot be accounted for exactly in terms of equation (16). The inability of (16) to explain the deviations may arise from variations in w, w' and dw'/dT with composition. That such a change occurs in w in going from pure benzene to pure diphenyl can be shown by considering ΔH_B at $X_D = 1$ and ΔH_D at $X_D = 0$. Equations (10) and (11) give

$$\Delta H_D = 2(z-1)\,Nw \quad \text{at} \quad X_D = 0,$$

$$\Delta H_B = zNw \quad \text{at} \quad X_D = 1.$$

These relations can also be obtained by a simple consideration of the lattice model and do not depend on the method of derivation of (10) and (11). Extrapolating the experimental results to these limiting concentrations we obtain 230 and 213 cal. for ΔH_D and ΔH_B respectively. Thus if we assume $z = 4$, Nw is 38 cal. in pure benzene and 53 cal. in pure diphenyl. Although this appears to be a considerable increase in w, the change is in fact small when

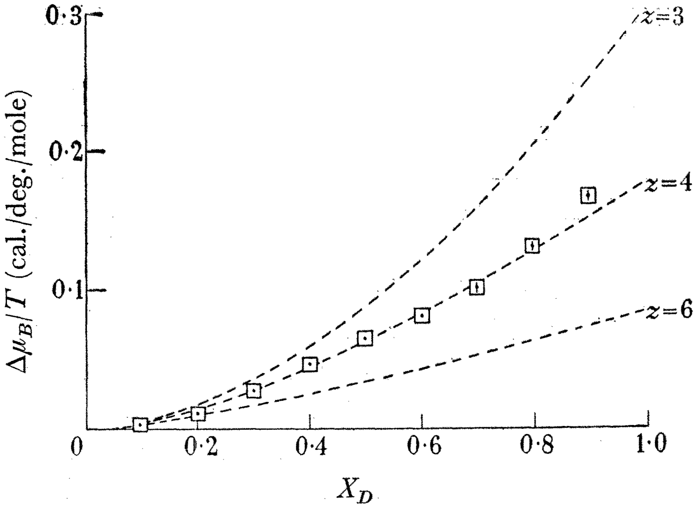

FIGURE 9. Comparison of theoretical and experimental non-ideal partial molar-free energies of benzene at 80° C.

considered as a variation in the terms which make up w, viz. w_{BB}, w_{DD} and w_{BD}. Thus from the lattice model of the system and the latent heats of vaporization L_B and L_D, it follows that

$$Nw_{BB}z = -2(L_B - \boldsymbol{R}T) = -14{,}000\,\text{cal.},$$

$$Nw_{DD}(z-1) = -(L_D - \boldsymbol{R}T) = -17{,}200\,\text{cal.}$$

With a co-ordination number of four we obtain for Nw_{BB} and Nw_{DD}, -3500 and -4300 cal. respectively, and from (14) we find that Nw_{BD} is about -4000 cal. The increase of 15 cal. in Nw can therefore arise from very small changes in these quantities.

Since we find that w differs at the extreme ends of the composition range it seems reasonable to conclude that there is a gradual variation throughout this range. Also it follows from the form of equation (16) that w' and dw'/dT are also functions of X_D. Hence to explain the behaviour of the present system statistically it would be necessary to remove the restriction that w, w' and dw'/dT are independent of composition which is a fundamental assumption when applying the quasi-chemical equation to obtain equations (10) and (17).

We have seen that with a particular value of w in the theoretical free-energy expression there is good agreement with the experimental values. This w could, however, be regarded as w' in Guggenheim's new formulation of w, in which case it would follow that variations in w' with composition are small and not sufficient to cause appreciable deviations from experiment in the expression for free energy. If this is the case then the variation of $-T(dw'/dT)$ with X_D must be of the same order as that of w. The deviations of ΔH_B and ΔS_B from the theory could then be interpreted in terms of similar changes in w and $-T(dw'/dT)$ respectively, in which case the deviations in both heat and entropy would have the same origin.

Variations in w with X_D of the order required could easily arise as a result of slight changes in molecular packing. Thus an extremely small expansion of the lattice could give the increase of 15 cal. in Nw as a result of slight changes in w_{BB}, w_{DD} and w_{BD}. This lattice expansion would mean an increased free volume for the benzene molecule and a corresponding increase in entropy as observed.

IV. SATURATED SOLUTIONS OF DIPHENYL IN BENZENE

By J. H. Baxendale and B. V. Enüstün

The vapour pressures of saturated solutions allow an additional confirmation of the accuracy of the experimental method in that the solubility and latent heat of fusion of diphenyl calculated from them can be compared with that from other observations.

Vapour pressures of saturated solutions

These were obtained in the usual way from 30 to 60° C, by measuring on a solution in contact with solid diphenyl which had been stirred for several hours to ensure equilibrium. The corrected vapour pressures are given in table 11 and are plotted in figure 10. It can be seen from this figure that if a solution of diphenyl in benzene with $X_D > 0{\cdot}7$ is cooled from 80° C the vapour pressure falls until the solution becomes saturated. It then increases with decreasing temperature as the solute crystallizes out, reaching a maximum at 48° C beyond which it falls again. This behaviour will be discussed subsequently.

Table 11. Solubility of diphenyl and saturation activity coefficients

temperature (° C)	P_s (mm.)	$\log_{10} \gamma_B^S$	X_D^S	$\log_{10} \gamma_D^S$
60·00	66·86	0·0366	0·8396	0·0018
57·52	77·65	—	—	—
55·01	83·79	—	—	—
50·00	90·97	0·0272	0·6803	0·0054
47·8	91·69	—	—	—
45·00	90·75	—	—	—
40·00	86·15	0·0208	0·5464	0·0105
30·00	69·82	0·0151	0·4324	0·0175

Solubilities of diphenyl

From the vapour pressures we have calculated a_B^S, the activity of benzene in the saturated solutions. The mole fraction of benzene at saturation x_B^S was obtained by extrapolation of the observations with lower concentrations of diphenyl at the same temperature. Since we find empirically that near the saturation point $\log a_B$ is linear with $\log X_B$ this can be done accurately. The solubility of diphenyl X^S_D then follows from X^S_B. The saturation activity coefficients of diphenyl, γ^S_D, have been calculated from ΔH_D and ΔS_D and the saturation temperatures. These data are given in table 11.

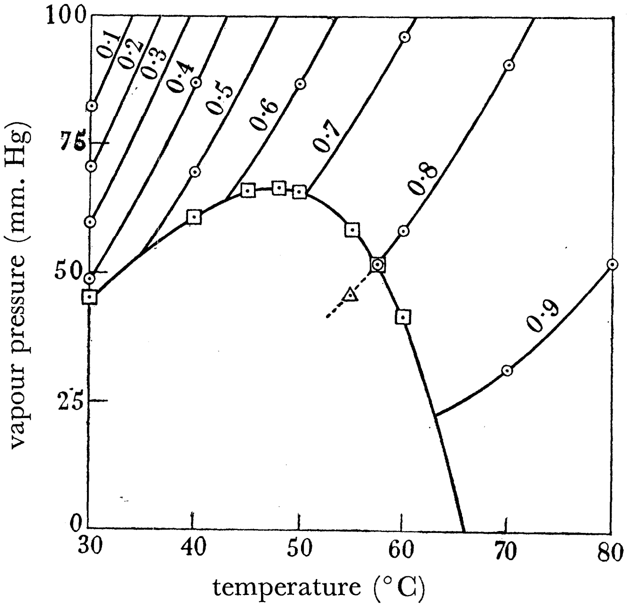

FIGURE 10. Variation with temperature of benzene vapour pressure over solutions of diphenyl. ⊙, unsaturated solutions; ⊡, saturated solutions; △, supersaturated solutions. The values of X_D are indicated on the curves.

Comparisons with previous results

As can be seen from figure 11, log X^S_B is linear with $1/T$, and the results of Warner *et al.* (1934) are in excellent agreement with the present ones. The log a^S_D curve is, however, not

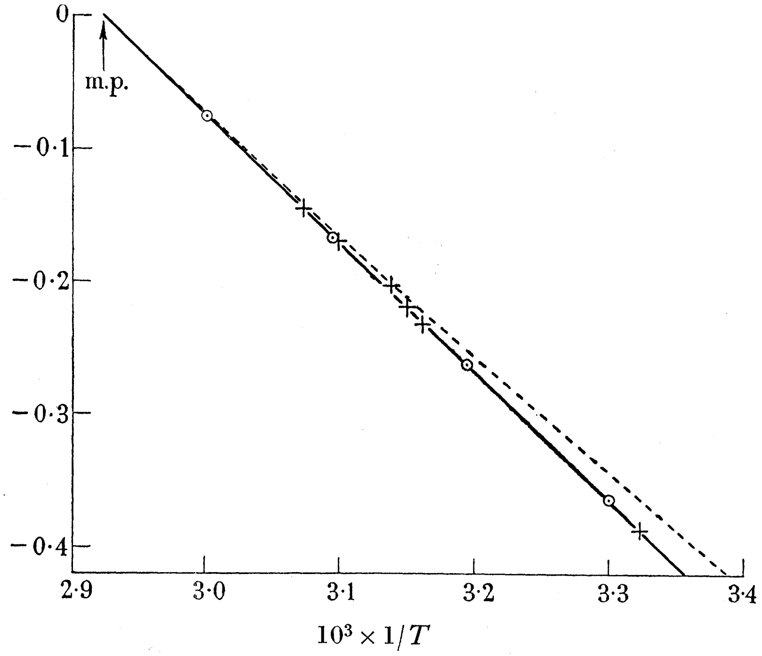

FIGURE 11. Variation with temperature of the solubility of diphenyl in benzene. ⊙, $\log_{10} X^S_D$ from present vapour-pressure data; +, $\log_{10} X^S_D$ observed by Warner *et al.* (1934); ----, $\log_{10} a^S_D$ from present data.

quite linear with $1/T$, and we have obtained L^f_D from the curve at various temperatures and plotted these in figure 12. Extrapolation to the melting-point gives a value of L^f_D in good agreement with that obtained calorimetrically by Spaght, Thomas & Parks (1932), but higher than the other values recorded in the literature. The difference in specific heats between liquid and solid diphenyl at the melting-point which can be obtained from figure 12 agrees with the value 8·7 cal./deg./mole obtained by Spaght *et al.* (1932). The fact that the values of a^S_D obtained by Warner *et al.* are higher than ours, in spite of the agreement on X^S_D, arises from the fact that they have used a lower value of L^f_D in their calculations.

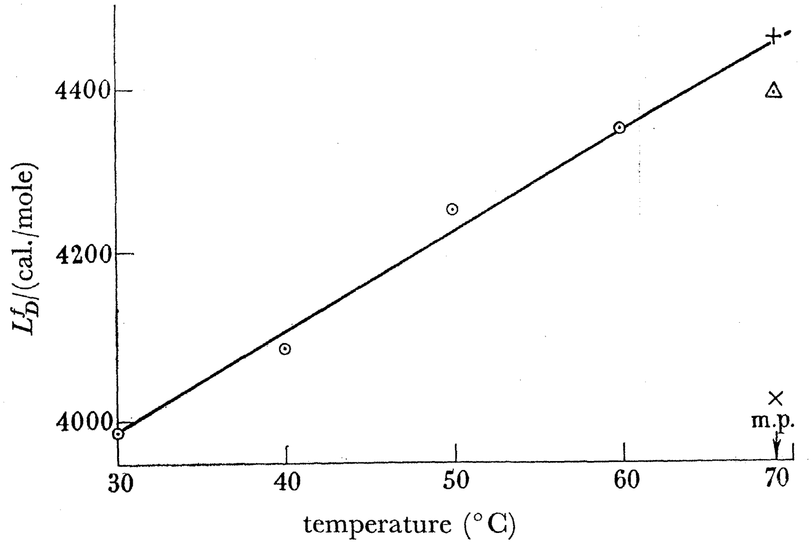

FIGURE 12. Variation of the latent heat of fusion of diphenyl with temperature. ⊙, from present observations; +, obtained by Spaght *et al.* (1932); ×, obtained by Washburn & Reed (1915); △, obtained by Ejkman (1889).

Thermodynamics of saturated solutions

The variation of the vapour pressure of saturated solutions with temperature has been considered previously by Brønsted (1937), Findlay (1938), and in more detail by Korvezee (1934, 1947). The relation between the saturation vapour pressure P_s and temperature T is given approximately by combining Raoult's law with the approximate equation for the ideal solubility of the solute D in the solvent B, viz.

$$\log X^S_D = \frac{L^f_D}{\boldsymbol{R}}\left\{\frac{1}{T_D}-\frac{1}{T}\right\},$$

where T_D is the melting-point of pure D. These lead to the equation

$$P_s = C\left[1-\exp\left\{\frac{L^f_D}{\boldsymbol{R}}\left(\frac{1}{T_D}-\frac{1}{T}\right)\right\}\right]\exp\left\{-\frac{L_B}{\boldsymbol{R}T}\right\}, \tag{18}$$

where C is defined by the approximate equation for the variation of the vapour pressure P of the pure solvent with temperature, viz.

$$P = C\exp\left\{\frac{-L_B}{\boldsymbol{R}T}\right\}.$$

In the exact derivation of P_s it is of course necessary to take into account the variation of L_B and L^f_D with temperature, the volume changes in the condensed phases and also the deviations of the vapour and solutions from ideality. Figure 10 is an example of the form of equation (18).

It can be shown from (18) that P_s has a maximum at $T_{\text{max.}}$ which is given by

$$\log \frac{L_B}{L_B+L_D^f} = \frac{L_D^f}{\mathbf{R}}\left(\frac{1}{T_D}-\frac{1}{T_{\text{max.}}}\right) \tag{19}$$

when the saturation concentration of D, X_D^S is $\frac{L_B}{L_B+L_D^f}$. It is also found that the P_s-T curve has a point of inflexion at T_i, a lower temperature than $T_{\text{max.}}$, which is given by

$$\frac{1}{T_i} = \frac{2}{T_m}-\frac{1}{T_D},$$

when

$$X_D^S = \left(\frac{L_B}{L_B+L_D^f}\right)^2.$$

An exact equation for X_D^S at $T_{\text{max.}}$ can be obtained by applying the Clapeyron equation to the saturated solutions, viz.

$$\frac{dP_s}{dT} = \frac{\Delta H}{T.\Delta V},$$

where ΔV is the volume change and ΔH the change in heat content when 1 mole of benzene is evaporated from the solution. ΔH is made up of the heat of evaporation of benzene $(L_B-\Delta H_B^S)$ and the accompanying heat of precipitation of the diphenyl-$(L_D^f+\Delta H_D^S)\,(X_D^S/X_B^S)$

i.e.

$$\Delta H = L_B-\Delta H_B^S-(L_D^f+\Delta H_D^S)\,\frac{X_D^S}{X_B^S},$$

where the value of each term is that at the temperature T. Hence at $T = T_{\text{max.}}$ when $dP_s/dT = 0$,

$$X_D^S = \frac{L_B-\Delta H_B^S+L_D+\Delta H_D^S}{L_B-\Delta H_B^S}.$$

A comparison of experimental determinations of $T_{\text{max.}}$ with those given by equation (19) has been made for systems of dihydric phenols and water, and of salts and water by Korvezee & Dingemans (1943) and have been discussed by Korvezee (1947).

From the approximate equation (19) given above we have calculated $T_{\text{max.}}$ to be 46° C for the benzene-diphenyl system, and if the exact form of the equations is used, 47·9° C is obtained compared with the observed value 47·8° C.

We have great pleasure in thanking Professor M. G. Evans for many helpful discussions on this work, and are grateful for his sustained interest and advice during the course of it.

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