EXPERIMENTAL INVESTIGATION OF THERMODYNAMIC PROPERTIES OF NON-IDEAL LIQUID MIXTURES

by Ian Brown, B.Sc. (Hons.)

Being a collection of published papers, unpublished
data and summaries, submitted in support of his
candidature for the Degree of Doctor of Science
of the University of Adelaide, November 1964.

PREFACE

The candidate is senior author of all the papers presented in this thesis. He was directly responsible for the inception and direction of the work described, with the exception of the theoretical part of item No. 6. With this exception, the thesis contains no material previously submitted for a Degree in any University by the candidate or by any other person.

References to published papers from which information was derived and acknowledgments of help received are given in the body of the thesis. The valuable assistance with the experimental work, given by the candidate's co-authors, is also gratefully acknowledged.

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SUMMARY

This experimental investigation of the thermodynamic properties of mixtures containing associated components was made to obtain some understanding of the factors governing the liquid-vapour equilibria of mixtures of this type which are important in industrial separations by distillation. This thesis is divided into four parts. Part I describes measurements of the thermodynamic properties of binary solutions of alcohols in benzene, n-hexane and other non-polar solvents. Part II describes similar measurements on solutions containing the polar liquids acetone, acetonitrile and nitromethane.

When this work was started only a limited amount of accurate isothermal data was available for systems of this type. Apparatus and methods were developed and precise measurements were made of liquid-vapour equilibria, calorimetric heats of mixing and volume changes on mixing of these systems over the full range of concentration at temperatures from 25° to 45°C. These data were used to calculate values of entropy changes on mixing and to determine the contributions of the enthalpy and entropy changes to the excess free energy of mixing.

This study of alcohol solutions had led to a better understanding of the contributions made to their thermodynamic properties due to the size and shape of the alcohol molecule and to the intermolecular interactions involving both the hydroxyl group and the solvent.

The study of solutions of the three polar liquids has shown that the intermolecular interactions governing their thermodynamic properties are complex. Values of

their properties were found to have appreciable contributions from both the break down of association of the polar component due to dilution by the solvent and from electron donor-acceptor interaction between solute and solvent. The relative importance of these contributions was found to vary considerably with the properties of both the solute and the solvent used.

The existing theories of solutions have been found to be inadequate to explain quantitatively the properties of these mixtures, but it is hoped that the data obtained in these investigations will make a useful contribution to the formulation of a new theory for solutions having associated components.

Part III of this work describes the application of various separation methods, particularly gas chromatography, to the separation and identification of the components of a Lurgi brown-coal tar. Methods are described for the identification of organic compounds by gas chromatography and for the quantitative classification of stationary-phase liquids used in this technique. A gas chromatographic method is also described for determining the changes in thermodynamic properties which occur in electron donor-acceptor interactions between the functional groups of solute molecules and polar stationary-phase solvents.

Part IV consists of two papers describing studies of the preparation of metaphosphoric acid and the pilot-plant production of furfural.

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Reprinted from the

AUSTRALIAN JOURNAL OF SCIENTIFIC RESEARCH

SERIES A — PHYSICAL SCIENCES

VOLUME 3, NUMBER 2, PAGES 306-323, 1950

LIQUID–VAPOUR EQUILIBRIA

I. THE SYSTEMS CARBON TETRACHLORIDE–CYCLOHEXANE AND WATER-ACETIC ACID

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I. THE SYSTEMS CARBON TETRACHLORIDE-CYCLOHEXANE AND WATER-ACETIC ACID

By I. BROWN* and A. H. EWALD*

[*Manuscript received January* 19, 1950]

Summary

An apparatus for the accurate determination of liquid-vapour equilibria is described. Data obtained with it for the system carbon tetrachloride-*cyclo*hexane at 70 °C. and the thermodynamic functions derived from these are shown to agree with the corresponding values determined by Scatchard, Wood, and Mochel(1). Equilibrium data of the system water-acetic acid have been measured at 760 mm. Hg, particular attention being given to high acetic acid concentrations. These results are compared with published values and the excess chemical potentials of the components have been calculated.

I. INTRODUCTION

The liquid-vapour equilibria of selected non-ideal liquid mixtures are being studied as part of an investigation of the processes of azeotropic and extractive distillation. A survey of the literature shows that the liquid-vapour equilibria of only very few systems have been measured with sufficient accuracy to yield significant values of the derived excess thermodynamic functions. These have been defined by Scatchard, Raymond, and Gilmann(2) : they are required to relate the properties of liquid mixtures to those of their components.

The most suitable form of apparatus for the determination of liquid-vapour equilibria is the recirculating type of still. This provides adequate samples of both the liquid and the condensed vapour but introduces the danger of the establishment of a false state of equilibrium due to enrichment of the vapour in the more volatile component by partial condensation ; alternatively the vapour may be impoverished with respect to this component by entrainment of liquid droplets. In a recent critical review Fowler(3) pointed out that these effects occur with several published still designs, and Garner(4) demonstrated that widely different results can be obtained for the same mixture by using different stills. In the present paper an improved equilibrium still is described, and data obtained with it show that this still permits the measurement of true liquid-vapour equilibrium concentrations, pressures, and temperatures.

II. APPARATUS

(*a*) *Equilibrium Still*

The most satisfactory stills are those of Scatchard, Raymond, and Gilmann(2) and Gillespie(5) (see also 6). Gillespie (personal communication, December 1947) realized, that in his still, samples taken from the boiler do not

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represent the liquid which is in equilibrium with the vapour leaving the disengagement chamber ; and he suggested the inclusion of a liquid trap between the disengagement chamber and the return line to the boiler(7). In a still modified in this manner the boiler and Cottrell pump may be regarded as merely providing a mixture of liquid and vapour in equilibrium which after splashing on to the thermometer is separated in the disengagement chamber to give samples of liquid and vapour which are in equilibrium, irrespective of any condensation or pressure effects in the pump-tube.

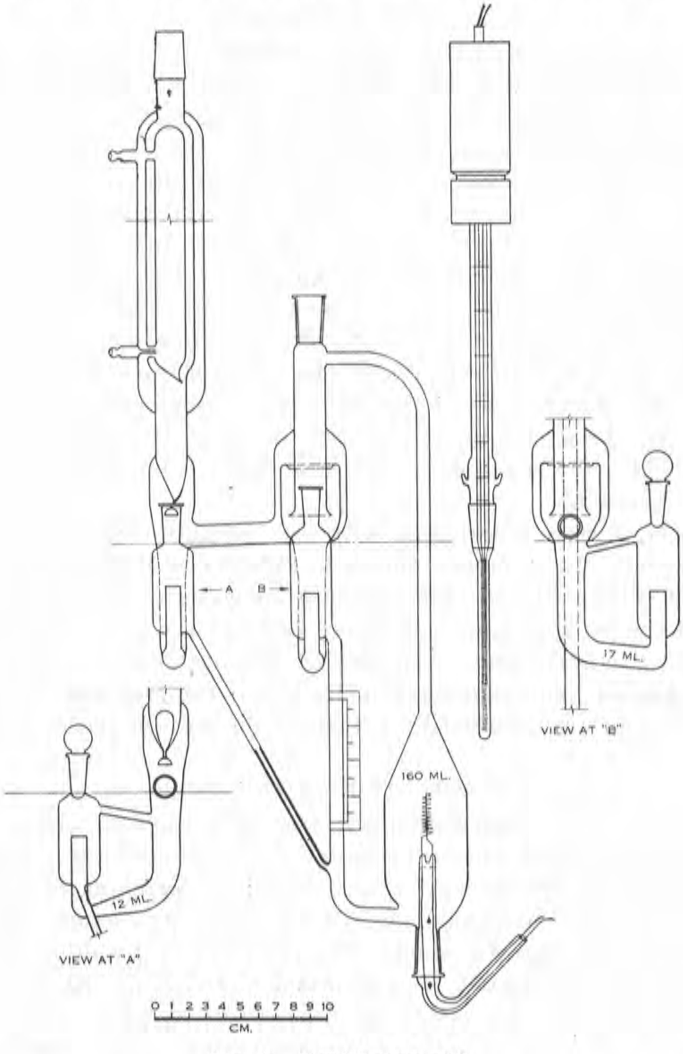

Fig. 1.—Equilibrium still.

The equilibrium still employed in this work is shown in Figure 1. The essential features of the still described by Gillespie(5) have been retained in the design, but a liquid trap has been included as suggested. A new kind of internal heater* was found necessary to obtain continuous nucleation and steady boiling, and the design of the boiler assembly* had to be altered to give satisfactory pumping at pressures down to 50 mm. Hg. The disengagement chamber was enlarged to accommodate a platinum resistance thermometer and the design of the sample traps was altered to eliminate stopcocks.

(*b*) *Auxiliary Equipment*

The apparatus for the control and measurement of pressure was essentially the same as that described by Scatchard, Raymond, and Gilmann(2) ; nitrogen was used as the confining gas. The mercury levels of the precision barometer were determined by means of two telescopes and verniers, sliding on a cathetometer with a calibrated scale. The mean temperature of the barometer was determined at each reading by thermometers, mounted as close as possible to the centre of the upper and lower barometer tubes, and immersed in mercury filled tubes of the same diameter as the barometer tubes. The mercury heights which could be measured to $\pm 0\cdot 04$ mm. were converted to standard mm. of mercury by the methods described by Beattie, Benedict, and Blaisdell(8) ; the pressures are correct to $\pm 0\cdot 05$ mm. Hg. Corrections were applied for the temperature and ruling errors of the cathetometer scale, the mean temperature of the mercury, the gravitational constant at the barometer, and the capillary depressions. The corrections due to the heights of confining gas and vapour were found to be negligible.

Temperatures were determined with the specially constructed Meyer type platinum resistance thermometer shown in Figure 1, a Tinsley vernier potentiometer, and a calibrated 100 ohm standard resistance. The thermometer was calibrated at the ice and steam points and compared with a standard resistance thermometer at temperatures up to 250 °C. Its resistance at the ice point was checked periodically and remained unchanged. Temperatures were measured to $\pm 0\cdot 003$ °C. and are recorded to $\pm 0\cdot 01$ °C. on the international scale.

III. OPERATION OF THE STILL

The optimum still charge was known after the initial trials and was measured by means of a level scale shown in Figure 1 ; a variation of 5 per cent. was permissible. Steady boiling was assured from the beginning by operating the internal heater at its maximum power input (40 watts) before connecting the still to the pressure control system. When the Cottrell pump was operating, both heaters were adjusted in accordance with the findings described subsequently in Section IV. Only small adjustments were required after the first 20 minutes of a run in order to maintain the system either at constant temperature or constant pressure.

* The boiler was wound with 4·6 m. of 0·405 mm. nichrome wire over a layer of asbestos tape. The wire was set in alundum cement and lagged with asbestos cloth and an outer cover of aluminium foil. The internal heater consisted of a coil of 25 cm. of 0·32 mm. platinum wire, with a short length of thick-walled soda-glass capillary over the central wire sealed to it at the lower end. Both heaters were controlled by variable voltage transformers. The Cottrell pump-tube and disengagement chamber were lagged with asbestos tape over a layer of aluminium foil.

On turning off the external heater in preparation for sampling, its large heat capacity caused boiling to continue for 1 to 2 minutes and, to avoid bumping at this stage, the internal heater was switched off only when the pumping in the Cottrell tube had almost ceased. The still was then vented to atmosphere through a drying tube and, when working at 760 mm. Hg, any subsequent distillation of vapour through the Cottrell tube was prevented by spraying water on the lagging of the tube. Samples were then withdrawn from the two traps.

When adjusting the composition of the still charge to that required for the next run, the volume of mixture to be removed, and the amount of pure component to be added were calculated, and only occasionally was a subsequent adjustment of the liquid level necessary.

IV. Still Performance Tests

(i) *Boiling.*—Test runs with water and aqueous solutions of ethanol and acetic acid showed that the internal heater gave adequate nucleation and smooth boiling at pressures from atmospheric to as low as 50 mm. Hg.

(ii) *Distillation and Liquid Flow-Rates.*—The distillation rate depended mainly on the external heating, while the rate at which the liquid circulated through the Cottrell tube was controlled by the internal heater and liquid level. Flow-rates through the liquid trap were measured, while the still was operating, by using a calibrated pump to force liquid from the trap to the return line at a rate sufficient to maintain a constant level in the trap. Distillation rates were obtained from the drop counter in the still. For dilute aqueous solutions liquid flow-rates were up to 430 ml./min. and distillation rates up to 3·8 ml./min., while with acetone the corresponding figures were 200 and 16·5 ml./min.

(iii) *Entrainment.*—The absence of entrainment at high liquid and vapour flow-rates was confirmed by the following tests.

The boiler and the liquid trap were filled with a 1 per cent. solution of flourescein in ethanol, and on operating the still at distillation rates up to 18 ml./min. and liquid flow-rates up to 400 ml./min., no colour could be detected in the vapour trap after 9 hours. A similar test with aqueous potassium permanganate also indicated no entrainment.

Furthermore, vapour samples from two runs with a 75 mol. per cent. solution of acetic acid in water, at distillation rates of 3·3 and 13·2 ml./min. respectively, had identical concentrations.

(iv) *Distillation in the Vapour Trap.*—Distillation from the liquid in the trap on to the walls of the vapour trap could conceivably cause impoverishment of the condensate sample. During one run with aqueous acetic acid the walls of the vapour trap were heated electrically to a temperature just above that of the condensing vapour, but this had no effect on the composition of the vapour sample.

(v) *Time Required to Reach Equilibrium.*—Measurement of the boiling temperature to ±0·005 °C. is not sufficiently sensitive to indicate the final approach to equilibrium ; two mixtures of widely different relative volatility (α)

were used in the following manner to determine the time required to reach equilibrium in the still.

Aqueous acetic acid (30 wt. %, $\alpha=1\cdot43$) was used in six runs lasting from 0·25 to 2·5 hours at a distillation rate of 7 ml./min., and samples from these were analysed with an accuracy of $\pm0\cdot23$ per cent. by the methods described later. After 2 hours no further change in the composition was found.

The second test mixture was a 30 mol. per cent. solution of nitrobenzene in *cyclo*hexane ($\alpha=30\cdot4$) which was distilled at a rate of 15 ml./min. Samples of 0·25 ml. were taken from the vapour trap at 3 minute intervals and analysed refractometrically with an accuracy of $\pm0\cdot05$ per cent. No change in composition was found after 13 minutes.

These findings are in marked contrast with the statements of Othmer(9) and Fowler(10) that 41·5 hours are required to reach equilibrium in a Gillespie still, but are in agreement with the findings of Rieder and Thompson(11) who found that 3 hours were adequate to give equilibrium for the system ethanol-water in such a still. The time required to reach equilibrium in any recirculating still will depend both on the ratio of the distillation rate to the volume of liquid in the vapour trap, and on the relative volatility of the mixture ; and will be small for high values of these ratios. The liquid flow-rate, which is always far greater than the distillation rate, will in no case be a controlling factor.

(vi) *Conclusion*.—The following conclusions were reached with regard to the operation of the still :

(1) The liquid level should be as low as is consistent with adequate pumping. Satisfactory operation was obtained with a total charge ranging from 182 to 193 ml.

(2) The internal heating should be as low as is consistent with even boiling and adequate wetting of the thermometer (2 to 20 watts).

(3) To obtain a high distillation rate the external heating should be as high as possible without causing surging of the liquid (80 to 300 watts).

V. THE SYSTEM CARBON TETRA CHLORIDE-CYCLOHEXANE

(*a*) *Purification of Components*

Commercial carbon tetrachloride was shaken with alcoholic potassium hydroxide, with 98 per cent. sulphuric acid, with an alkaline solution of potassium permanganate ; and the product finally dried over anhydrous calcium chloride, and distilled at 760 mm. Hg through a column of 25 mm. diameter, 1·5 m. long, and filled with 3 mm. single turn glass helices. A head fraction of 60 ml. was removed using a total reflux trap as described by Scatchard, Wood, and Mochel(12), and then a fraction boiling between 76·63 and 76·65 °C. (corr.) was distilled at a reflux ratio of 50 : 1. The boiling point, as determined in the equilibrium still, and the density of the product are compared with published values in Table 1.

*cyclo*Hexane (B.D.H.) was nitrated following the method of Scatchard, Wood, and Mochel(12) to remove aromatic impurities ; was dried over anhydrous magnesium sulphate ; and was fractionated at 760 mm. Hg at a reflux ratio of

100 : 1 in the column previously described. The fraction boiling at 80·70 to 80·71 °C. (corr.) was collected as product and no aromatic impurities were revealed by its ultraviolet absorption spectrum. The boiling point of the product, as determined in the equilibrium still, its freezing point, as found from a cooling curve, and its density are compared with published values in Table 1.

TABLE 1

COMPONENT PROPERTIES

	Carbon Tetrachloride		*cyclo*Hexane		
	Boiling Point (°C.)	d_4^{25}	Boiling Point (°C.)	Freezing Point (°C.)	d_4^{25}
This investigation	76·66	1·58429	80·72	6·54±0·02	0·77390
Scatchard, Wood, and Mochel(1)	76·687	1·58414	80·739	6·49	0·77383
Grimm(13)	76·71	1·58413	—	—	—
Rossini *et al.*(14)	—	—	80·738	6·55	0·77389

(*b*) *Experimental Procedure*

(i) *Analysis.*—Liquid compositions were determined from density measurements at 25·00±0·01 °C. Seven mixtures of the components were prepared by weighing in narrow-necked, stoppered 25 ml. flasks, allowance being made for the loss of first component in the air-vapour mixture displaced by the addition of the second component through a stainless steel cannula(15). The densities of the mixtures were determined in duplicate in single stem 10 ml. pyknometers fitted with glass caps. The meniscus level in the calibrated capillary stem (1·4 mm. diameter) was measured to ±0·02 mm. with a telemicroscope mounted on a cathetometer.

The measured densities were related to the compositions by equations (1) and (2) as suggested by Scatchard(16).

$$1/d = 1/d_0 + \triangle, \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\triangle = A.x_1x_2 + B.x_1x_2(x_1 - x_2), \quad \ldots\ldots\ldots\ldots \quad (2)$$

where $1/d_0$ is the specific volume, assuming the volume per mole to be additive, $\triangle$ is the deviation from this value, and x_1 and x_2 are the mol. fractions of carbon tetrachloride and *cyclo*hexane respectively. Values of $\triangle$ were determined from the densities and calculated compositions of the synthetic mixtures shown in Table 2 and the best values of the constants in equation (2) were found by the method of least squares to be : $A = +0·00479$, $B = -0·00107$.

The last column in Table 2 shows the differences between the densities calculated from equations (1) and (2) and the experimental values, and shows these to agree within the experimental probable error of ±0·00004 found from quadruplicate density measurements of each of the pure components.

TABLE 2

COMPOSITIONS AND DENSITIES AT 25 °C. OF SYNTHETIC MIXTURES OF CCl_4 AND C_6H_{12}

Mol. Fraction CCl_4	d_4^{25} exp.	△	$d_{calc.} - d_{exp.}$
0	0·77390	0	—
0·08969	0·83904	+0·00046	−0·00003
0·25593	0·96339	0·00101	−0·00001
0·39523	1·07117	0·00120	—
0·51572	1·16730	0·00119	+0·00008
0·64799	1·27611	0·00102	—
0·77261	1·38191	0·00074	+0·00007
0·88927	1·48426	0·00039	−0·00001
1	1·58429	0	—

The values of △ calculated by equation (2) and shown in Table 2 were plotted on a large scale *versus* density, and this graph was used to find d_0 for each mixture ; the composition was then calculated from the expression.

$$x_1 = \frac{d_0 V_2 - M_2}{(M_1 - M_2) - (V_1 - V_2) d_0}, \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

where x, M, V are mol. fraction, molecular weight, and molecular volume respectively, and where subscript 1 refers to carbon tetrachloride and subscript 2 to *cyclo*hexane. The experimental error in these compositions was calculated to be ±0·00014 by assuming the error in d_0 to be ±0·00005.

(ii) *Operation*.—The liquid and vapour equilibrium compositions of 12 mixtures were determined at 70 °C., and the vapour pressures of the pure components were measured in the still at 10 °C. intervals between 30 and 80 °C. The still was operated as previously described, with the pressure controlled to maintain a boiling temperature of 70·00±0·01 °C. A liquid throughput of 200–300 ml./min. and a distillation rate of about 16 ml./min. were used, and the still was run for 3 to 4 hours before sampling. The time required to reach equilibrium was estimated to be 1·5 to 2 hours for this system, by taking into consideration the value of α (1·13) and the distillation rate, as compared with those used in the tests described in Section IV (v).

Samples were taken by means of glass syringes fitted with stainless steel cannulae to permit direct injection into the pyknometers. The cannulae were inserted into the traps through rubber serum caps and were provided with small water-jackets through which ice-water was circulated. A sampling and injection rate of 12 ml./min. was sufficiently slow to cool the samples to below 25 °C. After the pyknometers had been placed in the constant temperature bath, the liquid level in the stem was brought close to the zero mark in one operation by withdrawing liquid through a fine capillary.

(c) *Results*

The vapour pressures of the pure components are shown in Table 3 and are consistently about 0·25 mm. higher than those given by Scatchard. This corresponds to the experimental error of ±0·01 °C. in the measurement of temperature.

TABLE 3

VAPOUR PRESSURES OF PURE COMPONENTS

Temperature (°C.)	Pressure (mm. Hg) (Standard)	
	Carbon Tetrachloride	*cyclo*Hexane
80·72	—	760·00
76·66	760·00	—
70·00	617·43	544·23
60·00	444·44	389·60
50·00	312·23	272·02
40·00	213·42	184·75
30·00	—	121·91

TABLE 4

CARBON TETRACHLORIDE–CYCLOHEXANE AT 70 °C.

Mol. Fraction CCl_4		Pressure (mm. Hg)	μ_1^E (cal./mol.)	μ_2^E (cal./mol.)	G_x^E (cal./mol.)	G_x^E exp. $-G_x^E$ calc.
Liquid x_1	Vapour y_1					
0·0538	0·0641	551·10	45·20	0·76	3·15	+0·47
0·1396	0·1622	560·58	38·54	1·37	6·56	+0·15
0·2327	0·2629	570·28	30·78	3·44	9·80	+0·13
0·2641	0·2968	573·20	30·43	3·24	10·42	−0·15
0·3135	0·3476	577·94	26·88	4·83	11·74	−0·06
0·4041	0·4388	585·90	21·49	7·77	13·32	−0·06
0·5153	0·5464	594·31	14·80	12·74	13·81	−0·29
0·5994	0·6259	600·32	10·92	17·98	13·75	+0·03
0·7012	0·7209	606·27	6·84	24·60	12·15	+0·00
0·8009	0·8125	611·19	3·06	35·59	9·54	+0·17
0·8995	0·9045	614·95	1·12	45·51	5·58	+0·19
0·9479	0·9500	616·17	0·17	53·18	2·93	−0·03

The liquid and vapour mol. fractions x_1 and y_1 and the total vapour pressure P of the mixture are shown in Table 4. The excess chemical potentials μ_1^E

and μ_2^E and the excess free energy G_x^E, which are the excess of these functions over their values in an ideal solution, are shown in columns 4, 5, and 6 and were calculated by the following equations :

$$\mu_1^E = RT \ln\gamma_1 = RT \ln \frac{Py_1}{P_1x_1} + C(V_1-\beta_1)(P_1-P), \ \ldots\ldots\ldots \ (4)$$

$$\mu_2^E = RT \ln\gamma_2 = RT \ln \frac{Py_2}{P_2x_2} + C(V_2-\beta_2)(P_2-P), \ \ldots\ldots\ldots \ (5)$$

$$G_x^E = x_1\mu_1^E + x_2\mu_2^E \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (6)$$

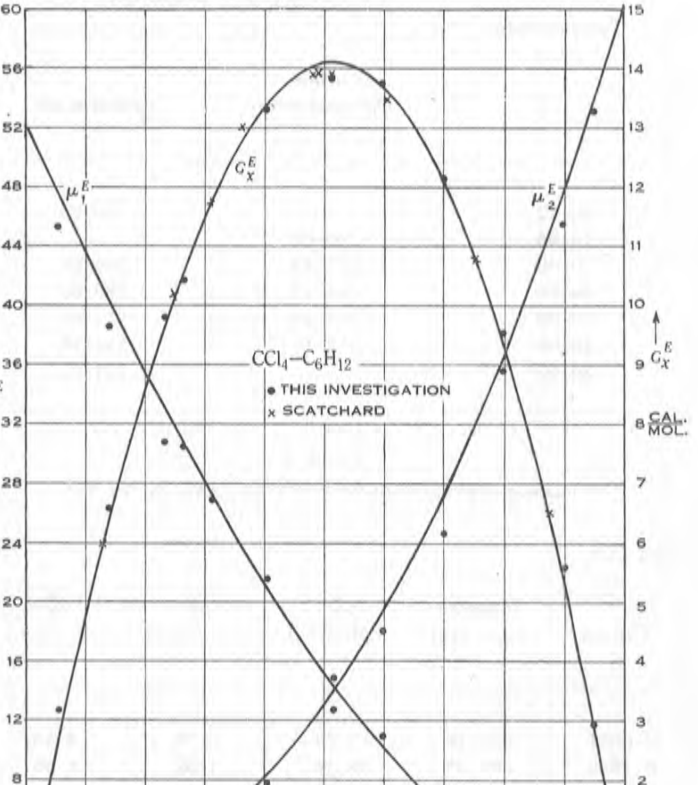

Fig. 2

The last term in equations (4) and (5) is a correction for the non-ideality of the vapour phase.

In these equations P is the total pressure in mm. Hg ; P_1, P_2, V_1, V_2 are the vapour pressures and liquid molar volumes of the pure components at 70 °C. ; γ_1 and γ_2 are the activity coefficients in the mixtures ; and β_1 and β_2 are the second virial coefficients in the equations of state for the pure components. The constant C converts mm. Hg-litres to calories ($C=0\cdot0318657$). The molar volumes of the pure liquids at 70 °C. were determined from published densities.

$V_1=0\cdot10276$ litre(17)

$V_2=0\cdot11519$ litre(18, 19, 20).

The virial coefficients were calculated from critical data by the Berthelot equation and the values, $\beta_1=-1\cdot054$ litres and $\beta_2=-1\cdot154$ litres, are in agreement with the experimental values found by Lambert *et al.*(21).

A three suffix Margules equation in the form given by Wohl(22) was fitted to the calculated values of G_x^E and the following equations obtained for the excess thermodynamic functions :

$$G_x^E=x_1x_2(60\cdot3978\ x_1+52\cdot2509\ x_2), \qquad (7)$$

$$\mu_1^E=x_2^2(52\cdot2509+16\cdot2938\ x_1), \qquad (8)$$

$$\mu_2^E=x_1^2(60\cdot3978-16\cdot2938\ x_2) \qquad (9)$$

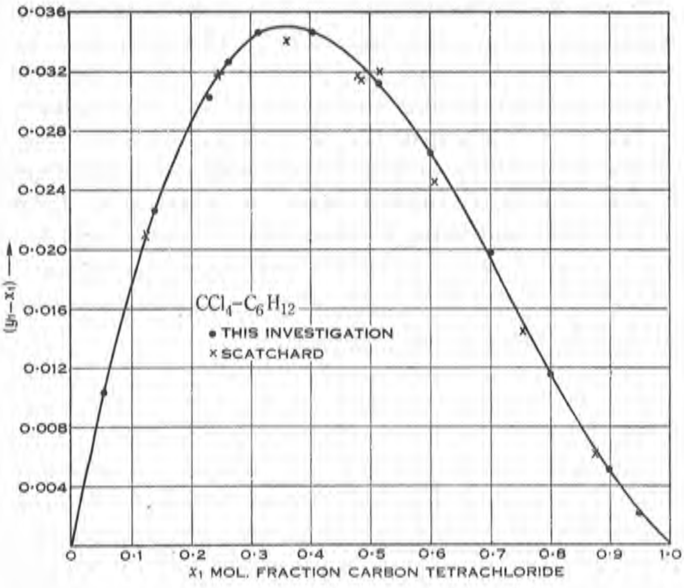

Fig. 3

Column 7 in Table 4 shows the differences between G_x^E calculated from equation (7) and from the experimental values. These are within the experimental error in G_x^E which was estimated to be $\pm1\cdot2$ cal./mol.

A comparison of these data with those obtained by Scatchard, Wood, and Mochel(1) is shown in Figure 2 in which the curves represent values of G_x^E, μ_1^E and μ_2^E calculated from equations (7), (8), and (9), and the points shown are values calculated from experimental data obtained in this investigation and by Scatchard. In Figure 3 these experimental data are plotted as (y_1-x_1) against x_1.

The internal consistency of the data was established by applying the Gibbs Duhem equation in two days. Equation (7) is an integrated form of this equation and was shown to represent the experimental values of G_x^E within the estimated experimental error; the values must thus be consistent among themselves and must represent the thermodynamically defined quantities. The second check was obtained by the method of Redlich and Kister(23). The experimental values of $RT \ln \gamma_1$ and $RT \ln \gamma_2$ were plotted separately against x_1 and the difference of the areas under the two curves was found. This amounted to 4·5 per cent., but it was estimated that experimental errors in $RT \ln \gamma_1$ and $RT \ln \gamma_2$ could cause a difference of about 18 per cent. in these areas.

VI. THE SYSTEM WATER-ACETIC ACID AT 760 MM. Hg

(a) *Purification of Components*

One component was freshly prepared conductivity water.

The other component, acetic acid obtained by hydrolysis of purified acetic anhydride (B.D.H., A.R.), was refluxed with 2 per cent. by weight of solid potassium permanganate as recommended by Bousfield and Lowry(24) and distilled from the residue. It was then fractionated at a reflux ratio of 40 : 1 through a 50 cm. column similar to that used for the carbon tetrachloride purification. The water content of the product was found by the Karl Fischer method to be 0·006 per cent. by weight, and the acid was finally dried by refluxing with 100 per cent. excess of purified acetic anhydride,* as recommended by Orton and Bradfield(25), but using concentrated sulphuric acid as catalyst.

The acid was then carefully fractionated through the 50 cm. column and a middle portion collected in a flask from which it was directly distilled into the equilibrium still and freezing point apparatus.

(b) *The Normal Boiling Point of Pure Acetic Acid*

The wide variation in the reported boiling points of even carefully purified samples of acetic acid (117·8–118·5 °C.) is due to the extreme difficulty of drying it. The only two determinations found, in which the same sample was used to determine both the boiling point and the freezing point, were those of Bousfield and Lowry(24) and Kendall and Brakeley(26). Their results, together with four values obtained in this investigation, are shown in Table 5.

Figure 4 shows a plot of boiling point *versus* freezing point of the samples of Table 5 together with their claimed accuracies. The most reliable values of the freezing point were considered to be those of de Visser(28) (16·5965 °C.) and MacDougall(29) (16·612, 16·616 °C.) and, assuming the latter to be correct, a straight line drawn through all the values shows the normal boiling point to

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* The acetic anhydride used in the final dehydration was obtained from fractionated B.D.H., A.R. anhydride which had been refluxed with carefully purified chromic anhydride, filtered, and refractionated. Since CrO_3 containing traces of water and sulphuric acid reacts with acetic anhydride with explosive violence, the chromic anhydride (B.D.H., A.R.) was recrystallized from water and dried at 110 °C.

TABLE 5

THE FREEZING POINT AND BOILING POINT OF ACETIC ACID

Sample	Boiling Point/760 (°C.)	Freezing Point (°C.)	Wt. % H_2O
1	$117 \cdot 85 \pm 0 \cdot 01$	$16 \cdot 56 \pm 0 \cdot 02$	0·0242*
2	117·90	16·60*	0·00742
3	117·92	16·60*	0·00064
4	117·95	16·60*	0·00753
Bousfield and Lowry ..	$117 \cdot 88 \pm 0 \cdot 05$	$16 \cdot 60 \pm 0 \cdot 005$	—
Kendall and Brakeley ..	$117 \cdot 8 \pm 0 \cdot 1$	$16 \cdot 57 \pm 0 \cdot 05$	—

* These values were determined from the cryoscopic constant for acetic acid 39·0°/g. mole(27) and the value of MacDougall (16·614 °C.) for the freezing point of the pure acid.

be $117 \cdot 95 \pm 0 \cdot 01$ °C. This agrees within $\pm 0 \cdot 01$ °C. with the value obtained in this investigation by extrapolation of a plot of liquid and vapour mol. fractions against boiling temperature.

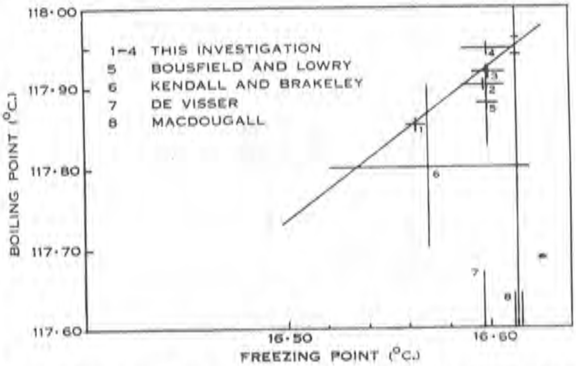

Fig. 4.—Acetic acid : boiling point and freezing point.

(c) *Experimental Procedure*

The still was operated for 3 to 4 hours at distillation rates of up to 13·2 ml./min. and liquid flow-rates of 200 to 300 ml./min. while the pressure was controlled at one standard atmosphere to within $\pm 0 \cdot 2$ mm. Hg.

The hygroscopic nature of concentrated acetic acid made it necessary to exclude contact with the atmosphere during sampling, and two syphons as shown in Figure 5 were used to withdraw samples of the required size by applying suction at *A* with a graduated glass syringe. *B* is a rubber stopper which closed the trap during sampling.

Mixtures containing less than 0·33 mol. fraction of water were sampled into dry, 100 ml. conical flasks which had been weighed and cooled. The flasks were stoppered and re-weighed after attaining room temperature, and the water in the samples estimated by the Karl Fischer method using an electrometric end point. The water equivalents of the Karl Fischer reagent and the aqueous methanol used for back titration were determined at the beginning, the middle, and the end of each series of titrations by means of water weighed out of a small weight pipette. Two empty flasks were titrated with each set of samples and allowance was made for these blank titres.

Samples containing a higher concentration of water were withdrawn into calibrated 100 ml. volumetric flasks, which had been half filled with cold distilled water and weighed. The weight of the samples was found by re-weighing the flasks ; and triplicate aliquots were titrated with decinormal barium hydroxide to a phenolphthalein end point. One sample was analysed by both this and the Karl Fischer method and the results were in agreement.

The analytical errors were estimated as follows :

(i) *Karl Fischer Method.*—Mixtures having mol. fractions of water between 0·33 and 0·1 were sampled and analysed in duplicate and the mean error was found to be ±0·16 per cent. which corresponds to ±0·0003 in mol. fraction. Only single samples of adequate size could be taken of mixtures containing less than 0·1 mol. fraction of water, and the analytical errors were estimated to be ±1 per cent. (±0·0001 in mol. fraction) in the range from 0·1 to 0·003 mol. fraction. At mol. fractions below 0·0004, even the largest sample that could be taken gave a titre which was comparable in size with the titre of the blank flasks, and the errors in this range were estimated to be ±40 per cent. which corresponds to ±0·0001 in mol. fraction.

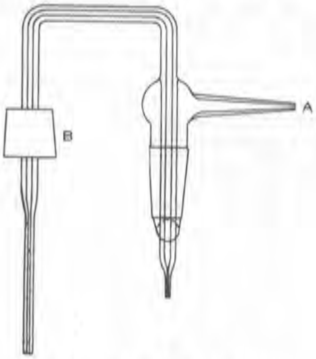

Fig. 5.—Sampling syphon.

(ii) *Barium Hydroxide Method.*—The errors were determined from analyses of duplicate samples, each titrated in triplicate, and were found to range from ±0·15 per cent. at a mol. fraction of water of 0·5 to ±0·06 per cent. at a mol. fraction of 0·99.

(*d*) *Results*

The results of 19 determinations of the liquid-vapour equilibrium compositions and temperatures for this system are shown in Table 6, together with the excess chemical potentials (μ^E) calculated from the experimental data by equations (**4**) and (**5**). The additional data used in these calculations were :

Water.—The molar volumes were calculated from published density values(30); the vapour pressures P_1 and virial coefficients β_1 were obtained from the equation of state of Keyes, Smith, and Gerry(31).

TABLE 6

WATER-ACETIC ACID AT 760 MM. Hg

Mol. Fraction of Water		Temperature (°C.)	Cal./Mol. (uncorr.)		Cal./Mol. (corr.)	
Liquid x_1	Vapour y_1		μ_1^E	μ_2^E	μ_1^E	μ_2^E
0·000210	0·000226	117·96	—414·8	—7·9	—406·6	—7·9
0·000213	0·000347	117·92	—91·9	+0·1	—83·8	+0·0
0·000247	0·000450	117·91	+4·8	+0·5	+3·4	+0·3
0·00340	0·00689	117·64	+85·0	+4·2	+93·0	+1·5
0·00545	0·01122	117·51	100·0	+4·2	108·1	+0·8
0·04741	0·09790	115·03	164·6	+27·4	170·5	+1·1
0·08120	0·1446	113·81	80·1	43·3	86·4	+6·1
0·1497	0·2382	111·51	51·8	69·8	57·0	+12·2
0·2198	0·3273	109·84	44·0	80·7	48·4	+14·4
0·2917	0·4071	108·16	37·3	99·0	40·9	+12·5
0·3378	0·4573	107·36	34·3	101·9	37·6	+8·1
0·4198	0·5496	105·85	48·5	98·4	51·1	—8·1
0·5359	0·6591	104·17	44·9	98·2	46·7	—22·3
0·6463	0·7524	102·86	37·8	94·1	39·1	—37·4
0·7388	0·8217	101·92	28·2	98·5	29·0	—40·8
0·8251	0·8783	101·24	14·1	129·7	14·6	—21·4
0·9210	0·9429	100·54	3·0	175·4	3·2	+21·0
0·9676	0·9761	100·24	0·1	200·0	0·2	+45·7
0·9891	0·9921	100·07	0·3	188·4	0·4	+33·6

Acetic Acid.—The molar volumes were calculated from density values of Young(32). Vapour pressures, measured in the equilibrium still over the range 100 to 118 °C., were used to determine the constants in the following equation:

$$\log P_2 \text{ (mm. Hg)} = 8\cdot11401 - 2046\cdot74 \,.\, \frac{1}{T} \text{ (°K.)}.$$

Values calculated from this equation agree with the values given by Stull(33).

The virial coefficients of acetic acid β_2 were calculated from those of water by the principle of corresponding states. The value of β_2 at the normal boiling point of acetic acid was determined from the vapour density of 0·00316 g./ml.(34). The ratio of β_2 to the virial coefficient of water at the same reduced temperature was found to be 42·798 and was assumed to remain constant from 100 to 118 °C. Values of β_2 calculated on this assumption ranged from —14·54 l./mol. at 100 °C. to —12·24 l./mol. at 118 °C., and are of the same magnitude as values obtained by extrapolating the experimental vapour density data of Ritter and Simons(35) (—13·87 to —12·88 l./mol.).

In Figure 6, values of the excess chemical potentials with and without the corrections for the non-ideality of the vapours are plotted against concentration. The calculated values of μ_2^E are somewhat indefinite due to the magnitude and the uncertainty of the virial coefficient of acetic acid. The Gibbs Duhem equation could not be used to test the consistency of the data due to this uncertainty and because the measurements were not made at constant temperature. The error in μ_1^E at $x_1=0\cdot003$ is ±15 cal./mol. or 15 per cent., but falls to $\pm2\cdot5$ cal./mol. (1·5 per cent.) at $x_1=0\cdot05$ and the maximum in the μ_1^E curve at this concentration is therefore based on experimentally significant values. At water concentrations below 0·003 mol. fraction the experimental error is large and the values of μ_1^E uncertain; however, the negative values obtained at the two lowest water concentrations may be significant as they lie on a smooth curve drawn through them and the three succeeding positive values. These negative values of μ_1^E also become plausible if one considers the very strong interaction between water and acetic acid molecules (cf. the very hygroscopic nature of concentrated acetic acid) while the maximum in the curve could indicate that superimposed on this interaction, which leads to a decrease in the free energy of the water molecules, there is the effect of the dissociation of the molecular complexes of the water, giving an increased free energy.

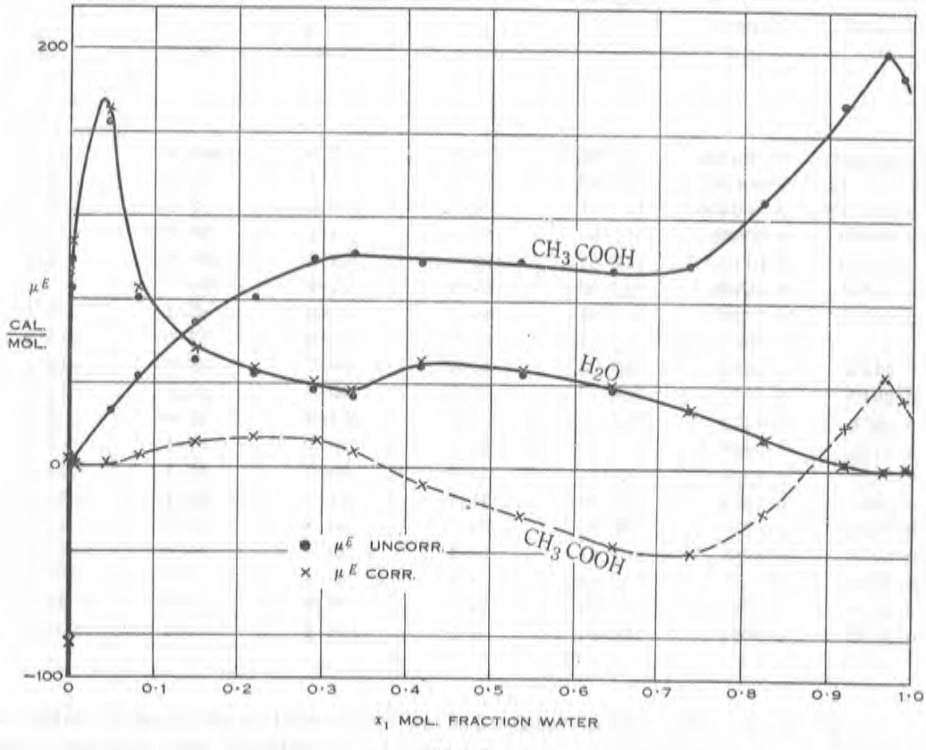

Fig. 6

(e) *Comparison of Results with Other Measurements*

Figure 7 shows a plot of $(y_1 - x_1)$ *versus* x_1 in which the curve represents the results obtained in this investigation. The results of Cornell and Montonna(36) and of York and Holmes(37) lie close to the curve while those of Povarnin and Markov(38), Othmer and Gilmont(39), and Pascal, Dupuy, and Garnier(40) show considerably higher values. The results of other workers, which have been included in a similar comparison by Othmer and Gilmont(39) have been omitted to simplify the figure. The high values of $(y_1 - x_1)$ obtained by some workers may be due to partial condensation giving enrichment of the vapour, while low values may be due to entrainment. It has already been shown that no entrainment occurs in the apparatus described here, even at distillation rates considerably higher than those used in the actual determinations ; while the design of the disengagement chamber eliminates the possibility of enrichment.

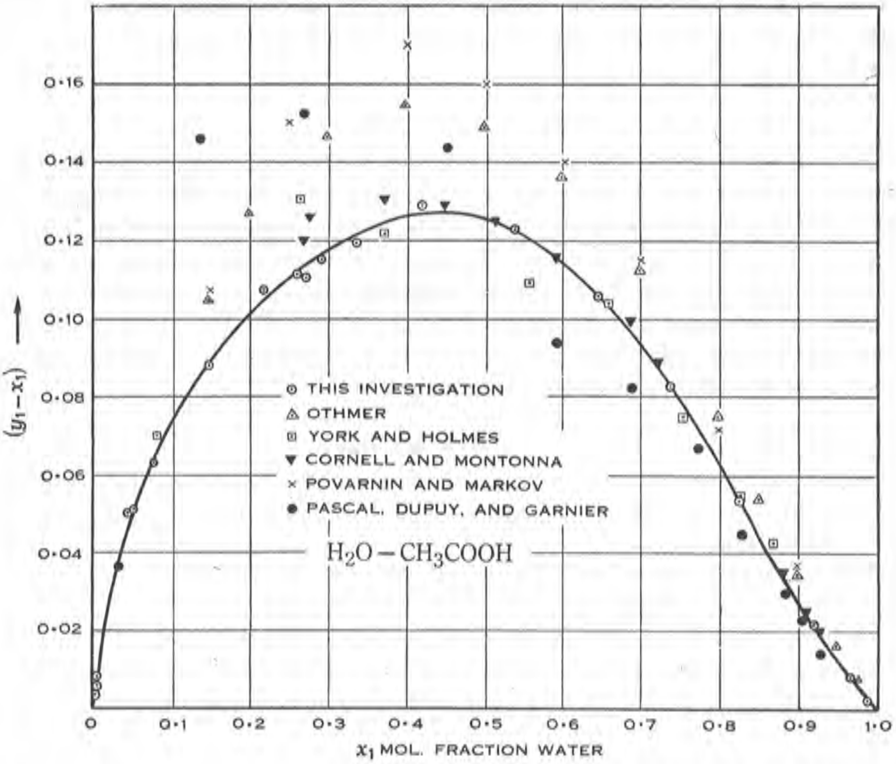

Fig. 7

VII. Conclusions

The liquid-vapour equilibrium still described in this paper has been shown to be free of the faults found in a number of other stills ; it was found to operate satisfactorily over a wide range of conditions, and to be suitable for the determination of precise equilibrium data both at constant pressure and at constant temperature. It has been shown that equilibrium is established in the still after approximately 2 hours of operation and that the contents of the liquid and vapour traps then have concentrations corresponding to a true liquid-vapour equilibrium.

The normal boiling point of acetic acid has been redetermined and an interpretation has been given for the variation with composition of the excess chemical potential of water in acetic acid solution.

The equilibrium still is now being used to investigate a series of binary mixtures of *n*-heptane with other non-polar components. The results obtained will be used to determine the relation between the thermodynamic properties of these mixtures and the physical properties of their components, and will be reported in a subsequent paper.

VIII. Acknowledgments

The authors thank the members of the instrument workshops, Division of Industrial Chemistry, C.S.I.R.O., for their assistance in the construction of apparatus and, in particular, Mr. K. A. Ophel for the construction of the resistance thermometer. They wish to thank Mr. D. T. C. Gillespie for valuable suggestions, and also members of the Chemical Physics Section of the abovementioned Division for spectroscopic measurements, and the staff of the Defence Research Laboratories, and the National Standards Laboratory, C.S.I.R.O., for their advice and for the calibration of instruments.

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Reprinted from the
AUSTRALIAN JOURNAL OF SCIENTIFIC RESEARCH
SERIES A — PHYSICAL SCIENCES
VOLUME 4, NUMBER 2, PAGES 198-212, 1951

LIQUID–VAPOUR EQUILIBRIA

II. THE SYSTEM BENZENE–*n*-HEPTANE

By I. BROWN and A. H. EWALD

Reprinted for
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Reprinted from the Australian Journal of Scientific Research, Series A, Physical Sciences, Volume 4, Number 2, pp. 198–212, 1951

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II. THE SYSTEM BENZENE–*n*-HEPTANE

By I. Brown* and A. H. Ewald*

[*Manuscript received January 25, 1951*]

Summary

Liquid-vapour equilibrium data for the system benzene–*n*-heptane have been measured at intervals over the whole composition range at 60 and 80 °C. and for equimolar mixtures at 50, 70, and 85 °C. The changes in the thermodynamic functions on mixing, both at constant pressure and at constant volume, have been calculated. The values of these changes on mixing at constant volume have been compared with values predicted from component properties. The conditions for azeotrope formation in this system have been defined.

I. Introduction

The liquid-vapour equilibrium concentrations for the system benzene–*n*-heptane were measured as part of an investigation of methods for predicting such data from the properties of the components of binary mixtures. This system was chosen as typical of non-polar systems having a large difference between the internal pressures of the components. The thermodynamic functions for mixing at constant pressure were calculated from the equilibrium data. In order to correct these functions to constant volume mixing conditions it was necessary to determine the coefficient of expansion of the mixture.

II. Experimental

(*a*) *Purification of Materials*

(i) *Benzene*.—Analytical reagent quality benzene was shaken with two portions of concentrated sulphuric acid, washed with sodium carbonate solution and with water, and dried over anhydrous calcium chloride. It was then fractionally crystallized four times and the product was fractionally distilled at a reflux ratio of 70 to 1 through a 1·2 m. column packed with 1·6 mm. Dixon packing ; head and tail fractions were rejected. The physical properties of the purified benzene are shown in Table 1.

(ii) n-*Heptane*.—*n*-Heptane (C.F.R. knock-rating quality) was fractionally distilled in the same column at total reflux. After the removal of three 60 ml. head fractions the column head temperature remained constant within ±0·01 °C. The distillate was then allowed to accumulate in a 500 ml. head trap and was removed after 24 hours operation at total reflux ; three batches of distillate were removed in this way. The physical properties of the bulked product are shown in Table 1.

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(*b*) *Vapour Pressures of the Components*

The vapour pressures of the purified components were measured at 10 degree intervals from 40 to 90 °C. in the apparatus previously described (Brown and Ewald 1950) and the boiling points were measured at 760 mm. Hg (Std.). The Antoine equation*

$$\log P = A - B/(C + t), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

was fitted to the vapour pressure data by the method of Willingham and Rossini (1945) and the constants were found to be :

	Benzene	*n*-Heptane
A	6·91279	6·88686
B	1214·57	1258·27
C	221·166	215·701

Vapour pressure values calculated from equation (1) were found to be 0·08 per cent. higher for benzene and 0·06 per cent. higher for *n*-heptane than those calculated in the same manner by Rossini *et al.* (1947).

TABLE 1

PHYSICAL PROPERTIES OF COMPONENTS

Physical Property	Benzene		*n*-Heptane	
	This Work	Rossini (1947)	This Work	Rossini
B.p./760 (°C.) ..	80·07±0·01	80·099	98·40	98·427
F.p. (°C.) ..	+5·48±0·02	+5·533	—	—
d_4^{25}	0·87359	0·87370	0·67956	0·67951
N_D^{25}	1·4979	1·49792	1·3851	1·38511

(*c*) *Analytical Method*

The compositions of liquid and vapour samples were determined from density measurements as described previously for the system carbon tetrachloride-*cyclo*hexane (Brown and Ewald 1950). Thirteen mixtures of benzene–*n*-heptane of known composition were used to determine the constants in equation (2) which expresses the change in specific volume on mixing as a function of composition.

$$\Delta = x_1x_2[0\cdot027243 + 0\cdot005472(x_1 - x_2) + 0\cdot004976(x_1 - x_2)^2 + 0\cdot007620(x_1 - x_2)^3]. \quad \ldots\ldots\ldots\ldots \quad (2)$$

In Table 2 are shown the mole fractions of benzene, the refractive indices and densities of the synthetic mixtures used for the density-composition calibration, as well as experimental values of Δ and the difference between the latter

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* A table of nomenclature is included at the end of this paper.

and values calculated from equation (2). The last column shows the per cent. change in molar volume on mixing at 25 °C.

TABLE 2

BENZENE-*n*-HEPTANE PROPERTIES OF MIXTURES OF KNOWN COMPOSITION

x_1	N_D^{25}	d_4^{25}	$\Delta_{\text{exp.}}$	$(\Delta_{\text{exp.}}-\Delta_{\text{calc.}})\times 10^4$	$\dfrac{100\ V_{25}^M}{\overset{\circ}{V}_{25}}$
0·94305	1·4863	0·85459	0·00239	+1·8	0·205
0·89286	1·4771	0·83920	0·00371	+0·5	0·313
0·87747	1·4746	0·83479	0·00396	—0·7	0·332
0·82371	1·4656	0·81984	0·00502	—0·6	0·413
0·77316	1·4579	0·80677	0·00578	—0·0	0·468
0·77128	1·4578	0·80634	0·00574	—0·7	0·465
0·65798	1·4420	0·78010	0·00671	+0·2	0·526
0·55918	1·4306	0·76002	0·00695	+0·6	0·531
0·43647	1·4179	0·73803	0·00654	—0·0	0·485
0·32594	1·4080	0·72078	0·00556	+0·5	0·403
0·21794	1·3995	0·70564	0·00402	—1·4	0·284
0·16094	1·3951	0·69827	0·00315	—0·2	0·220
0·08211	1·3901	0·68872	0·00176	+1·3	0·122

(*d*) *Equilibrium Measurements*

The apparatus and technique used for the liquid-vapour equilibrium measurements were identical with those used for the system carbon tetrachloride-*cyclo*hexane (Brown and Ewald 1950). Fourteen determinations were made at intervals over the whole composition range at 60 °C. and fifteen at 80 °C. Single determinations were also made at 50, 70, and 85 °C. for approximately equimolar mixtures. The equilibrium still was operated at a vapour throughout equivalent to approximately 15 ml. of condensate per minute and a period of at least three hours was allowed in each determination for the system to approach equilibrium.

(*e*) *The Volume Change on Mixing as a Function of Temperature*

Calculation of the excess thermodynamic functions for mixing at constant volume requires a knowledge of the volume change on mixing, V_t^M.

Values of V_t^M were computed at the required temperatures from measured values of the volume change on mixing at 25 °C., V_{25}^M, using equation (3).

$$V_t^M=K_t\,.\,V_{25}^M=K_t(x_1M_1+x_2M_2)\Delta.\ \ldots\ldots\ldots\ldots\ (3)$$

This involves the assumption that the ratio $V_t^M/V_{25}^M=K_t$ is a constant for all compositions (cf. Wood and Brusie 1943).

Values of K_t were computed at the various temperature levels from equation (4).

$$K_t=\frac{[x_1V_{1(25)}+x_2V_{2(25)}+\Delta(x_1M_1+x_2M_2)]\,[1+\varkappa(t-25)]-[x_1V_{1(t)}+x_2V_{2(t)}]}{(x_1M_1+x_2M_2)\Delta}.\ \ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

These were found to be as follows :

t (°C.)	25	50	60	70	80
K_t	1·0	0·756	0·720	0·830	0·931

Values of the molar volumes of the components, $V_{1(t)}$ and $V_{2(t)}$ were calculated from the density data given in I.C.T. (1928, p. 28) and by Egloff (1939) respectively and values of Δ were obtained from equation (**2**). The average coefficients of expansion, $\varkappa$, of a 49·7 mole per cent. benzene mixture were measured over the required temperature range in a Pyrex dilatometer with a bulb of 7 ml. capacity and a 30 cm. capillary stem of 1·88 mm. diameter. The dilatometer was calibrated with pure benzene over the range of 25 to 75 °C. During the calibration and determination it was immersed in a kerosene bath controlled to ±0·01 °C. and the meniscus height above a datum mark was measured with a cathetometer to ±0·05 mm. Values of the coefficients of expansion of this mixture over ranges from 25 to t °C. are shown in Table 3.

TABLE 3

AVERAGE COEFFICIENTS OF EXPANSION OF MIXTURE

Temp. (°C.)	$\varkappa$
44·94	0·001281
49·87	0·001285
59·78	0·001307
70·03	0·001341
75·00	0·001364
79·96	0·001385

III. RESULTS

(*a*) *Equilibrium Data*

Tables 4 and 5 show the experimental values of the equilibrium concentrations and total vapour pressures at temperatures of 60 and 80 °C. together with the relative volatilities calculated by equation (**5**).

$$\alpha=y_1x_2/y_2x_1. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{5})$$

The excess chemical potentials and excess free energy of mixing at constant pressure, which are also shown in these tables, are defined by Scatchard, Raymond, and Gilmann (1938) and represent the variations in the values of the chemical potentials and free energy of mixing from those of an ideal solution of the same composition. They were calculated by the use of the following equations :

$$\mu_1^E=RT\ln\gamma_1=RT\ln\frac{Py_1}{P_1x_1}+f(V_1-\beta_1)(P_1-P), \quad \ldots\ldots\ldots \quad (\mathbf{6})$$

$$\mu_2^E=RT\ln\gamma_2=RT\ln\frac{Py_2}{P_2x_2}+f(V_2-\beta_2)(P_2-P), \quad \ldots\ldots\ldots\ldots \quad (\mathbf{7})$$

$$G_{xp}^E=x_1\mu_1^E+x_2\mu_2^E. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{8})$$

The vapour pressure values required were calculated from equation (**1**). The second virial coefficients for benzene are those computed by Tompa (1948),

TABLE 4

BENZENE-n-HEPTANE. EQUILIBRIUM DATA AND DERIVED FUNCTIONS AT 60 °C.

x_1	y_1	P (mm. Hg)	μ_1^E (cal./mol.)	μ_2^E (cal./mol.)	G_{xp}^E (cal./mol.)	G_{xp}^E (difference)	y_1 (difference)	α
0·01789	0·04218	216·43	181·6	1·9	5·1	+0·5	—0·0063	2·417
0·04544	0·09996	224·86	160·9	4·4	11·5	+0·1	—0·0088	2·333
0·09274	0·19302	239·66	165·6	7·1	21·8	—0·2	—0·0105	2·340
0·18792	0·34165	266·92	146·4	15·4	40·0	—0·1	—0·0066	2·243
0·29336	0·47169	294·35	128·8	24·9	55·4	—0·1	—0·0071	2·150
0·38715	0·56254	315·58	107·1	39·1	65·4	+0·3	—0·0056	2·035
0·48775	0·64567	335·65	85·4	57·4	71·3	+0·2	—0·0030	1·914
0·57844	0·70782	350·83	62·1	87·6	72·8	+0·6	—0·0044	1·766
0·58017	0·70915	351·01	61·7	87·6	72·6	+0·4	—0·0043	1·765
0·68364	0·77608	365·93	39·7	125·8	67·0	—0·6	—0·0031	1·604
0·79118	0·84285	378·15	19·0	188·5	54·4	—0·5	—0·0025	1·410
0·89576	0·91354	387·64	6·0	270·3	33·5	+0·4	—0·0003	1·228
0·94253	0·94947	390·29	2·4	313·3	20·3	+0·5	+0·0003	1·147
0·97900	0·98021	391·51	0·4	361·2	7·9	+0·2	—0·0000	1·073

TABLE 5

BENZENE-n-HEPTANE. EQUILIBRIUM DATA AND DERIVED FUNCTIONS AT 80 °C.

x_1	y_1	P (mm. Hg)	μ_1^E (cal./mol.)	μ_2^E (cal./mol.)	G_{xp}^E (cal./mol.)	G_{xp}^E (difference)	y_1 (difference)	α
0·02113	0·04288	440·14	125·7	2·9	5·5	+0·4	—0·0054	2·076
0·04373	0·08641	452·34	125·8	5·1	10·4	+0·2	—0·0094	2·068
0·04580	0·09008	453·06	123·6	4·9	10·4	—0·3	—0·0096	2·060
0·09287	0·17231	478·77	120·5	11·3	21·5	+0·9	—0·0156	2·033
0·18947	0·32242	527·72	126·5	15·6	36·6	—0·7	—0·0117	2·035
0·28835	0·43994	572·65	105·7	28·2	50·5	+0·1	—0·0118	1·938
0·39089	0·54459	614·60	90·1	39·6	59·3	—0·5	—0·0074	1·863
0·49515	0·63154	651·90	68·2	62·0	65·1	+0·2	—0·0073	1·748
0·58192	0·69303	678·53	47·3	92·9	66·4	+0·9	—0·0104	1·622
0·61584	0·71970	688·11	43·5	97·9	64·4	—0·3	—0·0070	1·602
0·68479	0·76680	706·53	31·4	125·1	61·0	—0·1	—0·0061	1·513
0·79214	0·83614	730·14	12·2	191·5	49·5	+0·0	—0·0071	1·339
0·88321	0·90384	746·65	5·6	236·8	32·6	—0·1	—0·0013	1·243
0·94237	0·94939	754·04	1·3	288·6	17·9	—0·1	—0·0006	1·147
0·97934	0·98097	757·20	0·1	324·9	6·8	—0·1	—0·0002	1·091

while those for *n*-heptane were calculated from the Berthelot equation using the critical constants $T_c = 540$ °K. and $P_c = 26{\cdot}8$ atm. The liquid molar volumes of benzene and *n*-heptane were computed at the required temperatures as in Section II (*e*). Both the second virial coefficients and molar volumes used are shown in Table 6.

Table 6

SECOND VIRIAL COEFFICIENTS AND MOLAR VOLUMES (LITRES)

t (°C.)	Benzene		*n*-Heptane	
	β_1	V_1	β_2	V_2
50	—1·150	0·092	—1·831	0·152
60	—1·090	0·094	—1·716	0·154
70	—1·010	0·095	—1·610	0·157
80	—0·980	0·096	—1·514	0·159
85	—0·928	0·097	—1·469	0·159

It was found that the values of G^E_{xp} shown in Tables 4 and 5 could be expressed as a function of composition by equation (**9**)

$$G^E_{xp} = x_1x_2[a + b(x_1 - x_2) + c(x_1 - x_2)^2], \quad \ldots\ldots\ldots\ldots\ldots \quad (\mathbf{9})$$

where a, b, and c have the following values:

$$a = 718{\cdot}231 - 1{\cdot}297\ T,$$
$$b = 228{\cdot}223 - 0{\cdot}5084\ T,$$
$$c = \ 40{\cdot}667 - 0{\cdot}01713\ T.$$

These were obtained by using the method of least squares to find the best values of the coefficients at 60 and 80 °C. and by assuming these to vary linearly with temperature.

The corresponding equations for the excess chemical potentials are

$$\mu^E_1 = x^2_2[a - b + x_1(4b - c) + 6c(x^2_1 + \tfrac{1}{6}x_2 - x_1x_2)], \quad \ldots\ldots\ldots\ldots \quad (\mathbf{10a})$$

$$\mu^E_2 = x^2_1[a + b + x_2(-4b - c) + 6c(x^2_2 + \tfrac{1}{6}x_1 - x_1x_2)]. \quad \ldots\ldots\ldots\ldots \quad (\mathbf{10b})$$

In the seventh column of Tables 4 and 5 is shown the difference between values of G^E_{xp} calculated from equations (**6**), (**7**), and (**8**) and those calculated using equation (**9**). In the eighth column is shown the difference between the experimental values of the vapour concentration and those calculated using equation (**10**) together with values of P_1 and P_2 from equation (**1**), of β and V from Table 6, and experimental values of x_1 and P.

Table 7 shows additional equilibrium measurements for approximately equimolar mixtures at 50, 70, and 85 °C. The differences shown in the last column indicate that equation (**9**) is suitable for temperature interpolation; the differences at 50 and 85 °C. which involve a temperature extrapolation are larger than the standard deviations of G^E_{xp} (0·42 and 0·51 cal./g. mol. at 60 and 80 °C. respectively) but are still well within the estimated errors in G^E_{xp} (see Section III (*e*)).

TABLE 7

BENZENE-*n*-HEPTANE. EQUILIBRIUM DATA AND DERIVED FUNCTIONS AT OTHER TEMPERATURES

Temp. (°C.)	x_1	y_1	P (mm. Hg)	μ^E_1 (cal./mol.)	μ^E_2 (cal./mol.)	G^E_{xp} (cal./mol.)	G^E_{xp} (difference)
85	0·49246	0·62093	757·35	60·1	69·0	64·7	+1·4
80	0·49515	0·63154	651·90	68·2	62·0	65·1	+0·2
70	0·49080	0·63644	472·57	74·9	61·9	68·2	+0·2
60	0·48775	0·64567	335·65	85·4	57·9	71·3	+0·2
50	0·48616	0·65259	232·35	90·7	60·8	75·3	+1·0

(*b*) *The Excess Entropy of Mixing and Heat of Mixing at Constant Pressure*

The excess entropy of mixing may be obtained by differentiation of equation (**9**) with respect to temperature. Since $G^E_{xp}=H^M_{xp}-TS^E_{xp}$, we find that the temperature independent part of the coefficients of equation (**9**) represents H^M_{xp} and the temperature dependent part represents $-TS^E_{xp}$. We therefore have the equations

$$S^E_{xp}=x_1x_2[1\cdot297+0\cdot5084(x_1-x_2)+0\cdot01713(x_1-x_2)^2], \quad \ldots\ldots \quad (\mathbf{11})$$

and

$$H^M_{xp}=x_1x_2[718\cdot231+228\cdot223(x_1-x_2)+40\cdot667(x_1-x_2)^2]. \quad \ldots\ldots \quad (\mathbf{12})$$

Values of S^E_{xp} and H^M_{xp} calculated from these equations at even mole fractions are shown in Table 8.

(*c*) *Azeotrope Formation*

To determine the conditions for azeotrope formation for this system the values of the relative volatilities for temperatures of 60 and 80 °C. shown in Tables 4 and 5 were plotted against x_1 and the curves produced to $x_1=1$. Since the curves did not intersect the line $\alpha=1$ no azeotrope is formed even at 60 °C. The change of relative volatility with temperature was found by combining equations (**5**), (**6**), and (**7**) to give

$$RT\ln\alpha=RT\ln(P_1/P_2)+\mu^E_1-\mu^E_2-f[(V_1-\beta_1)(P_1-P)-(V_2-\beta_2)(P_2-P)]. \quad \ldots\ldots\ldots\ldots \quad (\mathbf{13})$$

As x_1 approaches unity, equation (**13**) reduces to

$$RT\ln\alpha=RT\ln(P_1/P_2)-\mu^E_2+f(V_2-\beta_2)(P_2-P_1). \quad \ldots\ldots \quad (\mathbf{14})$$

TABLE 8

BENZENE-*n*-HEPTANE. THERMODYNAMIC FUNCTIONS AT CONSTANT PRESSURE AND CONSTANT VOLUME
(cal./mol. and cal./deg. mol.)

x_1	G^E_{xp} (70 °C.)	S^E_{xp} (70 °C.)	H^M_{xp} (70 °C.)	G^E_{xv} (80 °C.)	G^E_{xv} (60 °C.)	S^E_{xv} (70 °C.)	H^M_{xv} (70 °C.)	$\mathbf{E}^M_{xv}$ (70 °C.)*	$\mathbf{S}^E_{xv}$ (70 °C.)*	$\mathbf{E}^M_{xv}-T\mathbf{S}^E_{xv}$*
0·02	4·97	0·016	10·52	8·62	8·54	—0·004	7·18	4·74	0·001	4·56
0·05	12·01	0·041	25·92	21·32	21·24	—0·004	19·80	11·61	0·010	8·15
0·1	22·71	0·081	50·55	41·63	41·46	—0·008	38·66	22·47	0·020	15·71
0·2	40·54	0·160	95·35	77·54	77·33	—0·011	73·79	41·66	0·036	29·27
0·3	54·00	0·230	133·02	105·63	105·63	—0·000	105·86	57·12	0·049	40·30
0·4	63·29	0·287	161·81	125·11	125·52	+0·021	132·35	68·34	0·058	48·54
0·5	68·27	0·324	179·56	135·83	136·71	+0·044	151·40	74·69	0·062	53·34
0·6	68·45	0·336	183·72	137·49	138·74	+0·062	159·49	75·40	0·061	54·36
0·7	63·07	0·316	171·37	128·95	130·31	+0·068	152·93	69·58	0·056	50·43
0·8	50·85	0·257	139·17	107·45	108·60	+0·058	127·89	56·07	0·044	41·00
0·9	30·45	0·154	83·42	67·57	68·23	+0·033	79·23	33·46	0·026	24·51
0·95	16·61	0·084	45·44	37·95	38·30	+0·017	44·06	18·22	0·014	13·52
0·98	7·00	0·035	19·11	16·30	16·44	+0·007	18·78	7·66	0·006	5·64

* Symbols in bold type refer to values predicted from component properties.

This and equation (**10b**) were used to calculate the following limiting values of α as x_1 approaches unity.

t (°C.) ..	80	60	50	40	30
α ..	1·059	1·033	1·018	1·003	0·988.

Graphical interpolation of these values shows that $\alpha=1$ at 38 °C., so that an azeotrope should form at high benzene concentrations below this temperature. The argument assumes the validity of equation (**10**) down to 38 °C.

No definite experimental evidence for azeotrope formation with this system has been published. Marschner and Cropper (1946) report an azeotrope which contains 99·5 mole per cent. benzene and boils at 80·1 °C. at 760 mm. Hg, but state that there is doubt as to its existence. Stage and Schultze (1944) found no azeotrope at 760 mm. Hg. Sieg (1950), who measured constant pressure equilibria from 760 to 300 mm. Hg (approximately 80 to 53 °C.) found no evidence of azeotrope formation.

(*d*) *Values of the Excess Thermodynamic Functions for Mixing at Constant Volume*

The thermodynamic functions calculated here from experimental data refer to mixing at constant pressure, while those predicted from the properties of the component liquids refer to constant volume conditions. In order to compare the two sets of functions it was therefore necessary to convert the former to constant volume conditions by use of the following relations of which equation (**15**) was given by Scatchard (1949).

$$G^E_{xv}=G^E_{xp}+\frac{V^M_t}{\omega}, \quad \ldots\ldots \quad (\mathbf{15})$$

$$S^E_{xv}=-[G^E_{xv}\,(80\ ^\circ\mathrm{C.})-G^E_{xv}\,(60\ ^\circ\mathrm{C.})]/20, \quad \ldots\ldots \quad (\mathbf{16})$$

$$H^M_{xv}=G^E_{xv}+TS^E_{xv}. \quad \ldots\ldots \quad (\mathbf{17})$$

Values of these excess functions for mixing at constant volume calculated using these equations are shown in Table 8. Values of V^M_t were computed from equation (**3**) and values of the isothermal compressibility of the mixture, ω, obtained from the compressibilities of the pure components assuming linear variation with mole fraction. The effect on G^E_{xv} and S^E_{xv} of using mole fractions rather than volume fractions is not significant. The compressibility data for benzene were obtained from I.C.T. (1928, p. 38) and those for *n*-heptane by graphical interpolation between the value at 99·5 °C. of Amagat given in I.C.T. (1928, p. 37) and values at 20, 30, 40, and 50 °C. calculated from the adiabatic compressibilities of Freyer, Hubbard, and Andrews (1929). The values used were as follows:

t (°C.)	ω Benzene (atm.$^{-1}$)	ω *n*-Heptane (atm.$^{-1}$)
80	156×10^{-6}	231×10^{-6}
60	128×10^{-6}	197×10^{-6}

(e) *Errors in the Derived Thermodynamic Functions*

Before the significance of the values of these functions could be determined it was necessary to evaluate the errors in them due to errors in the measured quantities from which they were calculated. For temperature, pressure, and composition the errors were ±0·01 °C., ±0·05 mm. Hg, and ±0·00025 mole fraction respectively, while in the derived functions for an equimolar mixture at an average temperature of 70 °C. they were :

Function	Absolute Error (±)
μ^E	2·0 cal./mol.
G^E_{xp}	2·0 cal./mol.
G^E_{vx}	3·9 cal./mol.
S^E_{xp}	0·20 cal./deg. mol.
S^E_{xv}	0·23 cal./deg. mol.

Values of μ^E_1 from equation (**6**) were less than, and those of μ^E_2 from equation (**7**) were greater than the corresponding values calculated from equation (**10**). Thus the experimental values show some thermodynamic inconsistency, which is probably due to low values of the vapour concentration (see Tables 4 and 5). This is more noticeable at low mole fractions of benzene where the relative volatility is higher than in benzene-rich solutions. It is probably due to evaporation of small amounts of benzene-rich mixture from the vapour trap during the sampling period.

(f) *Comparison of Thermodynamic Functions Calculated from Experimental Data with those Predicted from the Properties of the Component Liquids*

To make this comparison the following relation was employed :

$$G^E_{xp}=E^M_{xv}-TS^E_{xv}+\frac{V^\circ}{\omega}[\ln(1+V^M/V^\circ)-V^M/V^\circ], \quad \ldots\ldots \quad (\mathbf{18})$$

which follows from the relations given by Scatchard (1949). For this system the last term is of the order of 0·001 cal./mol. and can be neglected. The remaining terms on the right-hand side can be predicted from the properties of the components following the methods of Hildebrand and Scatchard (1936), Flory (1942), and Huggins (1942).

Values of E^M_{xv} can be calculated for regular solutions from the relation*

$$\mathbf{E}^M_{xv}=(x_1V_1+x_2V_2)v_1v_2D^2, \quad \ldots\ldots\ldots\ldots\ldots \quad (\mathbf{19})$$

where

$$D=(\Pi_1^{0\cdot5}-\Pi_2^{0\cdot5}) \text{ and } \Pi_1=\Lambda_1/V_1.$$

Values of $\mathbf{E}^M_{xv}$ at 70 °C. were calculated using values of Π_1 and Π_2 obtained from the heats of vaporization using the relation $\Lambda=L-RT$. Values of L at 70 °C. were determined from the vapour pressures using equation (**1**) and the relation

$$L_1=RT^2\frac{d\ln P_1}{dT}\left[1+\frac{P_1}{RT}(\beta_1-V_1)\right]. \quad \ldots\ldots\ldots\ldots\ldots \quad (\mathbf{20})$$

---

* Symbols in bold type indicate quantities predicted from component properties.

The values found were 7500 and 8116 cal./g. mol. for benzene and *n*-heptane respectively. Values of L were also calculated from the heats of vaporization at the normal boiling points given by Rossini *et al.* (1947) using the equation of Watson (1943) for extrapolation. They were 7486 and 8038 cal./g. mol. respectively. Using the values calculated from equation (**20**) it was found that $\Pi_1=71\cdot 87$ cal./ml., $\Pi_2=47\cdot 44$ cal./ml., and $D^2=2\cdot 528$. The excess entropy changes on mixing (shown in Table 8) which are due only to differences in the molar volumes of the components were obtained by the use of equation (**21**) which was derived by Flory and Huggins for polymer solutions.

$$\mathbf{S}^E_{xv}=R[x_1 \ln V_1+x_2 \ln V_2-\ln (x_1V_1+x_2V_2)]. \quad \ldots\ldots \quad (\mathbf{21})$$

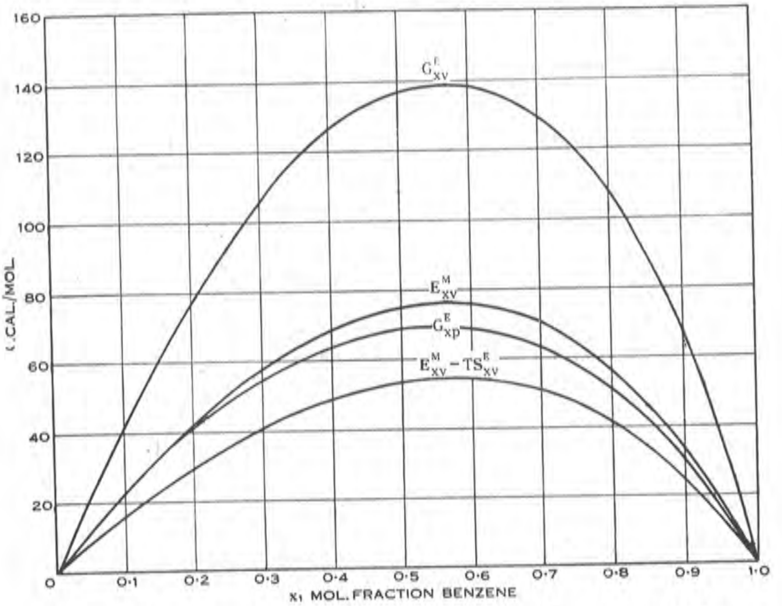

Fig. 1 —Benzene-*n*-heptane. Thermodynamic functions at 70 °C.

In comparing predicted values with values of G^E_{xp} calculated from the equilibrium data it is necessary to consider the errors that could occur in the predicted values of $\mathbf{E}^M_{xv}$. The fractional error in the internal energy of mixing determined from equation (**19**) is given by

$$\frac{\delta \mathbf{E}^M_{xv}}{\mathbf{E}^M_{xv}}=\frac{3\delta V}{V}+\frac{\Pi_1^{0\cdot 5}+\Pi_2^{0\cdot 5}}{\Pi_1^{0\cdot 5}-\Pi_2^{0\cdot 5}}\left[\frac{\delta V}{V}+\frac{\delta \Lambda}{\Lambda}\right], \quad \ldots\ldots\ldots\ldots\ldots \quad (\mathbf{22})$$

where $\delta V/V$ and $\delta\Lambda/\Lambda$ are the fractional errors in the molar volumes and energies of vaporization respectively. Thus the error in $\mathbf{E}^M_{xv}$ increases rapidly as the difference in the internal pressures becomes smaller. Using conservative estimates of the fractional errors in Λ and V of $0\cdot 004$ and $0\cdot 005$ respectively we find for the system benzene–*n*-heptane at 70 °C. that the error in $\mathbf{E}^M_{xv}$ at $x_1=0\cdot 5$ is $7\cdot 7$ cal./mol. ($10\cdot 2$ per cent.). For the system carbon tetrachloride-benzene where $D = 0 \cdot 475$ the error in $\mathbf{E}^{M}_{xv}$ would be as high as 36·6 per cent. Thus, it is not surprising that large differences are often found between experimental values of G^{E}_{xp} for regular systems and those calculated using equation (**19**). Conversely the apparent good agreement between internal pressures calculated from experimental values of G^{E}_{xp} and those calculated from calorimetric values of the heat of vaporization may be misleading (see, for example, Scatchard, Wood, and Mochel 1939*a*, 1939*b*).

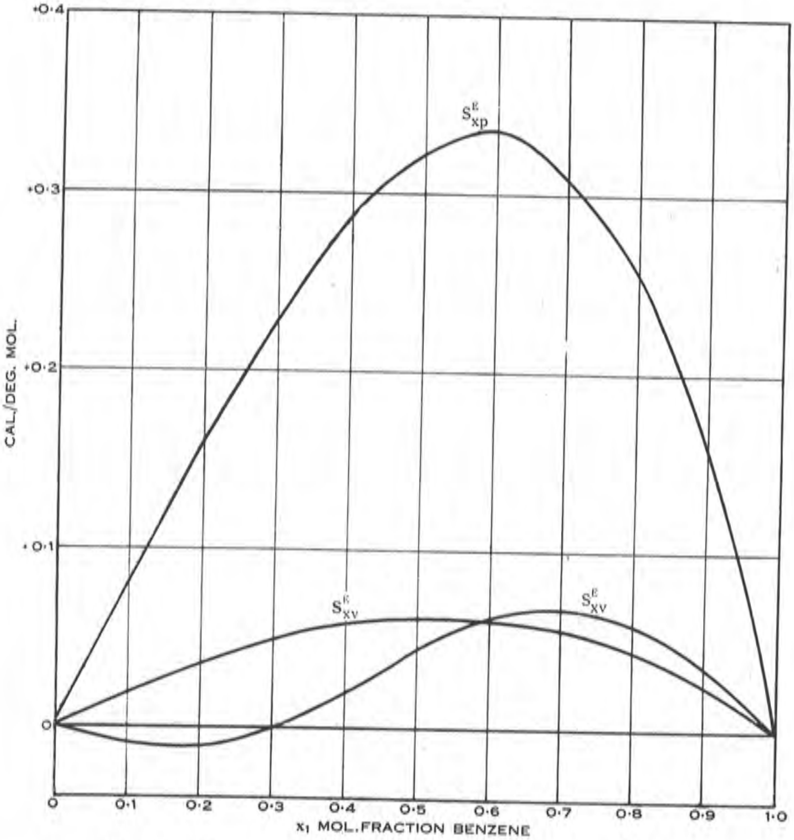

Fig. 2.—Benzene-*n*-heptane. Excess entropy at 70 °C.

A comparison of values of G^{E}_{xp} at 70 °C. determined from the experimental data with those predicted from the properties of the component liquids at the same temperature is shown in Figure 1.

IV. Discussion

The significance of the excess free energies of mixing at constant pressure and at constant volume is not affected by their errors which are of the order of 3 per cent. By comparison of values of G^{E}_{xv} and G^{E}_{xp} shown in Figure 1 it can be seen that $G^{E}_{xv} \approx 2G^{E}_{xp}$ or $G^{E}_{xp} \approx V^{M}_{t}/\omega$ (compare equation (**15**)), which is in agreement with the relation derived by Scatchard (1937).

For the excess entropy of mixing at constant pressure the error is about 0·20 cal./deg. mol. or equivalent to 70 per cent. of its maximum value. In spite of this large error, the experimental values prove S^E_{xp} to be positive. The error in S^E_{xv}, however, is 0·23 cal./deg. mol. and is equivalent to four times its maximum value; S^E_{xv} is therefore not significantly different from zero. The negative values of S^E_{xv} at low benzene concentrations shown in Figure 2 could be due to the relatively large experimental error at low benzene concentration. The excess entropy of this system is thus due mostly to the change of volume on mixing; but positive values of S^E_{xv}, if they should prove significant, could be due to the breakdown of order in the benzene as is suggested by Scatchard (1939*b*) for the system benzene-*cyclo*hexane.

It is only for regular solutions that the function E^M_{xv} is equal to the excess free energy of mixing. For this system, $\mathbf{E}^M_{xv}$ as calculated from equation (**19**) is equal to G^E_{xp} within the error of $\mathbf{E}^M_{xv}$, in agreement with the finding that $S^E_{xv} \approx 0$. The values of $\mathbf{S}^E_{xv}$ calculated by the Flory-Huggins equation (**21**) and shown in Figure 2 agree with experimental values as to sign and order of magnitude over most of the concentration range. This comparison does not provide a check whether the Flory-Huggins equation is applicable to systems of this type, because of the large experimental error in S^E_{xv}.

V. CONCLUSIONS

(1) An azeotrope in the system benzene–*n*-heptane should be found at high benzene concentrations at temperatures below 38 °C.

(2) The Hildebrand-Scatchard expression for the internal energy of mixing at constant volume gives a reasonable agreement with experimental values of the excess free energy of mixing at constant pressure for this system, but preliminary study of other systems shows the method to be unsuitable for precise prediction of excess free energies of near-regular solutions. The study of additional mixtures will be necessary to define the range of systems for which this method is useful.

(3) A wider study will also be required to test the combined use of the Hildebrand-Scatchard and Flory-Huggins theories in predicting the behaviour of non-regular systems. In future work it is proposed to measure calorimetrically the heats of mixing and also to measure the volume changes on mixing at the same temperature used for the liquid-vapour equilibrium measurements in order to obtain more accurate values of the excess entropy of mixing at constant volume.

VI. ACKNOWLEDGMENTS

The authors thank Mr. M. H. Taubert, chief chemist, Vacuum Oil Co., Melbourne, and Mr. J. Poppleton, assistant chief technical officer, Shell Co. of Australia Ltd., for gifts of *n*-heptane; also Mr. J. A. Barker and Dr. M. E. Winfield, Division of Industrial Chemistry, C.S.I.R.O., for valuable suggestions during the preparation of the manuscript.

VII. TABLE OF NOMENCLATURE

A, B, C = Constants in the Antoine equation (**1**),
$D = (\Pi_1^{0\cdot5}-\Pi_2^{0\cdot5})$,
E = Internal energy,
E = Internal energy predicted from component properties,
G = Free energy (Gibbs),
H = Enthalpy,
$K_t = V_t^M/V_{25}^M$,
L = Latent heat of vaporization,
M = Molecular weight,
N_D^{25} = Refractive index at 25 °C. for sodium D line,
P = Pressure,
P_1, P_2 = Vapour pressures of components 1 and 2,
R = Gas constant,
S = Entropy,
S = Entropy predicted from component properties,
T, t = Temperature °K., °C.,
V = Molar volume,
$V^\circ = x_1V_1+x_2V_2$,
d_4^{25} = Density at 25 °C. referred to water at 4 °C.,
f = Constant for converting from mm. Hg-litres to calories $=0\cdot0318657$,
v = Volume fraction,
x, y = Mole fraction in liquid and vapour respectively,
α = Relative volatility,
$\varkappa$ = Average coefficient of expansion,
β = Second virial coefficient in equation of state,
ω = Isothermal compressibility,
γ = Activity coefficient,
$\delta(\ )$ = Absolute error in ( ),
Δ = Change in specific volume on mixing at 25 °C.,
μ = Chemical potential,
Λ = Energy of vaporization,
Π = Internal pressure,

Superscripts

E = Change in excess of that for an ideal solution,
M = Change on mixing,

Subscripts

1, 2 refer to the more and less volatile component respectively,
x indicates a function of composition,
p indicates mixing at constant pressure,
v indicates mixing at constant volume,
t indicates a function of temperature,
c refers to critical state.

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Reprinted from the
AUSTRALIAN JOURNAL OF SCIENTIFIC RESEARCH
SERIES A — PHYSICAL SCIENCES
VOLUME 5, NUMBER 3, PAGES 530-540, 1952

LIQUID-VAPOUR EQUILIBRIA

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Reprinted for
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By I. BROWN*

[*Manuscript received March* 19, 1952]

Summary

Liquid-vapour equilibrium compositions and pressures and relevant thermodynamic functions are given for the systems benzene–*n*-heptane at 80 °C., *n*-hexane–chlorobenzene at 65 °C., and *cyclo*hexane–nitrobenzene at 80 °C. A comparison with values obtained previously for the first of these systems is used to demonstrate the improved performance of a new equilibrium still which is described. It is shown that consistent results can be obtained with the new still for miscible systems having a relative volatility in the range 1·0 to 14. Equilibrium data are also given for the system *n*-hexane–chlorobenzene at 760 mm. Hg to permit comparison with the performance of other equilibrium stills.

I. INTRODUCTION

The three binary systems studied were chosen to give a range of relative volatility from 1·0 to over 100, to determine the effect of relative volatility on the performance of the new equilibrium still. The need for a still that would give satisfactory performance with mixtures of high relative volatility was shown by the results of Brown and Ewald (1951) for the system benzene–*n*-heptane where inconsistency was found when the relative volatility was greater than 2·0.

II. APPARATUS

The equilibrium still of Brown and Ewald (1950), which will be referred to as still No. 1, suffered from two defects when used with the system benzene–*n*-heptane at low benzene concentrations. Errors in vapour concentration determinations were introduced by evaporation of small amounts of condensate from the vapour trap after the still was vented to atmosphere for sampling. Uneven boiling caused occasional hydraulic surges which led to temperature fluctuations and to difficulty in temperature measurement. With some systems of high relative volatility (e.g. acetone-water), it was also found that flash boiling occurred where the condensed vapour mixed with the hot liquid stream returning to the kettle.

These difficulties have been overcome by three major alterations to the still. The design of the new still, referred to as still No. 2, is shown in Figure 1.

The new type of sample trap has a small vapour hold-up, a small area of liquid free surface, and a magnetically operated ball valve to isolate the contents of the traps while the liquid and vapour streams are still circulating. This type

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of trap also prevents contamination of the samples by liquid draining down from the walls after the still circulation is stopped, and it allows the contents of the traps to be cooled before sampling.

To promote even boiling, finely powdered Pyrex glass has been sintered on to the walls of the kettle, the taper to the Cottrell pump tube made more gradual, and the operating liquid level raised.

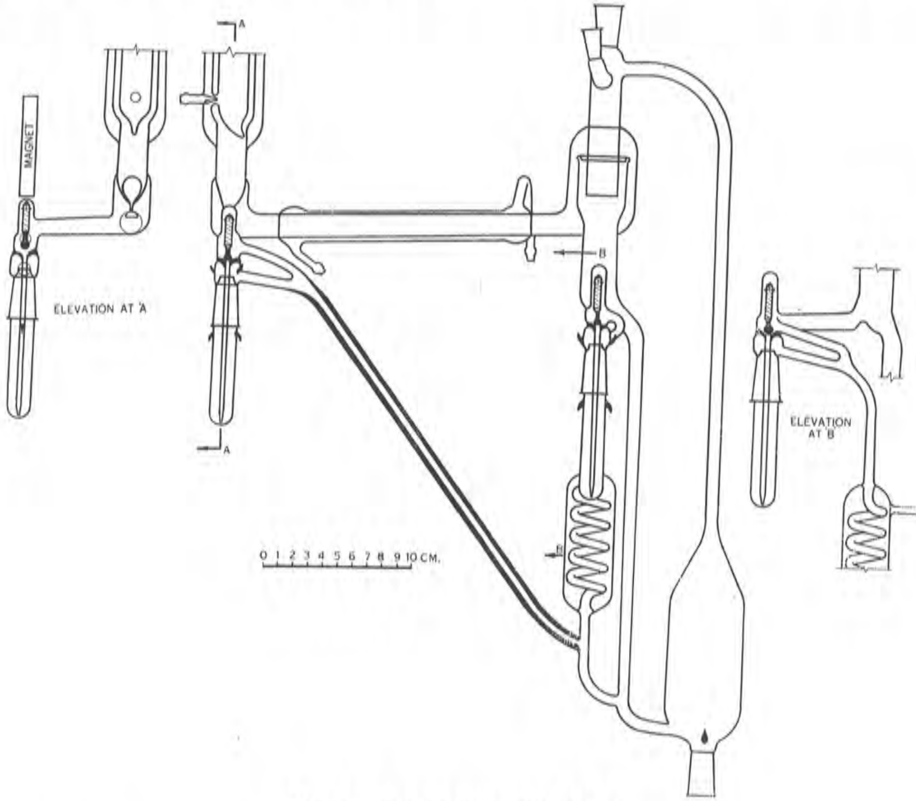

Fig. 1.—Equilibrium still No. 2.

Flash-boiling has been eliminated by the addition of a spiral heat-exchanger which cools part of the liquid return before it mixes with the condensed vapour that flows back to the kettle. A horizontal condenser aids cooling of the vapour sample and reduces the hold-up of liquid and vapour in the vertical condenser. A stoppered opening has also been provided for filling. The operating charge of the still is approximately 200 ml. of which 12 ml. is in each trap.

Operation of the still was commenced at atmospheric pressure and, when the traps filled, the pressure was gradually reduced to the required value or to that corresponding to the required temperature. The still was then allowed to function until a steady state was reached (1·5 to 4 hours); small adjustments of pressure were made if required. The valves on the traps were then closed, the still vented to atmosphere through a drying tube, and the contents of the traps cooled and sampled for analysis. During the run the temperature and pressure were measured using the methods previously described.

III. Purification and Properties of Components

(a) *Purification of Materials*

(i) *Benzene and* n-*Heptane*.—Details of the purification of these liquids and the physical properties of the products have already been given by Brown and Ewald (1951). The same samples were used in this work.

(ii) n-*Hexane*.—Spectroscopic grade *n*-hexane was fractionated at a reflux ratio of 75 to 1 through a 1·5 m., 25 mm. diameter column packed with 1·6 mm. Dixon packing. Samples of 10 ml. were collected and those with a boiling point of 68·72 to 68·75 °C. at 760 mm. Hg (uncorr.) and a refractive index n_D^{25} 1·3720 to 1·3723 were retained. This material was twice shaken for 5 hours at 45 °C. with redistilled chlorosulphonic acid to remove methyl*cyclo*pentane, as proposed by Shepard and Henne (1930), and the product, after separation, was washed with concentrated sulphuric acid, water, 10 per cent. sodium hydroxide, and water, and finally dried over anhydrous calcium chloride. The product was then refractionated through the same column at a reflux ratio of about 100 to 1; head and tail fractions were rejected. The physical properties of the product were as follows:

Property	This Sample	Rossini *et al.* (1947)
B.p./760 (°C.)	68·67	68·742
d_4^{25}	0·65480	0·65482
n_D^{25}	1·3722	1·37226

(iii) *Chlorobenzene*.—Reagent grade chlorobenzene was fractionated at a reflux ratio of about 30 to 1 through a 50 cm., 25 mm. diameter column packed with 3 mm. glass Fenske helices, and head and tail fractions were rejected. The product was shaken twice with 10 per cent. aqueous sodium hydroxide, washed, and dried over anhydrous calcium chloride, and refractionated through the same column at a reflux ratio of about 40 to 1. The physical properties of the product are given below and compared with values by various authors reported by Timmermans (1950).

Property	This Sample	Timmermans (1950)
B.p./760 (°C.).. ..	131·72	131·687 to 132·00
d_4^{25}	1·10112	1·10110
n_D^{25}	1·5219	1·52190

(iv) cyclo*Hexane*.—Details of the purification and physical properties of this liquid have been described previously by Brown and Ewald (1950). The refractive index of the purified liquid was n_D^{25} 1·4233, as compared with the value of 1·42354 given by Rossini *et al.* (1947).

(v) *Nitrobenzene*.—Reagent grade nitrobenzene was shaken with three lots of 1N aqueous sodium carbonate, with 1N sulphuric acid, with water, and then dried over anhydrous calcium chloride. It was fractionated at 3 mm. Hg at a reflux ratio of about 30 to 1 through the column used for the chlorobenzene; head and tail fractions were rejected. The physical properties of the product were as follows:

Property	This Sample	Timmermans (1950)
F.p. (°C.)	+5·69	5·67 to 5·77
B.p./760 (°C.).. ..	210·66	210·85
d_4^{25}	1·19833	1·1983 to 1·1986
n_D^{25}	1·5499	1·55006

(b) *Vapour Pressures of Components*

The vapour pressures of the components were measured in the equilibrium still using the same temperature and pressure measuring equipment as described previously. The results are shown in Table 1. The Antoine equation*

$$\log P = A - B/(C+t), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

was fitted to the vapour pressure data for each component by the method of Willingham *et al.* (1945) and the values of the constants found are given in Table 2.

Table 1

MEASURED VAPOUR PRESSURES OF PURIFIED COMPONENTS (STANDARD MM. Hg)

Benzene		*n*-Hexane		Chlorobenzene		Nitrobenzene	
t (°C.)	P	t (°C.)	P	t (°C.)	P	t (°C.)	P
40·00	182·93	36·44	243·09	62·04	72·43	134·10	82·23
50·00	271·52	41·05	291·20	62·06	72·48	139·75	100·30
60·00	391·74	44·45	331·27	66·38	86·69	145·17	120·64
70·00	551·25	47·32	368·46	74·13	117·91	149·73	140·20
80·00	758·44	48·98	391·25	81·60	156·48	154·61	164·01
80·07	760·00	50·60	414·71	89·06	204·36	159·77	192·80
n-Heptane		53·04	451·99	94·04	242·84	164·45	222·33
40·00	92·51	55·53	493·24	94·47	246·45	168·72	252·39
50·00	141·64	55·69	495·74	98·79	284·73	172·96	285·04
60·00	210·32	57·79	532·74	103·18	328·29	178·48	333·44
70·00	303·79	60·21	577·82	106·25	361·75	182·07	367·64
80·00	428·20	60·58	585·04	110·35	410·99	185·70	405·18
90·00	590·14	62·33	619·81	114·48	465·85	188·90	441·33
91·00	608·55	64·24	659·78	115·89	485·69	192·98	490·74
98·40	760·00	65·44	685·70	117·94	515·85	196·63	538·87
*cyclo*Hexane		65·76	692·93	121·10	565·34	200·41	592·53
30·00	121·91	67·55	733·75	123·39	606·63	203·88	645·62
40·00	184·75	67·67	736·17	126·18	652·69	206·62	690·23
50·00	272·02	68·70	761·15	128·45	695·11	209·49	739·54
60·00	389·60			130·37	732·69	210·626	759·98
70·00	544·23			131·40	753·43	210·629	760·04
80·72	760·00			131·70	759·54		
				131·73	760·28		

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* A table of nomenclature is included at the end of this paper.

The standard deviations in fitting the vapour pressure data for these substances were less than the estimated experimental errors due to errors in the measurement of the temperature and pressure, which were ±0·01 °C. and ±0·05 mm. Hg respectively.

TABLE 2

VALUES OF CONSTANTS IN ANTOINE EQUATION

Substance	A	B	C
Benzene	6·91279	1214·57	221·166
n-Heptane	6·88686	1258·27	215·701
n-Hexane	6·84625	1151·74	221·777
Chlorobenzene	6·99893	1444·75	219·113
*cyclo*Hexane	6·85366	1208·47	223·465
Nitrobenzene	7·08937	1726·66	199·613

(c) *Virial Coefficients and Molar Volumes*

The second virial coefficients in the equations of state for the vapours of the components were estimated from critical data using the Berthelot equation. The critical data for nitrobenzene were calculated by the method of Meissner (1949), which gave T_c 716 °K. and P_c 47 atm. The virial coefficient values for benzene were those estimated by Tompa (1948). The values used are shown in Table 3.

The liquid molar volumes used in calculating the thermodynamic functions were obtained by graphical interpolation of published density data given by Timmermans (1950), I.C.T. (1928), and Egloff (1939). The values used are also given in Table 3.

TABLE 3

LIQUID MOLAR VOLUMES AND SECOND VIRIAL COEFFICIENTS (LITRES)

Substance	t (°C.)	V	β
Benzene	80	0·096	—0·980
n-Heptane	80	0·159	—1·514
n-Hexane	65	0·140	—1·227
Chlorobenzene	65	0·106	—1·633
*cyclo*Hexane	80	0·117	—1·085
Nitrobenzene	80	0·108	—2·089

IV. ANALYTICAL METHODS

The liquid and vapour samples from the system benzene–n-heptane were analysed by density measurements as described previously. The other systems were analysed by refractive index measurements. Mixtures were made by weighing the components, and compositions calculated allowing for air buoyancy and for the weight of air-vapour mixture of the first component displaced on adding the second. The composition *versus* refractive index data that were used for the preparation of large-scale graphs are given in Table 4.

TABLE 4

COMPOSITION VERSUS REFRACTIVE INDEX

n-Hexane–Chlorobenzene		*cyclo*Hexane–Nitrobenzene	
x_1	n_D^{25}	x_1	n_D^{25}
0·0000	1·5219	0·0000	1·5499
0·1059	1·5031	0·1139	1·5342
0·1987	1·4872	0·2186	1·5202
0·2841	1·4733	0·2554	1·5155
0·3941	1·4557	0·3138	1·5076
0·4675	1·4445	0·4100	1·4951
0·6174	1·4222	0·5046	1·4828
0·7080	1·4098	0·6020	1·4704
0·8598	1·3894	0·7036	1·4580
0·9284	1·3809	0·7933	1·4467
1·0000	1·3722	0·8843	1·4362
		1·0000	1·4233

V. LIQUID–VAPOUR EQUILIBRIUM DATA

The equilibrium data were measured by the method described in Section II. The excess chemical potentials, the excess free energy of mixing at constant pressure, and the relative volatility were calculated from the measured liquid and vapour concentrations, pressures, and temperatures using equations (2) to (5).

$$\mu_1^E = RT \ln \gamma_1 = RT \ln (Py_1/P_1x_1) + f(V_1 - \beta_1)(P_1 - P), \quad \ldots\ldots (2)$$

$$\mu_2^E = RT \ln \gamma_2 = RT \ln (Py_2/P_2x_2) + f(V_2 - \beta_2)(P_2 - P), \quad \ldots\ldots (3)$$

$$G_{xp}^E = x_1\mu_1^E + x_2\mu_2^E, \quad \ldots\ldots (4)$$

$$\alpha = y_1x_2/y_2x_1. \quad \ldots\ldots (5)$$

The vapour pressures of the pure components were calculated from equation (1) using the values of the constants given in Table 2.

The values of the excess free energy of mixing at various concentrations were fitted by the method of least squares to equation (6) or the equivalent equation with b and c set equal to zero. Using the values of the constants so obtained, fitted values of the excess chemical potentials were calculated from equations (7) and (8).

$$G_{xp}^E = x_1x_2[a + b(x_1 - x_2) + c(x_1 - x_2)^2], \quad \ldots\ldots (6)$$

$$\mu_1^E = x_2^2[a - b + c + (4b - 8c)x_1 + 12cx_1^2], \quad \ldots\ldots (7)$$

$$\mu_2^E = x_1^2[a - 3b + 5c + (4b - 16c)x_1 + 12cx_1^2]. \quad \ldots\ldots (8)$$

(a) *The System Benzene–*n*-Heptane at* 80 °C.

The results obtained with this system using the new still are given in Table 5. The first three columns show the liquid and vapour concentrations and the pressure; the next four show the excess chemical potentials, the excess free energy of mixing, and the relative volatility. The last column shows the difference between G^E_{xp} calculated from equations (**2**) to (**4**) and that from equation (**6**). The values of the constants (cal./mol.) found in fitting the data to equation (**6**) were $a=+254\cdot3$, $b=+64\cdot3$, $c=+12\cdot3$.

TABLE 5

BENZENE–*n*-HEPTANE AT 80 °C. RESULTS WITH NEW STILL (NO. 2)

x_1	y_1	P (mm. Hg)	μ_1^E (cal./mol.)	μ_2^E (cal./mol.)	G^E_{xp} (cal./mol.)	α	ΔG^E_{xp} (cal./mol.)
0·0464	0·0988	454·62	181·7	0·9	9·2	2·253	+0·1
0·0861	0·1729	476·25	172·1	2·0	16·6	2·219	+0·2
0·2004	0·3473	534·38	147·9	7·3	35·4	2·123	+0·2
0·2792	0·4412	569·49	126·6	13·8	45·3	2·038	—0·6
0·3842	0·5464	613·53	103·3	27·9	56·9	1·931	+0·1
0·4857	0·6304	650·16	78·6	49·4	63·6	1·806	+0·5
0·5824	0·7009	679·74	55·8	76·7	64·5	1·680	—0·0
0·6904	0·7759	708·78	36·1	112·0	59·6	1·553	—0·4
0·7842	0·8384	729·77	20·9	154·9	49·8	1·428	—0·1
0·8972	0·9149	748·46	4·8	241·9	29·2	1·232	+0·3

A comparison is given in Table 6 of the fitted values of G^E_{xp} calculated from equation (**6**) using these values of the constants, with the corresponding data obtained previously using still No. 1. The estimated error in G^E_{xp} was 2·0 cal./mol. and the standard deviation in fitting the results was 0·5 cal./mol. (No. 1) and 0·4 cal./mol. (No. 2). This comparison shows a significant difference between the two sets of results at concentrations of benzene below a mole

TABLE 6

BENZENE–*n*-HEPTANE AT 80 °C. COMPARISON OF G^E_{xp} (CAL./MOL.)

x_1	G^E_{xp} (Still No. 1)	G^E_{xp} (Still No. 2)	Difference (No. 1—No. 2)
0·1	21·9	19·0	2·9
0·2	38·9	35·2	3·7
0·3	51·7	48·4	3·3
0·4	60·4	58·1	2·3
0·5	65·0	63·6	1·4
0·6	65·1	64·2	0·9
0·7	59·9	59·2	0·7
0·8	48·3	47·6	0·7
0·9	28·9	28·2	0·7

fraction of 0·4. This is the composition range where the relative volatility was highest for this system.

The thermodynamic consistency of the data obtained with the two stills was compared by considering the differences between the experimental values of the excess chemical potentials from equations (**2**) and (**3**) and the fitted values from equations (**7**) and (**8**). These differences $\Delta\mu^E$ are shown in Table 7. Before the significance of these differences could be determined it was necessary to evaluate the errors in the values of the excess chemical potentials due to errors in the measured quantities from which they were calculated. For temperature, pressure, and composition the errors were $\pm 0 \cdot 01$ °C., $\pm 0 \cdot 05$ mm. Hg, and $\pm 0 \cdot 00025$ mol. fraction respectively. The corresponding errors, $\delta\mu^E$ in the excess chemical potentials also appear in Table 7.

TABLE 7

BENZENE–n-HEPTANE AT 80 °C. ERRORS IN EXCESS CHEMICAL POTENTIALS (CAL./MOL.)

x_1	$\Delta\mu_1^E$ (No. 1)	$\Delta\mu_1^E$ (No. 2)	$\delta\mu_1^E$	$\Delta\mu_2^E$ (No. 1)	$\Delta\mu_2^E$ (No. 2)	$\delta\mu_2^E$
0·05	—98	—9·0	3·8	+4	+0·6	1·2
0·1	—79	—9·0	3·2	+9	+1·0	1·4
0·5	—10	—4·5	1·7	+10	+5·0	1·9
0·9	—1	—0·1	1·0	+7	+4·0	3·4

These results show that the values obtained using still No. 2 are considerably more consistent than those obtained using still No. 1. The consistency of the results was also tested by the method of Redlich and Kister (1948) ; the experimental values of $(\mu_1^E - \mu_2^E)$ were plotted against x_1 and the areas above and below datum were measured. The ratio of these areas was 1·83 for still No. 1, while for the new still it was 1·09.

(*b*) *The System* n-*Hexane–Chlorobenzene at* 65 °*C*.

The results obtained with this system are shown in Table 8. The accuracy of these excess free energy data did not justify the use of the three-constant equation (**6**). The data were fitted by the method of least squares to the simpler equation

$$G_{xp}^E = a x_1 x_2 \, ;$$

the value of a was found to be +414 cal./mol.

The consistency of the data was tested by plotting experimental values of $(\mu_1^E - \mu_2^E)$ against x_1 and measuring the areas above and below datum. This ratio was found to be 1·00.

(*c*) *The System* n-*Hexane–Chlorobenzene at* 760 *mm. Hg*

The equilibrium data for this system were measured at $759 \cdot 8 \pm 0 \cdot 4$ mm. Hg to enable a comparison to be made with results obtained using other equilibrium

TABLE 8

n-HEXANE–CHLOROBENZENE AT 65 °C.

x_1	y_1	P (mm. Hg std.)	μ_1^E (cal./mol.)	μ_2^E (cal./mol.)	G_{xp}^E (cal./mol.)	α	ΔG_{xp}^E (cal./mol.)
0·083	0·544	166·4	344	2·1	30·4	13·2	—1·0
0·144	0·679	222·3	315	2·5	47·4	12·6	—3·6
0·201	0·744	264·1	265	11·6	62·5	11·5	—4·0
0·284	0·803	319·7	210	35·8	85·3	10·2	+1·1
0·394	0·852	382·3	148	69·8	100	8·86	+1·6
0·438	0·866	403·9	123	92·1	106	8·27	+3·9
0·485	0·882	428·3	106	102	104	7·93	+0·6
0·540	0·896	453·8	81·3	133	105	7·30	+2·4
0·591	0·910	477·9	65·4	143	97·3	7·02	—2·8
0·679	0·929	516·3	36·6	198	88·6	6·19	—1·7
0·806	0·957	578·0	14·1	270	63·7	5·37	—1·0
0·927	0·984	638·4	2·7	345	27·6	4·72	—0·3

stills. The pressure was controlled by a modification of the manostat described by Gould and Evans (1933). The results are given in Table 9. These data were shown to be consistent by the method of Herington (1951).

TABLE 9

n-HEXANE–CHLOROBENZENE AT $759 \cdot 8 \pm 0 \cdot 4$ MM. Hg

x_1	y_1	P (mm. Hg)	t (°C.)	μ_1^E (cal./mol.)	μ_2^E (cal./mol.)	α
0·018	0·118	759·7	127·56	376	1·3	7·45
0·049	0·282	759·4	121·06	353	4·0	7·62
0·081	0·406	759·6	115·66	328	2·7	7·74
0·109	0·491	759·9	111·53	310	0·3	7·87
0·146	0·577	759·8	106·62	289	3·9	7·96
0·200	0·666	759·8	101·04	255	6·0	7·97
0·309	0·769	759·7	92·70	184	42·1	7·42
0·419	0·835	759·7	86·84	129	70·5	6·98
0·516	0·872	759·7	82·66	90·3	120	6·38
0·591	0·896	759·7	80·19	65·0	162	5·94
0·593	0·896	760·0	80·13	62·6	160	5·89
0·594	0·896	760·1	80·17	61·0	156	5·91
0·644	0·912	759·8	78·31	47·7	183	5·70
0·737	0·934	760·0	75·70	23·6	256	5·06
0·790	0·950	760·1	74·17	16·3	255	5·09
0·793	0·950	760·4	74·14	14·3	278	4·96
0·847	0·965	759·4	72·72	5·9	276	4·91

(*d*) *The System* cyclo*Hexane–Nitrobenzene at* 80° *C.*

This system was chosen to test the performance of the still with a mixture of very high relative volatility. The results are given in Table 10. The excess free energy data were fitted by the method of least squares to the equation that was used for the system *n*-hexane–chlorobenzene; the value of a was found to be 1630 cal./mol. The difference between the experimental and fitted values of G^E_{xp} shown in the last column of Table 10 are less than the estimated errors in G^E_{xp} of approximately 60 cal./mol.

TABLE 10

*cyclo*HEXANE–NITROBENZENE AT 80 °C.

x_1	y_1	P (mm. Hg)	μ^E_1 (cal./mol.)	μ^E_2 (cal./mol.)	G^E_{xp} (cal./mol.)	α	ΔG^E_{xp} (cal./mol.)
0·145	0·973	322·6	490	130	182	213	—20
0·440	0·985	556·2	369	380	375	83·6	—27
0·490	0·985	573·1	314	465	391	68·4	—16
0·573	0·985	600·3	236	606	394	50·0	—5
0·686	0·985	630·3	143	867	371	30·1	+19
0·773	0·983	654·1	83	1210	339	17·0	+52
0·891	0·991	689·9	25	1290	162	13·9	+4

The upper limit of relative volatility for satisfactory performance of the still could not be defined by these results as the relative volatility was too high over most of the composition range. The upper limit for α is somewhere in the range covered by this system and is probably close to 14.

Difficulty was experienced in operating the still at low *cyclo*hexane concentration due to the large differences in vapour pressure and density of the components. The condensed vapour returned to the kettle unevenly giving irregular boiling.

VI. CONCLUSIONS

The results that have been given for these three binary systems show that the new equilibrium still gives consistent data over a wider range of relative volatility than still No. 1. Thermodynamically consistent results can be obtained with the apparatus described for miscible systems having a relative volatility from 1·0 to 14. The still is satisfactory for obtaining accurate data at ordinary pressures both for thermodynamic investigation of liquid mixtures and for plant design.

VII. ACKNOWLEDGMENTS

The author thanks all those who helped with this work, particularly Miss P. C. Miller for curve fitting and Messrs. O. H. Rigby, G. English, L. N. Sutton, and F. W. Wheatley for their help in the purification of the components and in the equilibrium measurements; also Mr. D. T. C. Gillespie for suggestions during the development of the apparatus.

VIII. TABLE OF NOMENCLATURE

$A, B, C,$=constants in the Antoine equation (1),
$a, b, c,$=constants in equations (6), (7), and (8),

G=free energy (Gibbs),

n_D^{25}=refractive index at 25 °C. for sodium D line,

P=pressure,

P_1, P_2=vapour pressures of components 1 and 2,

R=gas constant=$1 \cdot 9872$ cal./deg. mol.,

T, t=temperature °K., °C. (0 °C.=$273 \cdot 16$ °K.),

V=molar volume,

d_4^{25}=density at 25 °C. referred to water at 4 °C.,

f=constant for converting from mm. Hg–litres to calories=$0 \cdot 0318657$,

x, y=mole fraction in liquid and vapour respectively,

α=relative volatility,

β=second virial coefficient in equation of state,

γ=activity coefficient,

$\delta(\ )$=absolute error in ( ),

$\triangle(\ )$=difference between fitted and experimental values of ( ),

μ=chemical potential,

Superscript

E=excess change above that for an ideal solution,

Subscripts

1, 2 refer to the more and less volatile components respectively,

x indicates a function of composition,

p indicates mixing at constant pressure.

c refers to the critical state.

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SEAMER AND ARUNDEL STS., GLEBE, SYDNEY

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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 7, NUMBER 3, PAGES 264–268, 1954

LIQUID–VAPOUR EQUILIBRIA

IV. THE SYSTEM ETHANOL + BENZENE AT 45 °C

By I. Brown and F. Smith

Reprinted for
the Commonwealth Scientific and Industrial Research Organization, Australia

Reprinted from the

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LIQUID–VAPOUR EQUILIBRIA

IV. THE SYSTEM ETHANOL+BENZENE AT 45 °C

By I. Brown* and F. Smith*

[*Manuscript received March* 31, 1954]

Summary

New liquid-vapour equilibrium data are given for the system ethanol+benzene at 45·00 °C. These data are used to calculate the excess free energy of mixing for this system.

I. Introduction

Liquid-vapour equilibrium data for this system have been measured at constant pressure by a number of workers, notably by: Tyrer (1912*a*, 1912*b*), Fritzweiler and Dietrich (1933), Uchida and Tezuka (1938), Ellis (1951, 1952), and Yerazunis (in press). Their measurements are not entirely in agreement. The only measurements at constant temperature, however, are those of Lehfeldt (1898) which we have shown to be thermodynamically inconsistent by the method of Herington (1947) and Redlich and Kister (1948). The present measurements were made to provide reliable isothermal values of the excess free energy of mixing required for an investigation of the thermodynamic properties of alcohol solutions.

II. Experimental

(*a*) *Apparatus*

The liquid-vapour equilibrium and vapour pressure measurements were made using the equilibrium still described by Brown (1952), pressure and temperature measurements were made by the methods of Brown and Ewald (1950), and the analysis by refractive index measurements using a Bellingham and Stanley Pulfrich type refractometer maintained at 25·00±0·01 °C.

(*b*) *Purification and Properties of Components*

The ethanol was purified by the method of Barker, Brown, and Smith (1953) and the benzene as described by Brown and Ewald (1951). The physical properties of the components are shown in Table 1.

(*c*) *Analytical Method*

The liquid and vapour samples were analysed by refractive index measurements. Eleven mixtures were made by weighing, allowing for the buoyancy of the air and the weight of air-vapour mixture of the first component displaced on adding the second. The refractive index-composition data are given in Table 2, where x_1 is the mole fraction of ethanol in the mixture.

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In order to use the data in Table 2 for the analysis of liquid and condensed vapour samples a direct plot of refractive index against composition was impracticable. A graph against refractive index of the difference Δ_0 between the measured refractive index and the value calculated assuming a linear relationship with mole fraction also involved too many significant figures. A quadratic in n was taken out and values of the residual Δ were calculated using equation (**1**)

TABLE 1

PHYSICAL PROPERTIES OF COMPONENTS

Property	Ethanol	Benzene
B.p./760 mm Hg (°C)	78·29	80·07
$d_4^{25\cdot00}$	0·78511	0·873~~50~~64
$n_D^{25\cdot00}$	1·35929	1·49803
Vapour pressure 45·00 °C ..	172·87	223·74

$$\Delta = n - n_2 + x_1(n_2 - n_1) + 2\cdot777(n - n_2)(n - n_1), \qquad \ldots\ldots \; (\mathbf{1})$$

where n, n_1, and n_2 are the measured refractive indices of the mixture, pure ethanol, and pure benzene respectively. The calculated values of Δ shown in Table 2 were plotted against n. The composition of the samples was then determined from (**1**) using the graph to determine values of Δ.

TABLE 2

REFRACTIVE INDEX-COMPOSITION DATA

x_1	$n_D^{25\cdot00}$	Δ
0·0000	1·49803	0·00000
0·0451	1·49401	+0·00072
0·0957	1·48885	+0·00080
0·1991	1·47790	+0·00087
0·2890	1·46776	+0·00070
0·3928	1·45533	+0·00041
0·4966	1·44219	+0·00017
0·5984	1·42815	−0·00021
0·6940	1·41392	−0·00058
0·8059	1·39555	−0·00099
0·9052	1·37772	−0·00088
0·9487	1·36923	−0·00073
1·0000	1·35929	0·00000

III. LIQUID-VAPOUR EQUILIBRIUM DATA

The liquid-vapour equilibrium data are shown in Table 3 where x_1 and y_1 are the mole fractions of ethanol in the liquid and vapour respectively, P is the total pressure in standard mm Hg, and α is the relative volatility given by $\alpha = (y_1x_2)/(y_2x_1)$.

TABLE 3

ETHANOL+BENZENE AT 45·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0374	0·1965	271·01	6·286	1335	5·4	55·1
0·0972	0·2895	296·53	3·782	1030	24·6	122·3
0·2183	0·3370	306·55	1·820	633·9	93·0	211·1
0·3141	0·3625	309·33	1·242	455·2	156·7	250·5
0·4150	0·3842	309·59	0·8791	315·9	236·2	269·3
0·5199	0·4065	307·46	0·6327	204·5	333·7	266·5
0·5284	0·4101	306·99	0·6205	198·8	340·3	265·5
0·6155	0·4343	302·05	0·4796	128·2	433·0	245·4
0·7087	0·4751	291·81	0·3720	74·0	540·2	209·8
0·8102	0·5456	271·08	0·2811	30·5	674·8	152·8
0·9193	0·7078	227·72	0·2127	6·2	829·5	72·6
0·9591	0·8201	203·28	0·1944	1·8	882·7	37·8

These data show that an azeotrope is formed at 45·00 °C having a mole fraction of ethanol of 0·375 and at a total pressure of 309·75 mm Hg.

IV. DERIVED THERMODYNAMIC FUNCTIONS

The excess chemical potentials μ_1^E and μ_2^E and the excess free energy of mixing G_x^E were calculated from the equilibrium data using equations (2), (3), and (4). The values obtained (cal/g-mol) are given in Table 3.

$$\mu_1^E = RT \ln (Py_1/P_1x_1) + (\beta_{11} - V_1)(P - P_1) + P\delta_{12}y_2^2, \quad \ldots\ldots (2)$$

$$\mu_2^E = RT \ln (Py_2/P_2x_2) + (\beta_{22} - V_2)(P - P_2) + P\delta_{12}y_1^2, \quad \ldots\ldots (3)$$

$$G_x^E = x_1\mu_1^E + x_2\mu_2^E, \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where P_1 and P_2 are the vapour pressures of the pure components, β_{11}, β_{22}, β_{12} are the second virial coefficients in the equations of state for the pure and mixed vapours, V_1 and V_2 are the liquid molar volumes.

$$\delta_{12} = 2\beta_{12} - \beta_{11} - \beta_{22}, \qquad T\ °\mathrm{K} = t\ °\mathrm{C} + 273\cdot 16.$$

The values of V_1 and V_2 were calculated from density data given by Timmermans (1950), the value of β_{11}(ethanol) was calculated by the method used by Barker, Brown, and Smith (1953), and that for benzene from the relation given by Allen, Everett, and Penney (1952), that is,

$$\beta_{22} = 0\cdot 070 - \frac{13\cdot 2 \times 10^4}{T^2} \qquad \mathrm{l/mole}.$$

To form an approximate estimate of β_{12} the following assumptions were made :

(i) That the second virial coefficient which ethanol would have if it did not form hydrogen bonds is given by the Berthelot equation, $\beta'_{11} = B_1 - A_1/T^2$.

(ii) That the mixed virial coefficient β_{12} is given by an equation of the Berthelot type, $\beta_{12} = B_{12} - A_{12}/T^2$.

(iii) That the values of B_{12} and A_{12} are given by the following combinations of the Berthelot constants for ethanol and benzene as determined from critical data.

$$B_{12}=\left(\frac{B_1^{\frac{1}{3}}+B_2^{\frac{1}{3}}}{2}\right)^3, \quad \left[\frac{A}{B^2}\right]_{12}=\sqrt{\left[\frac{A}{B^2}\right]_1\times\left[\frac{A}{B^2}\right]_2}.$$

Values of second virial coefficients and molar volumes at 45 °C (l.) used are :

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
$-1\cdot970$	$-1\cdot236$	$-0\cdot919$	$+1\cdot367$	$0\cdot060$	$0\cdot092$

The excess free energy data at 45·00 °C were fitted by the method of least squares to equation (**5**) :

$$G_x^E=x_1x_2[a+b(x_1-x_2)+c(x_1-x_2)^2+d(x_1-x_2)^3]. \quad \ldots . \quad (5)$$

The values of the constants and the standard deviation σ of the fit were (in cal/g-mol) :

	a	b	c	d	σ
Two constant equation	$+1092\cdot4$	$-217\cdot4$	0	0	$5\cdot6$
Three constant equation	$+1072\cdot7$	$-218\cdot0$	$+162\cdot0$	0	$2\cdot3$
Four constant equation	$+1071\cdot7$	$-170\cdot6$	$+166\cdot6$	$-136\cdot3$	$0\cdot9$

Values of the second derivative of the total free energy of mixing with respect to x_1 were also calculated and these gave no change of sign, showing that equation (**5**) with the above values of the constants does not indicate separation into two liquid phases.

The method of Herington (1947) and Redlich and Kister (1948) was used to test the thermodynamic consistency of the results which was shown to be satisfactory as the ratio of the areas above and below datum in a plot of $(\mu_1^E-\mu_2^E)$ against x_1 was 1·015.

The errors in G_x^E due to the errors in the measured quantities were estimated to be of the order of 3·5 cal/mole of which approximately half is due to errors in the refractometric analysis.

V. CONCLUSIONS

Thermodynamically consistent values are given for the liquid-vapour equilibrium and excess free energy of mixing for the system ethanol+benzene at 45 °C. These data will be used to calculate the excess entropy of mixing for this system as soon as heat of mixing measurements have been completed. This system forms an azeotrope at 45·00 °C having a mole fraction of ethanol of 0·375 and a total pressure of 309·75 mm Hg.

VI. ACKNOWLEDGMENTS

The authors thank Mr. W. Fock for his help in testing the data of Lehfeldt, Mr. O. H. Rigby for his help in the purification of the components, and Mr. J. A. Barker for his help with the preparation of the manuscript.

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AUSTRALASIAN MEDICAL PUBLISHING CO. LTD.
SEAMER AND ARUNDEL STS., GLEBE, SYDNEY

Reprinted from the Australian Journal of Chemistry, Volume 9, Number 1, pp. 141–142, 1956

CORRIGENDA

VOLUME 7, NUMBER 3, PAGES 264–8

Liquid-Vapour Equilibria. IV. The System Ethanol+Benzene at 45 °C. By I. Brown and F. Smith

VOLUME 8, NUMBER 4, PAGES 501–5

Liquid-Vapour Equilibria. VII. The Systems Nitromethane+Benzene and Nitromethane+Carbon Tetrachloride at 45 °C. By I. Brown and F. Smith

VOLUME 8, NUMBER 3, PAGES 361–9

Heats of Mixing of Alcohol Solutions. By I. Brown and W. Fock

The density values of some pure components, with densities below 1·0, given in the above three papers are low. In Table 1 of the first two papers the density (d_4^{25}) of benzene was given as 0·87359 and 0·87366 respectively; these should be 0·87366. In Table 1 of the third paper the following corrections apply:

Benzene: *For* 0·87359 *read* 0·87364.
Acetone: *For* 0·78494 *read* 0·78501.
2,2,4-Trimethylpentane: *For* 0·68766 *read* 0·68778.

These errors were brought about by the use of a table of buoyancy corrections given by Roeder (1953). His method greatly simplified the calculation of the corrections. Unfortunately, the values of the corrections given in Table 1 of his paper apply only to densities from 1·00 to 1·50 and not also to densities below 1·0 as he states.

The values given in his table were calculated from his expression $d=P'/V+K$, where d is the corrected density, P' is the difference in weights of the full and empty pyknometer, and V is the true volume of the pyknometer in ml. The correction factor K is given by

$$K=\lambda\left(1-\frac{P'}{V}\cdot\frac{1}{\sigma}\right),$$

where λ is the air density, assumed to be the same at the two weighings, and σ is the density of the weights (8·4 for the tabulated values given).

Densities calculated by these formulae are correct to 3 in the fifth decimal place provided the air density at the two weighings does not differ by more than 0·000005.

A correct set of K values for densities less than 1·00 can be calculated from the formula. As an example, for an air density of 0·00120 the correction for a P'/V of 1·50 would be 0·00099, while that for a P'/V of 0·50 would be 0·00113 and not 0·00099 as given in Roeder's table.

To confirm the density of highly purified benzene two separate samples were prepared by the method of Brown and Ewald (1951) with an additional fractional distillation before crystallization. The freezing curve of these samples was measured in an apparatus the same as that of Herington and Handley (1950) using a calibrated platinum resistance thermometer and a calibrated Mueller bridge. The purity of the benzene was determined by the method of Mair, Glasgow, and Rossini (1941). The densities were measured by the method of Brown and Ewald (1950) and the refractive indices using a calibrated Hilger-Chance precision refractometer.

Benzene Sample	Purity Mol. (%)	$d_4^{25\cdot00}$	$n_D^{25\cdot00}$
A	99·98±0·01	0·87374	1·49799
B	99·98	0·87370	1·49801

The accuracy of the thermodynamic data reported in the above papers is unaffected by these density errors as density values were not used for analysis but only as criteria of purity of the components.

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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 12, NUMBER 3, PAGES 407–412, 1959

LIQUID-VAPOUR EQUILIBRIA

IX. THE SYSTEMS n-PROPANOL+BENZENE AND n-BUTANOL+BENZENE AT 45°C

By I. BROWN and F. SMITH

Reprinted for the
Commonwealth Scientific and Industrial Research Organization
Australia

LIQUID-VAPOUR EQUILIBRIA

IX. THE SYSTEMS *n*-PROPANOL+BENZENE AND *n*-BUTANOL+BENZENE AT 45 °C

By I. Brown* and F. Smith*

[*Manuscript received March* 4, 1959]

Summary

Liquid-vapour equilibrium data are given for the systems *n*-propanol+benzene and *n*-butanol+benzene at 45·00 °C. The data are used to calculate the excess free energy of mixing for these systems.

I. Introduction

Liquid-vapour equilibria for the system *n*-propanol+benzene have been determined at 20 °C by Tryhorn and Wyatt (1928), at 40·0 °C by Lee (1931), and at 10 degree intervals from 0 to 70 °C by Schmidt (1926). Measurements have also been made at atmospheric pressure by Wehe and Coates (1955) and Bonauguri, Bicelli, and Spiller (1951) and at elevated pressures by Kumarkrishna Rao, Swami, and Narasinga Rao (1957).

The liquid-vapour equilibria for the system *n*-butanol+benzene have been determined at 20 °C by Tryhorn and Wyatt (1928) and at 25 °C by Allen, Lingo, and Felsing (1939). Measurements have also been made at atmospheric pressure by Bonauguri, Bicelli, and Spiller (1951) and by Shemilt (personal communication).

The present measurements were made to obtain values of the excess free energy of mixing at 45 °C as no published data of sufficient accuracy were available at this temperature. The data obtained here will be discussed in a subsequent paper together with those obtained previously for other alcohol systems.

II. Experimental

(*a*) *Apparatus*

The liquid-vapour equilibrium and vapour pressure measurements were made using the equilibrium still described by Brown (1952); pressure measurements were made by the methods of Brown and Ewald (1950) and the temperatures were measured with a calibrated Myer type platinum resistance thermometer and calibrated Mueller bridge using the methods described by Brown and Smith (1957). Liquid and vapour samples were analysed by refractive index measurements using a Hilger-Chance precision refractometer maintained at 25·00±0·01 °C.

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(b) *Purification and Properties of Components*

Benzene was purified by the method described by Brown and Ewald (1951). *n*-Propanol usually contains allyl alcohol as its major impurity and removal of this as the close-boiling azeotrope with *n*-propanol is wasteful if the allyl alcohol content is high even when an efficient distillation column is used. The method of Kretschmer (1951) gave a product with a high density and refractive index when the initial allyl alcohol content was above about 1 per cent. The method finally employed was to fractionally distil a sample containing less than 1 per cent. of allyl alcohol using the column described by Brown and Ewald (1951) operated at a reflux ratio of 75 : 1 and rejecting the head fractions with a high density. *n*-Butanol was purified by distillation using the same column.

TABLE 1

PHYSICAL PROPERTIES OF COMPONENTS

Property	Benzene	*n*-Propanol	*n*-Butanol
Boiling point/760 mm Hg (°C) ..	80·04	97·08	117·52
$d_4^{25\cdot00}$	0·87372	0·79958	0·80579
$n_D^{25\cdot00}$	1·49798	1·38312	1·39730
Vapour pressure 45·00 °C ..	223·64	69·35	25·34

The physical properties of the liquids used are shown in Table 1. The vapour pressures of the sample of benzene were checked at 45 °C and at the normal boiling point and found to be in good agreement with the values previously obtained by us. The vapour pressures of the alcohols were measured over a range of temperatures and the values found are given in Tables 2 and 3. These values were fitted by the method of Willingham *et al.* (1945) to the Antoine equation

$$\log_{10} P = A - \frac{B}{C+t},$$

where P is in standard mm Hg and t is in °C. The values of the constants found and σ, the standard deviation of the fit, are also presented in Tables 2 and 3.

TABLE 2

VAPOUR PRESSURE OF *n*-PROPANOL

t (°C)	P (mm Hg)	t (°C)	P (mm Hg)	Antoine Equation Constants
97·10	760·51	70·09	246·25	
97·09	760·05	65·80	201·52	$A=7\cdot83230$
97·08	760·25	61·51	163·90	$B=1485\cdot84$
94·36	685·12	54·52	115·55	$C=203\cdot00$
91·13	603·59	48·18	82·64	$\sigma=0\cdot14$ mm Hg
86·00	491·03	48·16	82·47	
81·11	400·38	48·14	82·43	
74·56	301·35			

TABLE 3
VAPOUR PRESSURE OF n-BUTANOL

t (°C)	P (mm Hg)	t (°C)	P (mm Hg)	Antoine Equation Constants
117·56	760·35	79·02	157·68	$A=7\cdot56483$ $B=1416\cdot99$ $C=184\cdot99$ $\sigma=0\cdot21$ mm Hg
113·26	651·47	79·00	157·38	
108·23	540·33	75·39	132·70	
103·30	446·65	70·15	102·52	
97·33	351·47	64·74	77·79	
89·14	248·72	64·56	77·06	

(c) *Analytical Methods*

Mixtures were prepared from weighed amounts of the components and their compositions were calculated allowing for air buoyancy and for the weight of air-vapour mixture of the first component displaced on adding the second, their compositions and refractive indices are given in Tables 4 and 5. The method of Brown and Smith (1954) was employed to calculate the composition of the liquid and vapour samples from the refractive index measurements.

TABLE 4
n-PROPANOL + BENZENE: REFRACTIVE INDEX—COMPOSITION DATA

x_1	$n_D^{25\cdot00}$	x_1	$n_D^{25\cdot00}$
0·0530	1·49221	0·5063	1·44344
0·1080	1·48644	0·6146	1·43103
0·2041	1·47629	0·7075	1·42008
0·3150	1·46450	0·7928	1·40968
0·4180	1·45328	0·8914	1·39730
0·4998	1·44416	0·9492	1·38981

TABLE 5
n-BUTANOL + BENZENE: REFRACTIVE INDEX—COMPOSITION DATA

x_1	$n_D^{25\cdot00}$	x_1	$n_D^{25\cdot00}$
0·0478	1·49239	0·4973	1·44542
0·0987	1·48672	0·6060	1·43473
0·2007	1·47571	0·6960	1·42608
0·3096	1·46434	0·8093	1·41526
0·3986	1·45528	0·9034	1·40636
0·4881	1·44635	0·9546	1·40159

III. RESULTS

The liquid-vapour equilibrium data are given in Tables 6 and 7 where x_1 and y_1 are the mole fractions of the alcohol in the liquid and vapour respectively, P is the total pressure in standard mm Hg, and α is the relative volatility given by $\alpha=y_1x_2/y_2x_1$.

From graphs of the data shown in Table 6 it was concluded that the system *n*-propanol+benzene forms an azeotrope at 45·00 °C at a mole fraction of *n*-propanol of 0·132 and at a pressure of 239·0 mm Hg.

Graphs of the data given in Table 7 indicate that if an azeotrope is formed at 45 °C in the system *n*-butanol+benzene it is at a mole fraction of butanol less than 0·01.

TABLE 6

n-PROPANOL+BENZENE 45·00 °C : EXPERIMENTAL DATA AND DERIVED FUNCTIONS

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0470	0·0843	235·26	1·867	1138·6	6·2	59·4
0·0977	0·1194	238·35	1·252	903·1	24·3	110·2
0·2144	0·1560	237·55	0·6770	572·1	83·1	187·9
0·2973	0·1728	234·89	0·4938	422·5	134·0	219·8
0·4061	0·1935	229·51	0·3509	282·0	210·0	239·2
0·4807	0·2080	224·13	0·2837	206·0	268·7	238·5
0·5252	0·2185	220·42	0·2528	170·5	307·5	235·5
0·6053	0·2402	211·04	0·2061	113·3	378·7	218·1
0·7033	0·2790	194·66	0·1632	62·2	475·8	184·9
0·7982	0·3437	170·06	0·1324	29·1	576·1	139·5
0·9140	0·5252	122·08	0·1041	3·6	704·1	63·8

TABLE 7

n-BUTANOL+BENZENE 45·00 °C : EXPERIMENTAL DATA AND DERIVED FUNCTIONS

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0538	0·0323	221·29	0·5870	1042	7·8	63·4
0·0974	0·0432	218·90	0·4184	842·7	23·7	103·5
0·1986	0·0579	212·80	0·2480	559·0	71·6	168·4
0·3007	0·0684	205·68	0·1708	380·4	129·5	204·9
0·4004	0·0779	197·33	0·1265	255·6	194·4	218·9
0·4915	0·0885	187·62	0·1005	174·8	259·8	218·0
0·6003	0·1054	171·29	0·0784	101·7	343·4	198·3
0·7072	0·1311	148·84	0·0625	47·8	434·0	160·9
0·8206	0·1893	114·04	0·0511	18·6	533·1	110·9

IV. DERIVED THERMODYNAMIC FUNCTIONS

The excess chemical potentials μ_1^E and μ_2^E and the excess free energy of mixing G_x^E were calculated from the equilibrium data using equations (**2**), (**3**), and (**4**) of Brown and Smith (1954). The values obtained (cal/g-mol of mixture) are shown in Tables 6 and 7. The liquid molar volumes V_1 and V_2 required for these calculations were obtained from densities given by Timmermans (1950). The value of the second virial coefficient for benzene vapour at 45 °C was obtained from equation (**A5**) of Allen, Everett, and Penney (1952). The second virial coefficients for *n*-propanol and *n*-butanol were calculated by corresponding states from the experimental data of Kretschmer and Wiebe (1954) for ethanol and *iso*propanol. The values of the critical data used for *n*-propanol were those of Kobe and Lynn (1953) and for *n*-butanol those of Singh and Shemilt (1955). An attempt was made to estimate the value of the second virial coefficient for *n*-butanol at 45 °C from the high temperature P-V-T data of Shemilt, Esplen, and Singh (1959) using the method of David and Hamann (1957). Values of $(Z-1)V^*$ were plotted against $1/V^*$ for values of T^* from 0·84 to 0·92, where $Z=PV/RT$, $V^*=V/V_c$, and $T^*=T/T_c$. The plots curved badly at low values of $1/V^*$ for T^* above about 0·9 and the data were not available at sufficiently low temperatures to enable a virial coefficient value at 45 °C ($T^*=0{\cdot}578$) to be obtained. The second virial coefficient, β_{12}, in the equation of state for the mixed vapours, and the allied coefficient δ_{12} were calculated by the method used by Brown and Smith (1954).

For the system *n*-propanol+benzene at 45·00 °C the values of the second virial coefficients and molar volumes (l/mol) were taken to be:

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−3·23	−1·23	−1·09	+2·29	0·08	0·092

For the system *n*-butanol+benzene the values used were:

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−4·88	−1·23	−1·18	+3·76	0·094	0·092.

V. DISCUSSION

The excess free energy data were fitted by the method of least squares to equation (**1**)

$$G^E_x=x_1x_2[a+b(x_1-x_2)+c(x_1-x_2)^2]. \qquad \ldots\ldots\ldots\ldots \quad (\mathbf{1})$$

For the system *n*-~~butanol~~ propanol+benzene at 45·00 °C the values of the constants (cal/g-mol) and the standard deviation of the fit (σ) were:

a	b	c	σ
+949·2	−224·2	+136·6	1·9 .

These values do not indicate separation into two liquid phases. The thermodynamic consistency of the data was tested by the method used previously, Brown and Smith (1954) and found to be satisfactory; the ratio of areas above and below datum on a plot of $\mu^E_1-\mu^E_2$ against x_1 was 1·03. Errors in G^E_x due to errors in the directly measured quantities were estimated to be ±3·5 cal/mol. Values of G^E_x at 40 °C were calculated from the data of Lee (1931), these were about 4 per cent. higher than the values given here. Values of G^E_x were also calculated from the less accurate data of Schmidt (1926) at 20 and at 40 °C using the method of Barker (1953). These data give values of G^E_x at $x_1=0{\cdot}5$ of 270 cal/mole at 20 °C and 280 cal/mole at 40 °C compared with the value of 237·3 at 45 °C found in this work.

For the system *n*-butanol+benzene at 45·00 °C the values of the constants obtained by fitting the excess free energy data to equation (**1**) were:

a	b	c	σ
+861·5	−250·3	+142·5	1·8.

In the test for thermodynamic consistency the ratio of the areas was 1·04 and the errors in G_x^E due to those in the measured quantities were estimated to be ±3 cal/mole at $x_1=0\cdot2$ and ±7 cal/mole at $x_1=0\cdot8$. Values of G_x^E calculated from the data of Allen, Lingo, and Felsing (1939) for this system at 25 °C are about 20 per cent. higher than those given here.

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6

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THERMODYNAMIC PROPERTIES OF ALCOHOL SOLUTIONS

THE SYSTEM ETHANOL + CARBON TETRACHLORIDE

Reprinted from the *Faraday Society Discussion*, 1953, No. 15

THERMODYNAMIC PROPERTIES OF ALCOHOL SOLUTIONS

THE SYSTEM ETHANOL + CARBON TETRACHLORIDE

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Received 21*st January*, 1953

New liquid-vapour equilibrium data for the system ethanol + carbon tetrachloride are presented and used to derive values of the changes in free energy, heat and entropy on mixing. These results are then used for further examination of a theory of solutions of alcohols.

A theory of solutions containing alcohols previously developed by one of us[1] was applied to the system methanol + carbon tetrachloride. For a further examination of the theory it appeared desirable to compare systems in which different alcohols were dissolved in the same non-polar solvent. Liquid-vapour equilibrium measurements were therefore made on the system ethanol + carbon tetrachloride.

Equilibrium concentrations and pressures were measured at 45° C and 65° C and used to derive values for the free energy, heat and entropy changes on mixing. The thermodynamic functions were then compared with corresponding values calculated for a lattice model in which the alcohol molecules have different kinds of contact points representing hydroxyl hydrogen, oxygen and hydrocarbon parts of alcohol molecules.

EXPERIMENTAL

The liquid-vapour equilibrium data for this system were measured at 45·00° C and 65·00° C using the equilibrium still described by Brown.[2] Pressure and temperature measurements were made by the methods of Brown and Ewald [3] and the liquid and condensed vapour samples were analyzed by density measurements.

PURIFICATION AND PHYSICAL PROPERTIES OF LIQUIDS.—The column described by Brown and Ewald [4] was used with a total reflux trap to fractionate technical-grade absolute alcohol until all water and benzene had been removed, as shown by boiling point and u.-v. absorption measurements. The fractionation of ethanol was continued at a reflux ratio of 100/1. The product was dried over aluminium ethylate and sealed in flasks in an atmosphere of carbon dioxide.

Analytical-grade carbon tetrachloride was shaken with alcoholic potassium hydroxide, concentrated sulphuric acid, alkaline permanganate, dried over anhydrous calcium chloride and fractionated using the same column operating at a reflux ratio of 70/1. The properties of the purified liquids are shown in table 1.

The vapour pressures P_1 and P_2 of the components were measured in the equilibrium still at intervals of approximately 20 mm Hg from 90 to 770 mm Hg. The data were fitted by the method of Willingham *et al.*[5] to the Antoine equation,

$$\log_{10} P = A - B/(C + t),$$

where P is in standard mm Hg and t in degrees centigrade. The values of the constants found and the standard deviation, σ, of the fit are also given in table 1, together with the calculated vapour pressures at 45·00° C and 65·00° C.

TABLE 1.—PROPERTIES OF COMPONENT LIQUIDS

property	ethanol	carbon tetrachloride
d_4^{25}	0·78511	1·58429
n_D^{25}	1·3596	1·4578
b.p./760 mm	78·29	76·65
Antoine equation constants A	8·11219	6·85906
Antoine equation constants B	1592·19	1196·60
Antoine equation constants C	226·062	224·138
σ mm Hg	0·16	0·21
v.p. 45° mm Hg	173·09	258·84
v.p. 65° mm Hg	438·42	525·48

ANALYTICAL METHOD.—The compositions of the liquid and condensed vapour samples were determined from density measurements as described previously for the system carbon tetrachloride + cyclohexane.[3] Nineteen mixtures of known composition were used to determine the values of the constants in eqn. (1) which expresses the change in specific volume on mixing as a function of the mole fractions of alcohol x_1 and carbon tetrachloride x_2.

$$\Delta = -\,x_1x_2[0{\cdot}002277 + 0{\cdot}00916\,(x_1 - x_2) + 0{\cdot}00466\,(x_1-x_2)^2+0{\cdot}00830\,(x_1-x_2)^3]. \quad (1)$$

The standard deviation in fitting these data was 0·00010 in Δ. In table 2 are shown the mole fractions of alcohol, the densities and refractive indices of the mixtures and the percentage volume change on mixing at 25·00° C calculated from the fitted values of Δ from eqn. (1).

Equilibrium data.—The results of the equilibrium measurements are shown in table 3 (45° C) and in table 4 (65° C). These tables give the mole fractions of alcohol in the liquid x_1 and in the vapour y_1, the total pressure P and the relative volatility α calculated from eqn. (2)

$$\alpha = y_1 x_2 / y_2 x_1. \tag{2}$$

The results show that an azeotrope is formed at 45° when $x_1 = 0{\cdot}324$ and with a total pressure of 351·1 mm Hg, while at 65° the values are $x_1 = 0{\cdot}393$ and $P = 760{\cdot}5$ mm Hg.

Table 2.—Density and refractive index of mixtures

x_1	d_4^{25}	n_{D}^{25}	$100\,V^m/V^\circ$
0·0000	1·58429	1·4578	0·0
0·0516	1·55779	1·4540	+ 0·061
0·1083	1·52845	1·4504	+ 0·089
0·1490	1·50658	1·4477	+ 0·091
0·1925	1·48245	1·4447	+ 0·080
0·2545	1·44660	1·4402	+ 0·057
0·2970	1·42133	1·4371	+ 0·037
0·3288	1·40134	1·4348	+ 0·020
0·3836	1·36619	1·4303	− 0·010
0·4412	1·32638	1·4256	− 0·041
0·4999	1·28451	1·4201	− 0·073
0·5433	1·25102	1·4162	− 0·096
0·6028	1·20361	1·4105	− 0·127
0·6462	1·16671	1·4060	− 0·148
0·6969	1·12152	1·3994	− 0·168
0·7662	1·05527	1·3924	− 0·183
0·8038	1·01687	1·3873	− 0·183
0·8547	0·96217	1·3808	− 0·168
0·8919	0·91999	1·3758	− 0·144
0·9459	0·85506	1·3678	− 0·087
1·0000	0·78511	1·3596	0·0

Derived thermodynamic functions.—The excess chemical potentials μ_1^E and μ_2^E and the excess free energy of mixing G_x^E were calculated from the equilibrium data using eqn. (3), (4) and (5). The values obtained are also shown in tables 3 and 4.

$$\mu_1^E = RT \ln (Py_1/P_1x_1) + (\beta_{11} - V_1)(P - P_1) + P\delta_{12}y_2^2, \tag{3}$$

$$\mu_2^E = RT \ln (Py_2/P_2x_2) + (\beta_{22} - V_2)(P - P_2) + P\delta_{12}y_1^2, \tag{4}$$

$$G_x^E = x_1\mu_1^E + x_2\,\mu_2^E, \tag{5}$$

Table 3.—Experimental data and derived functions at 45° C

x_1	y_1	P mm Hg	α	μ_1^E cal/mole	μ_2^E cal/mole	G_x^E cal/mole
0·0459	0·2178	328·31	5·79	1388·0	22	85
0·1015	0·2649	342·23	3·19	1034·0	47	147
0·1924	0·2981	348·98	1·78	716·0	98	217
0·2912	0·3178	350·97	1·13	498·0	166	262
0·3950	0·3356	350·47	0·774	338·0	249	284
0·4069	0·3369	350·51	0·741	322·0	260	285
0·5155	0·3577	346·88	0·523	203·0	361	280
0·6095	0·3823	339·65	0·397	126·0	460	257
0·7264	0·4335	321·69	0·288	60·0	597	207
0·8362	0·5269	286·53	0·218	22·0	737	139
0·8984	0·6244	253·77	0·188	8·2	818	91
0·9644	0·8137	205·65	0·161	−0·2	909	32
0·9788	0·8790	192·73	0·157	−1·2	924	18

where P is the total pressure, P_1 and P_2 are the vapour pressures of the pure components, β is the second virial coefficient in the equation of state and V_1 and V_2 are the liquid molar volumes.

$$\delta_{12} = 2\beta_{12} - \beta_{11} - \beta_{22}\,;\ T^\circ\,\mathrm{K} = t^\circ\,\mathrm{C} + 273{\cdot}16\,;\ 1\ \mathrm{cal} = 4{\cdot}1840\ \mathrm{joule\ (abs).}$$

Values of the second virial coefficient for ethanol, β_{11}, were determined from the experimental heat of vaporization data of Fiock, Ginnings and Holton [6] and the values of the constants in the Antoine equation given above. They were approximately 5 % less than values determined by corresponding states from virial coefficient data of Lambert [7] on methanol. The values of the virial coefficients for carbon tetrachloride were calculated from the Berthelot equation. Values of β_{12} were calculated by the method of Scatchard and Ticknor.[8] The liquid molar volumes of the components were calculated from density data given by Timmermanns.[9] The values used are shown in table 5.

TABLE 4.—EXPERIMENTAL DATA AND DERIVED FUNCTIONS AT 65° C

x_1	y_1	P mm Hg	α	μ_1^E cal/mole	μ_2^E cal/mole	G_x^E cal/mole
0·0517	0·2312	678·54	5·52	1300·0	26	94
0·1039	0·2987	721·28	3·68	1042·0	43	147
0·1977	0·3427	748·32	2·12	724·0	98	222
0·2960	0·3700	757·36	1·40	511·0	166	268
0·3913	0·3903	759·79	0·996	361·0	244	290
0·4007	0·3908	760·82	0·959	346·0	255	291
0·5076	0·4159	756·18	0·691	225·0	355	289
0·5995	0·4424	745·46	0·530	145·0	454	268
0·6999	0·4878	720·63	0·409	83·0	570	229
0·7075	0·4917	716·86	0·400	78·0	579	224
0·7123	0·4942	716·91	0·395	77·0	586	223
0·8255	0·5794	657·86	0·291	27·0	744	153
0·8939	0·6730	595·71	0·244	9·1	847	98
0·9596	0·8327	508·51	0·210	1·2	945	39
0·9763	0·8925	481·24	0·202	0·3	970	23

TABLE 5.—VALUES OF VIRIAL COEFFICIENTS AND MOLAR VOLUMES IN LITRES

	45° C	65° C
β_{11}	− 1·970	− 1·620
β_{22}	− 1·235	− 1·087
β_{12}	− 0·945	− 0·830
δ_{12}	1·315	1·048
V_1	0·060	0·061
V_2	0·100	0·102

The excess free energy data at 45° C and at 65° C were fitted separately by the method of least squares to eqn. (6).

$$G_x^E = x_1x_2[a + b(x_1 - x_2) + c(x_1 - x_2)^2 + d(x_1 - x_2)^3]. \tag{6}$$

The values of the constants and the standard deviation of the fit were (in cal/mole)

constant	45° C	65 67° C
a	+ 1120·9	+ 1151·5
b	− 218·0	− 208·0
c	+ 275·0	+ 254·0
d	− 291·0	− 240·0
σ	3·0	3·0

Values of the total free energy of mixing were also calculated and plotted against x_1 to show that eqn. (6) did not indicate separation into two liquid phases.

The heat of mixing and the excess entropy of mixing at 45° C were determined on the assumption that G^E_x varied linearly with temperature. They were given as functions of composition by eqn. (7) and (8).

$$H^M_x = x_1x_2[633 - 390\,(x_1 - x_2) + 610\,(x_1 - x_2)^2 - 1100\,(x_1 - x_2)^3], \tag{7}$$

$$TS^E_x = x_1x_2\,[-\,488 - 170\,(x_1 - x_2) + 330\,(x_1 - x_2)^2 - 810\,(x_1 - x_2)^3]. \tag{8}$$

Values of G^E_x, H^M_x and TS^E_x at 45° C were calculated from eqn. (6), (7) and (8) and are compared below with the corresponding theoretical results.

THERMODYNAMIC CONSISTENCY AND ERRORS.—The thermodynamic consistency of the data was checked by the method of Kretschmer and Wiebe [10] and found to be satisfactory. The magnitudes of the errors in the derived functions were estimated assuming the following errors in the measured quantities: 0·0001 g in weighing, 0·00005 g/ml in density, 0·05 mm Hg in the pressure, 0·015° in the temperature and 50 ml in the virial coefficients. The average errors in the derived quantities at 45° C were found to be 1·5 cal/mole in G^E_x and 45 cal/mole in H^M_x and TS^E_x.

STATEMENT OF THEORY.—The theoretical treatment used here follows that previously published.[1] It is based on the usual lattice model, generalized, however, to allow a molecule to have contact points of several types, such that contact points of one type have a definite interaction energy with those of another type. Thus an alcohol (A) molecule is assumed to have one H contact point, two O contact points and $(q_Az - 3)$ I contact points, representing respectively hydroxyl hydrogen, oxygen and hydrocarbon parts of the molecule. Here q_Az is the total number of contact points on the molecule, given for a molecule occupying r_A sites on a z-coordinated lattice by

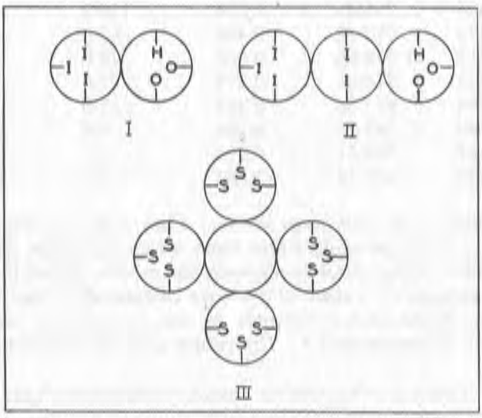

FIG. 1.—Geometrical models for molecules.
I. methanol; II. ethanol; III. carbon tetrachloride.

$$q_Az = r_Az - 2r_A + 2.$$

The non-polar solvent molecule (S) is assumed to have only one type of contact point. These models are illustrated in fig. 1.

The interactions considered are the hydrogen bond H—O, of strength U_1; a non-specific interaction, effective for all alcohol-solvent contacts, of strength U_3; and an additional specific interaction between hydroxyl hydrogen and solvent molecule, of strength U_2 (thus the energy of an H—S contact is $U_2 + U_3$). The energies U_1, U_2, U_3 do not represent the *total* interaction energies; U_1, for example, is the difference between the energy of an H—O contact and the arithmetic mean of the energies of H—H and O—O contacts. Of the remaining interactions, those between identical contact points are made to vanish by the choice of energy zero, and the H—I and O—I interactions are neglected for reasons of simplicity.

It has been shown [1] that for this model the excess chemical potentials and the heat of mixing are given by eqn. (9*a*), (9*b*) and (10). The parameters X_H . . . X_S are defined as solutions of eqn. (11), and $X_H^1 \ldots X_S^1$ are solutions of the corresponding equations for the pure components. The notation η_i has been used for exp $(-U_i/kT)$, with $i = 1, 2, 3$.

$$\mu_A^E = RT\Big[\ln (X_H/x_AX_H^1) + 2\ln (X_O/x_AX_O^1) + (q_Az - 3)\ln (X_I/x_AX_I^1) + (\tfrac{1}{2}z - 1)r_A \ln\Big(\frac{r_Ax_A + r_Sx_S}{r_A}\Big)\Big], \tag{9a}$$

$$\mu_S^E = RT\Big[q_Sz\ln (X_S/x_SX_S^1) + (\tfrac{1}{2}z - 1)r_S\ln\Big(\frac{r_Ax_A + r_Sx_S}{r_S}\Big)\Big], \tag{9b}$$

$$H_x^M = -2RT[(X_HX_O - x_AX_H^1X_O^1)\eta_1\ln\eta_1 + X_HX_S\eta_2\ln\eta_2 + X_S(\eta_2X_H + X_O + X_I)\eta_3\ln\eta_3], \tag{10}$$

$$\left.\begin{aligned} X_H[X_H + \eta_1X_O + X_I + \eta_2\eta_3X_S] &= x_A/2 \\ X_O[\eta_1X_H + X_O + X_I + \eta_3X_S] &= x_A \\ X_I[X_H + X_O + X_I + \eta_3X_S] &= (q_Az - 3)x_A/2 \\ X_S[\eta_2\eta_3X_H + \eta_3X_O + \eta_3X_I + X_S] &= q_Szx_S/2 \end{aligned}\right\} \tag{11}$$

The values $z = 4$, $r_A = 2$ for methanol and 3 for ethanol, and $r_S = 5$ for carbon tetrachloride, have been used throughout.

NUMERICAL RESULTS.—For comparison with the present results on ethanol + carbon tetrachloride, interaction energies were determined which fitted the data of Scatchard and Ticknor[8] on methanol + carbon tetrachloride more accurately than the values previously used.[1] For a given value of U_1, U_2 was determined to give TS_x^E correctly for the equimolar mixture at 35° C, and U_3 was then determined to give G_x^E correctly for the equimolar mixture. The resulting values of U_1, U_2 and U_3 then fitted the data satisfactorily over the whole composition range. Several sets of values of U_1, U_2 and U_3, which fitted the data equally well, are shown in table 6. Clearly the data determine $(U_1 - U_2)$ and U_3, but not U_1 and U_2. Later calculations were therefore simplified by proceeding as if U_2 was zero. The extent of the agreement between experimental values for methanol + carbon tetrachloride at 35° C and theoretical values calculated with the interaction energies of table 6 is shown in fig. 2.

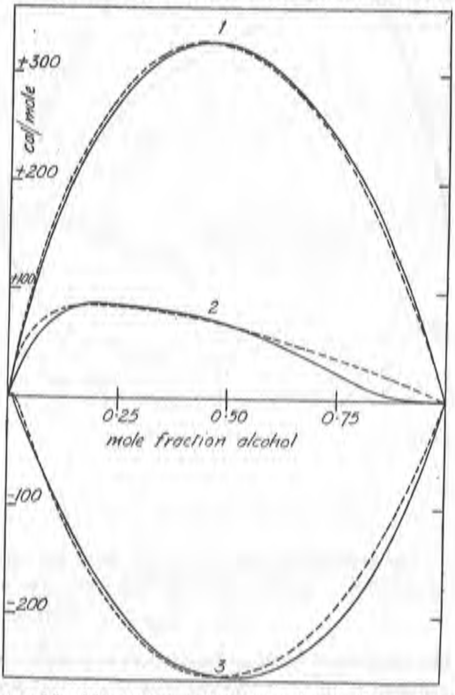

FIG. 2.—Comparison of experimental and theoretical results for methanol + carbon tetrachloride at 35° C.

Experimental values (solid curves) of Scatchard and Ticknor,[8] theoretical values (dotted curves) calculated for $U_1 = -3520$ cal/mole, $U_2 = 0$, $U_3 = 4{\cdot}7$ cal/mole.

1. G_x^E; 2. H_x^M; 3. TS_x^E.

TABLE 6.—INTERACTION ENERGIES FOR METHANOL + CARBON TETRACHLORIDE

U_1 (cal/mole)	U_2 (cal/mole)	U_3 (cal/mole)	$U_1 - U_2$ (cal/mole)
− 3520	0	4·7	− 3520
− 4000	− 477	4·6	− 3523
− 5000	− 1466	4·7	− 3534
− 6000	− 2463	4·6	− 3537

It was hoped that these same interaction energies might give reasonable agreement with the experimental results for ethanol + carbon tetrachloride. The extent to which this is so is shown in fig. 3. The differences between experimental and theoretical results are, for the equimolar mixture: in G_x^E, 18 cal/mole compared with the estimated experimental error of 1·5 cal/mole, and in H_x^M and TS_x^E respectively 78 cal/mole and 96 cal/mole, compared with the estimated experimental error of 45 cal/mole.

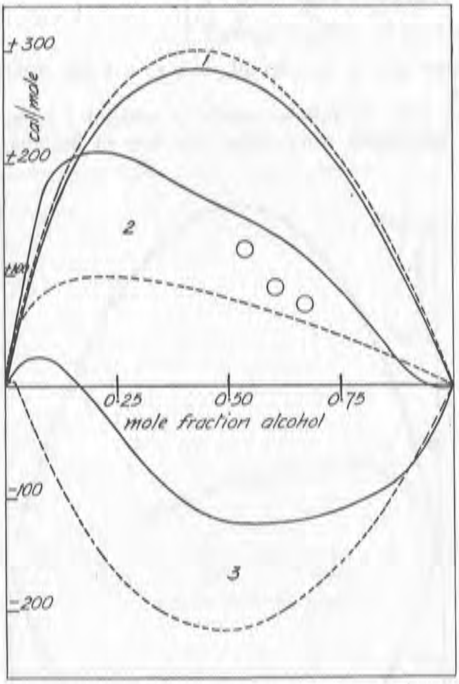

FIG. 3.—Comparison of experimental and theoretical results for ethanol + carbon tetrachloride at 45° C.

Experimental values (solid curves) from eqn. (6), (7), (8); theoretical values (dotted curves) calculated for methanol interaction energies,

$$U_1 = -3520 \text{ cal/mole}, \quad U_2 = 0, \quad U_3 = 4{\cdot}7 \text{ cal/mole}.$$

1. G_x^E; 2. H_x^M; 3. TS_x^E.

Circles represent results of calorimetric measurements of heat of mixing at 45·0° C.

The interaction energies which gave the most satisfactory fit of the experimental data for ethanol + carbon tetrachloride were also determined. They were

$$(U_1 - U_2) = -2750 \text{ cal/mole}, \quad U_3 = 9{\cdot}4 \text{ cal/mole}.$$

The agreement between theoretical and experimental results with these interaction energies is shown in fig. 4. The value of $(U_1 - U_2)$ depends strongly on the value of TS_x^E, and so is likely to be considerably in error. There is, however, a significant difference between the values found with methanol and with ethanol.

The values found for $(U_1 - U_2)$ are smaller than the usual estimates of hydrogen-bond strengths. Thus Mecke and Nückel,[11] on the basis of spectroscopic data, estimate 4,700 cal/mole for methanol in carbon tetrachloride. This value, however, is probably dependent on the method used for interpreting the data.

If our description of the molecular interactions is correct, U_3 should represent approximately the interaction between carbon tertachloride and a non-aromatic hydrocarbon. Values of G_x^E were therefore calculated for a binary solution in which both molecules occupied five lattice sites, the interaction energy between unlike molecules having the value 4·7 cal/mole in the first instance, and 9·4 cal/mole in the second instance. For the equimolar mixture at 40° C the values of G_x^E found were 14 cal/mole and 28 cal/mole respectively. The corresponding value for the system cyclohexane + carbon tetrachloride is given by Scatchard [12] as 16 cal/mole. The similarity of this value with the above calculated values suggests that our interpretation of the interactions in the alcohol solutions is reasonable.

DISCUSSION

For the two systems methanol + carbon tetrachloride and ethanol + carbon tetrachloride, if the interaction energies $(U_1 - U_2)$ and U_3 are chosen so that the theoretical and experimental values of G_x^E, H_x^M and TS_x^E agree for the equimolar mixture, then the theoretical and experimental values are in reasonable agreement over the whole composition range. In view of the complicated unsymmetrical behaviour of the thermodynamic functions, this is very satisfactory.

The values of $(U_1 - U_2)$ are reasonable, though smaller than usual estimates of hydrogen-bond strengths. The values of U_3 are similar to the value that could have been estimated from the behaviour of the system carbon tetrachloride + cyclohexane. However, it is not possible satisfactorily to fit both alcohol systems with a single set of interaction energies. This fact is probably due to a combination of several of the following factors: (i) experimental errors, (ii) inadequacy of the geometrical models, (iii) insufficient detail in the interactions considered, (iv) inadequacy of the quasichemical approximation, (v) neglect of vibrational, or free-volume contributions, (vi) neglect of long-range interactions, (vii) the possibility that the molecular interactions are in fact different in the two systems.

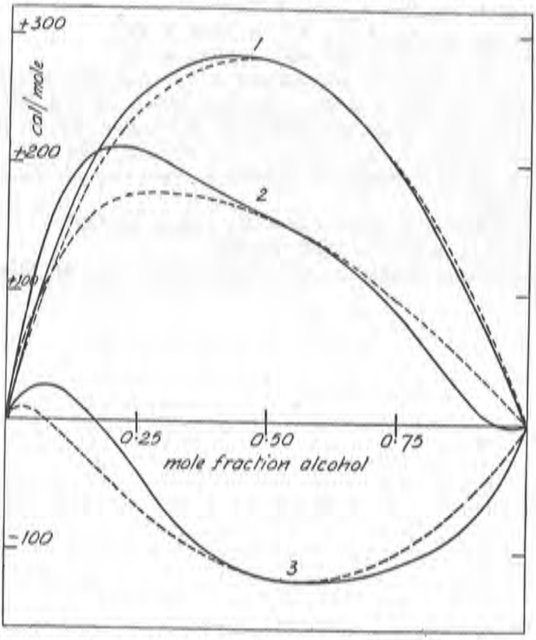

FIG. 4.—Comparison of experimental and theoretical results for ethanol + carbon tetrachloride at 45° C.

Experimental values (solid curves) from eqn. (6), (7), (8); theoretical values (dotted curves) calculated for $U_1 = -2750$ cal/mole, $U_2 = 0$, $U_3 = 9{\cdot}4$ cal/mole.

1. G_x^E; 2. H_x^M; 3. TS_x^E.

It is hoped to remove the first of these possibilities by making calorimetric measurements of the heat of mixing for ethanol + carbon tetrachloride,* and to investigate the seventh by making measurements on ethanol + benzene, for comparison with the results of Scatchard [8] on methanol + benzene, and on systems containing higher alcohols.

The authors thank Mr. W. Fock for his help with curve-fitting of vapour pressures and calculation of virial coefficients, Mr. O. H. Rigby for his help with purification of liquids, and Mr. J. P. Shelton for ultra-violet absorption measurements.

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* The results of three preliminary calorimetric measurements of the heat of mixing at 45° C of this system are shown as circles in fig. 3. They are just within the estimated uncertainty of the values derived from free energy measurements, but are uniformly lower than these values. It therefore seems probable that part of the apparent difference in interaction energies between the methanol and ethanol systems is due to experimental error in the heat of mixing values derived from the free energy measurements.

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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 8, NUMBER 3, PAGES 361-369, 1955

HEATS OF MIXING OF ALCOHOL SOLUTIONS

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Reprinted for
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HEATS OF MIXING OF ALCOHOL SOLUTIONS

By I. Brown* and W. Fock*

[*Manuscript received March* 21, 1955]

Summary

A calorimeter for the measurement of the heats of mixing of binary liquid systems at temperatures from 20 to 45 °C is described.

Heats of mixing have been measured for approximately equimolar mixtures of benzene+carbon tetrachloride at 25 °C, benzene+ethylene dichloride at 25 °C, acetone+chloroform at 25 °C, and ethanol+carbon tetrachloride at 45 °C. Measurements have been made at intervals over the whole composition range of the systems ethanol+2,2,4-trimethylpentane at 25 °C and ethanol+benzene at 45 °C.

I. Introduction

The accurate determination of heats of mixing at elevated temperatures was required for a study of the thermodynamic properties of binary mixtures of alcohols and polar liquids. Measurements become more difficult as the temperature is raised owing to the increased vapour pressure and the expansion of the liquids. Temperatures up to 45 °C were chosen so that the heats of mixing could be measured without undue difficulty.

For accurate measurements using reasonably small quantities of material, it is desirable to eliminate the latent heat effect due to evaporation and that due to a change in vapour composition on mixing. It is also necessary to keep exchange of heat between the calorimeter and its surroundings to a minimum. The bell type of apparatus used by Tompa (1952), the U tube type used by Scatchard *et al.* (1952) and Thacker and Rowlinson (1954), and the apparatus of Cheesman and Whitaker (1952) have been designed to overcome one or more of these difficulties. Adcock and McGlashan (1954) have recently described an apparatus of the bell type which gives accurate results over a wide range of temperatures and uses small quantities of liquid.

The apparatus described here is of the U tube type, using mercury to separate the liquids to be mixed and two expansion capillaries of the type used by Cheesman and Whitaker (1952) to prevent mixing of the vapour phases. Temperature changes are measured with a thermistor, and thermal insulation is provided by a high vacuum.

II. Apparatus

The assembly of the apparatus is shown diagrammatically in Figure 1, the whole being installed in a constant temperature room held at 20±0·2 °C. The mixing cell *A* is mounted on a pinion shaft *B*, which passes through a double

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* Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

Wilson seal in the back of a cast aluminium alloy vacuum box *C*, having a heavy brass cover *D*. The box is mounted in a thermostat bath *E* filled with high-flashpoint " Kerosene ", which is maintained at the desired temperature to $\pm 0\cdot005$ °C ; fluctuations within the box itself are considerably less. The aluminium box is evacuated at *G* by a 4 in. diameter oil diffusion pump which reduces the pressure in the box to less than $0\cdot05\mu$. All " Hycar " or " Neoprene " vacuum gaskets are rectangular in section and fitted into carefully lapped grooves. The cell contents are mixed and stirred by the oscillating mechanism *F* which consists of a synchronous motor driving a rack and pinion through a reduction gear and crank. The shaft is oscillated through an angle of 220° at a frequency of 4·5 c/min.

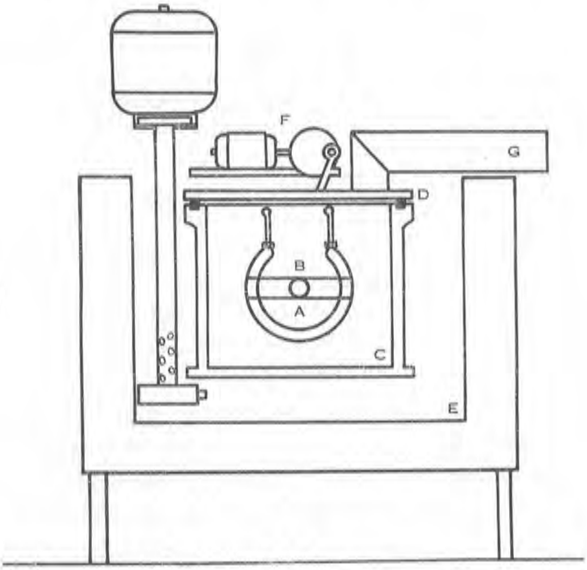

Fig. 1.—Assembly of apparatus.

The mixing cell is shown in Figure 2. It is made from 16 mm diameter stainless steel tube with screwed outlets welded to each end. These are closed by 1·0 mm internal diameter glass capillaries mounted in conical collars and attached by mild steel union nuts. A 0·75 mm " Teflon " gasket between the polished metal and glass surfaces provides a seal. These gaskets are sliced from a machined " Teflon " tube on a lathe by a razor, as striations in peeled " Teflon " sheet permit leakage into the vacuum system. The thermistor is mounted, just clear of the bottom, in a stainless steel pocket welded into the cell. A few drops of silicone oil in this pocket improve thermal conduction.

All protuberances are kept as small as possible and made of high thermal conductivity material to ensure rapid temperature equalization of the cell and its contents.

The lower half of the cell is coated with " Araldite " synthetic resin, over which the 12Ω heater is wound non-inductively from 116 cm of 0·25 mm silkcovered manganin wire. A further coat of " Araldite " separates the heater from a layer of copper foil strip wound around it to improve the heat conduction into the cell.

The cell is mounted in a cradle of glass fibre sheet bonded with synthetic resin and is surrounded by a loose radiation shield of thin aluminium foil.

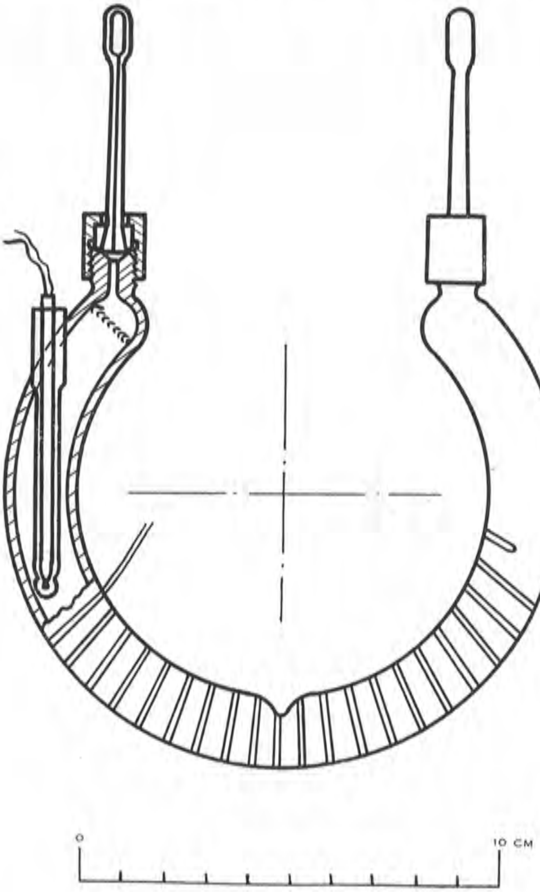

Fig. 2.—Mixing cell.

Flexible electrical leads connect the thermistor and heater to a six-pin connector under the vacuum box lid, whence connections to the external circuits are made through glass-metal seals soldered into the lid.

The thermistor used is a S.T.C. type F1512/300, having a resistance of 104,000Ω at 25 °C and 45,000Ω at 45 °C. The resistance measuring circuit consists of a Wheatstone bridge, one arm of which contains the thermistor, a 10,000Ω decade box, and a microammeter in series. The current through this arm is preset to 20 μA at balance by altering the voltage applied to the bridge, this low value is chosen to minimize the heating effect in the thermistor bead while still giving sufficient sensitivity. The detector is a reflecting galvanometer with a sensitivity of 1500 mm/μA at 1 m. Overall sensitivity is 1 to 2Ω/mm.

The heater circuit is shown in Figure 3. Both the cell heater H and the dummy heater D are wound from 116 cm of 0·25 mm diameter manganin wire and have a resistance of 11·866Ω at 25 °C, and 11·868Ω at 45 °C. The dummy heater is mounted in the thermostat bath. A steady direct current is supplied by a lead-acid accumulator. The heater current is evaluated by measuring the potential across a calibrated standard 2Ω resistance R using a Tinsley portable potentiometer P. A double-pole, double-throw mercury switch S is used to substitute the cell heater for the dummy and also to start and stop an electronic interval timer T. The timer is comprised of six Eccles-Jordan trigger circuits, the last of which operates a mechanical indicator. The interval timer can measure intervals to $\pm 0 \cdot 02$ sec; it is operated from the power mains at a frequency of 50 c/s.

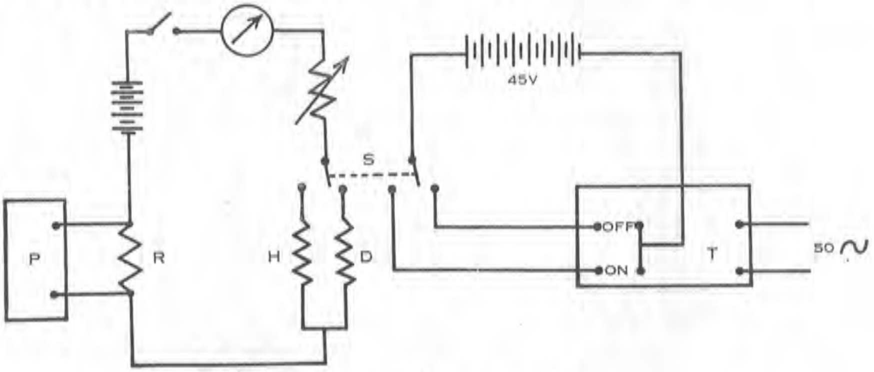

Fig. 3.—Heater circuit.

III. Purification of Liquids

The purification and physical properties of the ethanol, benzene, and carbon tetrachloride have been described previously (Brown and Smith 1954*a*, 1954*b*). Analar chloroform and ethylene dichloride were washed with dilute sodium carbonate solution and with water, and were then fractionally distilled. Analar acetone was fractionally distilled and the middle fraction dehydrated by the method of Thirion and Craven (1952).

A batch of 95 per cent. pure 2,2,4-trimethylpentane was shaken with concentrated sulphuric acid, washed with dilute sodium carbonate solution and water, and fractionally distilled.

The densities and refractive indices of the liquids used are shown in Table 1.

IV. Experimental Procedure

The mixing cell is filled by means of a hypodermic syringe with a bent needle. A charge of 170 g of mercury is used for most experiments except those where large heats of mixing are encountered, when about twice this amount is used. The cell is weighed after the mercury and each component have been introduced. When working at elevated temperatures a calculated amount of each component is removed after preliminary weighing to allow for thermal expansion and the cell is then reweighed. The weight of each component can be measured to ±10 mg.

After filling, the cell is mounted on the pinion shaft in the vacuum box and all electrical connections are made. After allowing the cell to reach operating temperature (about 2 hr) the vacuum box is evacuated by the roughing pump and left overnight with a current of 20μA flowing through the thermistor circuit. The box is further evacuated using the diffusion pump, which after an hour reduces the pressure to below 0·05μ. A further period of 2 hr is allowed for thermistor stabilization ; a current of from 0·1 to 0·2 A flowing in the dummy circuit allows the heater current to stabilize.

At the start of the run the bridge is balanced with about 5000Ω in series with the thermistor, further balancing being done by altering this series resistance. Readings are taken at 1 min intervals. At 5 min, the cell oscillating mechanism is set in motion, and further readings of the resistance are taken every minute.

Table 1

PHYSICAL PROPERTIES OF COMPONENT LIQUIDS

Liquid	n_D^{25}	d_4^{25}
Ethanol	1·35929	0·78511
Benzene	1·49803	0·87364
Carbon tetrachloride ..	1·45734	1·58435
Chloroform	1·44329	1·4807~~3~~7
Ethylene dichloride	1·44228	1·245~~46~~50
Acetone	1·35599	0·78501
2,2,4-Trimethylpentane ..	1·38908	0·68778

At 25 min, current is passed through the cell heater for a period of from ½ to 3 min depending on the mixture, and resistance readings taken for a further 20 min. During the heating period the potential across the standard resistance is measured by the potentiometer.

When the cell is charged with pure liquids the mol fraction of the resulting mixture is in the range 0·4 to 0·6. To obtain mixtures with higher or lower mol fractions, one side of the cell is filled with a mixture whose heat of mixing is known from a previous run.

For systems with a negative heat of mixing two procedures have been used. The first is similar to that used normally. The second is done in two stages : the resistance change on mixing is determined first, and the cell allowed to regain its equilibrium temperature overnight ; the oscillation is then continued and the resistance change on heating determined in the usual manner. The two methods showed no significant difference in their results.

V. Calculations

For a mixture with positive heat of mixing, Figure 4 records a typical set of measurements of resistance at different times.

To determine the resistance change on mixing, a point D is chosen 10 min after mixing commences, and the line ED extrapolated to intersect a vertical line through B at C. The resistance change on heating is found in a similar way by extrapolating to the vertical line corresponding to the cessation of the heat input. The temperatures corresponding to the points B, C, E', and F were found from a calibration of the thermistor, and were used to determine the temperature changes on mixing and heating: K and L degrees respectively. The heat of mixing in absolute joules per g mol of mixture is then given by:

$$H^M = KI^2R\theta/LM,$$

where I is the heater current and R its resistance, θ the duration of current flow through the heater, and M is the total number of moles of the mixture.

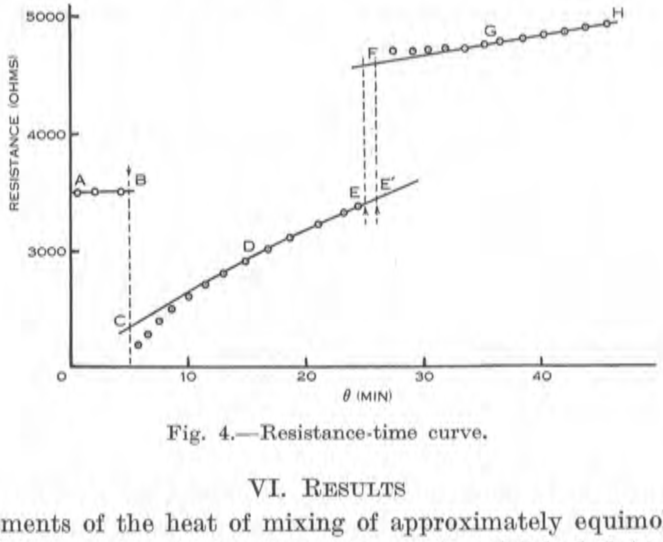

Fig. 4.—Resistance-time curve.

VI. RESULTS

Measurements of the heat of mixing of approximately equimolar mixtures of three systems were made for comparison with published data. To enable this to be done at the experimental mol fractions, graphs of published values of H^M/x_1x_2 were drawn and the values read off at the required concentrations. In all cases x_1 represents the mol fraction of the first mentioned component.

(a) *Benzene and Carbon Tetrachloride*

Author	Temperature (°C)	H^M (J/mol) at $x_1=$		
		0·567	0·576	0·580
Present work	25·0	107	110	110
Cheesman and Whitaker (1952)	24·7	106	106	106
Hirobe (1926)	25·0	105	105	105
Boissonas and Cruchard (1944)	25·0	108	108	108

The temperature variation of the heats of mixing of this system is illustrated by these results and those of Cheesman and Whitaker (1952) at 17·8 °C, Schulze (1951) at 15 °C, and Scatchard, Wood, and Mochel (1940) at 55 °C. In comparison with these, the results of Vold (1937) at 25 °C are low, while those of Baud (1915) at 15 to 20 °C and Schmidt (1926) at 18 °C are high.

(*b*) *Benzene and Ethylene Dichloride*

Author	Temperature (°C)	H^M (J/mol) at $x_1 =$	
		0·525	0·526
Present work	25·0	63·3	61·6
Cheesman and Whitaker (1952)	24·7	60·1	60·1
Korvezee, Ruiter, and Stuyts (1953)	24·7	60·5	60·5

(*c*) *Acetone and Chloroform*

Author	Temperature (°C)	H^M (J/mol) at $x_1 =$	
		0·467	0·474
Present work	25·0	—2000	—1965
Hirobe (1926)	25·0	—1955	—1950
Schmidt (1926)	14·0	—2280	—2280

The values of Carroll and Mathews (1924) at 60 °C when plotted as H^M/x_1x_2 are not self-consistent.

(*d*) *Ethanol and Carbon Tetrachloride at 45·0 °C*

x_1	H^M (J/mol)
0·537	511*
0·550	480
0·605	368*
0·671	273

* Previously reported : *Disc. Faraday Soc.* **15** : 142 (1953).

(e) *Ethanol and 2,2,4-Trimethylpentane at 25·0 °C*

x_1	$H^M(a)$ (J/mol)	$H^M(b)$ (J/mol)
0·117	537	887
0·233	645	1004
0·425	661	975
0·703	491	690
0·783	405	544
0·869	289	355
0·950	134	113

$H^M(a)$ are the values obtained in this work, while those shown in comparison are calculated from the excess free energies of mixing obtained by Kretschmer and Wiebe (1948).

(f) *Ethanol and Benzene at 45·0 °C*

x_1	H^M (J/mol)	x_1	H^M (J/mol)
0·130	1047	0·639	920
0·189	1231	0·651	899
0·276	1298	0·653	861
0·330	1320	0·857	390
0·547	1096	0·940	173
0·549	1098		

The values of published data are compared below at 0·5 mol fraction.

Author	Temperature (°C)	H^M (J/mol)
Present work	45	1170
Pahlke (1935)	20	760
Perrakis (1925)	20	675
Vialla (1914)	20	470
Winkelmann (1873)	15	465
Winkelmann (1873)	5	410
Winkelmann (1873)	0	390

The results of Carroll and Mathews are not self-consistent ; those of Pahlke and Perrakis at 20 °C, which cover different ranges of concentration, appear to be in reasonable agreement.

VII. Errors

The maximum errors in the values of the heats of mixing due to errors in the measured quantities have been determined. For the systems *a*, *b*, *c*, and *d* the errors are approximately 3 per cent., and for the others the error is 2 per cent. at the middle of the concentration range, and 3 per cent. at the extremities. The major contribution to the error is the uncertainty in extrapolation of the resistance-time curves (about two-thirds of the error); the error due to weighing is the next most important.

VIII. Conclusion

The apparatus described is capable of yielding useful heat of mixing data at temperatures up to 45 °C. Increased accuracy could probably be obtained by the simultaneous mixing and addition of heat as used by Adcock and McGlashan (1954). The accuracy is far greater than that which could be obtained from calculations based on free energy data at two adjacent temperatures.

IX. Acknowledgments

The authors wish to thank Mr. O. H. Rigby and Mr. J. A. Barker for their help with this work, and also the members of the workshop staff who helped with the building of the apparatus.

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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 9, NUMBER 3, PAGES 364-372, 1956

THERMODYNAMIC PROPERTIES OF ALCOHOL SOLUTIONS

II. ETHANOL AND *iso*PROPANOL SYSTEMS

By I. Brown, W. Fock, and F. Smith

Reprinted for
the Commonwealth Scientific and Industrial Research Organization, Australia

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THERMODYNAMIC PROPERTIES OF ALCOHOL SOLUTIONS

II. ETHANOL AND ISOPROPANOL SYSTEMS

By I. Brown,* W. Fock,* and F. Smith*

[*Manuscript received March* 16, 1956]

Summary

New experimental data are given for the heats of mixing of the systems ethanol + toluene at 35 °C, ethanol + methyl*cyclo*hexane at 35 °C, and *iso*propanol + benzene at 45 °C and for the liquid-vapour equilibrium data for the latter system at 45 °C.

These data have been used together with previously published data to calculate the excess free energy, heat and excess entropy of mixing at even mole fractions for the above systems. These functions have also been calculated from published data for the systems ethanol + benzene at 45 °C and ethanol + 2,2,4-trimethylpentane at 25 °C.

I. Introduction

The present work forms part of a programme of measurement of the thermodynamic properties of alcohol solutions. Data for the system ethanol + carbon tetrachloride have been given in Part I of this series by Barker, Brown, and Smith (1953) and by Brown and Fock (1955).

II. Apparatus and Methods

Heats of mixing for the systems ethanol + benzene and ethanol + 2,2,4-trimethylpentane were measured previously by Brown and Fock (1955). For the other systems the methods of Brown and Fock (1956) were used.

Table 1

isopropanol + benzene

Refractive index ; composition data

x_1	$n_D^{25\cdot00}$	x_1	$n_D^{25\cdot00}$
0·0528	1·49150	0·4980	1·43899
0·1067	1·48511	0·5017	1·43853
0·2087	1·47317	0·5983	1·42681
0·3057	1·46182	0·7131	1·41256
0·3931	1·45149	0·8053	1·40083
0·4898	1·43997	0·9033	1·38805
0·4932	1·43952	0·9494	1·38189

The liquid-vapour equilibrium measurements for the system *iso*propanol + benzene were made by using the apparatus and methods of Brown and Smith (1955). The analysis was by refractive index measurements with a Hilger-Chance precision refractometer maintained at 25·00 ± 0·01 °C. The refractive index and composition data for this system are given in Table 1 ;

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they were obtained from mixtures prepared by weighing. The method of Brown and Smith (1954) was employed to calculate the composition of the liquid and vapour samples.

III. Components

The ethanol, benzene, and 2,2,4-trimethylpentane were purified by the methods described by Brown and Smith (loc. cit.) and Brown and Fock (loc. cit.). The *iso*propanol (Analar quality) was purified by distillation and was dried by azeotropic distillation with purified benzene in a 1·2 m column packed with 1·6 mm Dixon packing, operated at a reflux ratio of 50 : 1. The toluene was distilled using the same column and the centre fraction was scrubbed with concentrated sulphuric acid, washed, dried, and refractionated. The methyl*cyclo*hexane was purified in the same way as the toluene.

The density and refractive index values for the purified components are shown in Table 2.

Table 2

PHYSICAL PROPERTIES OF COMPONENTS

Component	$d_4^{25\cdot 00}$	$n_D^{25\cdot 00}$
Ethanol	0·78511	1·35928
*iso*Propanol	0·78089	1·37503
Benzene	0·87370	1·49799
Toluene	0·86224	1·49406
Methyl*cyclo*hexane	0·76515	—
2,2,4-Trimethylpentane . .	0·68778	1·38905

The vapour pressure of *iso*propanol was measured by using the equilibrium still. The vapour pressure data are shown in Table 3. These data were fitted by the method of Willingham *et al.* (1945) to the Antoine equation

$$\log P = A - \frac{B}{C+t},$$

where P is in standard mm Hg and t in °C. The values of the constants, the standard deviation σ of the fit, the calculated values of the boiling point at 760 mm Hg, and the vapour pressure at 45 °C are also given in Table 3.

Table 3

VAPOUR PRESSURE OF ISOPROPANOL

t (°C)	P (mm Hg)	Antoine Equation Constants
41·31	111·51	
44·99	135·87	$A = 7\cdot 76677$
45·18	137·44	$B = 1371\cdot 59$
49·09	168·41	$C = 198\cdot 490$
57·72	259·00	$\sigma = 0\cdot 12$ mm Hg
64·93	363·11	
70·35	462·34	B.p./760 mm Hg (°C), 82·23
75·10	566·93	V.p. 45·00 °C (mm Hg), 136·05
78·48	652·61	
82·17	758·13	
82·26	760·51	

IV. Experimental Results

(a) *Heats of Mixing*

The results of the heat of mixing measurements for the systems ethanol+toluene at 35 °C, ethanol+methyl*cyclo*hexane at 35 °C, and *iso*propanol+benzene at 45 °C are given in Tables 4, 5, and 6 respectively ; x_1 is the mole fraction of the alcohol and H^M is the heat of mixing in joules per mole (J/mol) of mixture

Table 4

HEATS OF MIXING

Ethanol+toluene 35·00 °C

x_1	H^M (J/mol)	x_1	H^M (J/mol)
0·122	859	0·676	631
0·217	983	0·681	612
0·379	998	0·691	586
0·603	738	0·873	264
0·605	740		

Table 5

HEATS OF MIXING

Ethanol+methyl*cyclo*hexane 35·00 °C

x_1	H^M (J/mol)	x_1	H^M (J/mol)
0·129	574	0·712	478
0·247	685	0·719	515
0·426	695	0·719	506
0·657	553	0·723	470
0·665	529	0·888	276
0·670	541	0·892	257

Table 6

HEATS OF MIXING

*iso*Propanol+benzene 45·00 °C

x_1	H^M (J/mol)	x_1	H^M (J/mol)
0·118	1163	0·495	1687
0·131	1213	0·499	1638
0·233	1552	0·571	1548
0·284	1637	0·581	1521
0·490	1655	0·816	866

Ethanol + Methylcyclohexane[*] Heats of Mixing (j/mole)

25.0°C		35.0°C		45.0°C	
x_{alc}	H^M	x_{alc}	H^M	x_{alc}	H^M
0.234	547	0.229	633	0.227	770
0.245	547	0.247	651	0.246	795
0.421	576	0.413	667	0.410	802
0.428	575	0.432	673	0.430	811
0.681	471	0.680	532	0.679	622
0.691	456	0.692	521	0.680	625
0.692	461	0.693	519	0.692	611
		0.873	282	0.868	329

[*] Unpublished data measured by the methods of Brown, I. and Fock, W. Aust. J. Chem. 14 : 387 (1961).

(b) *Liquid-Vapour Equilibrium Data*

The liquid-vapour equilibrium data for the system *iso*propanol+benzene at 45 °C are given in Table 7; x_1 and y_1 are the mole fractions of *iso*propanol in the liquid and vapour respectively, P is the total pressure in standard mm Hg and α is the relative volatility.

Graphs of the data in Table 7 show that *iso*propanol+benzene forms an azeotrope at 45·00 °C, having a mole fraction of 0·296 *iso*propanol at a total pressure of 273·4 mm Hg.

TABLE 7

EXPERIMENTAL DATA AND DERIVED FUNCTIONS

*iso*Propanol+benzene at 45·00 °C

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0472	0·1467	252·50	3·470	1108·3	6·0	58·0
0·0980	0·2066	264·13	2·397	889·8	22·8	107·8
0·2047	0·2663	272·06	1·410	601·6	71·8	180·3
0·2960	0·2953	273·40	0·9966	436·3	126·7	218·3
0·3862	0·3211	272·22	0·7517	317·8	187·4	237·8
0·4753	0·3463	269·49	0·5848	227·8	256·6	242·9
0·5504	0·3692	264·92	0·4781	164·5	321·2	235·0
0·6198	0·3951	259·35	0·4007	118·8	387·8	221·1
0·7096	0·4378	247·70	0·3187	69·0	483·5	189·4
0·8073	0·5107	227·14	0·2491	30·3	601·8	140·4
0·9120	0·6658	189·28	0·1922	6·8	744·1	71·7
0·9655	0·8252	159·80	0·1687	0·8	821·8	29·1

V. EXCESS FREE-ENERGY DATA

The values of the excess chemical potentials μ_1^E, μ_2^E and the excess free energy of mixing G_x^E for the system *iso*propanol+benzene were calculated from the data given in Table 7, using equations (**1**), (**2**), and (**3**):

$$\mu_1^E=RT\ln Py_1/P_1x_1+(\beta_{11}-V_1)(P-P_1)+P\delta_{12}y_2^2+\tfrac{1}{3}D_{11}\{(4y_1^3-3y_1^4)P^3-P_1^3\}, \quad \ldots\ldots (\mathbf{1})$$

$$\mu_2^E=RT\ln Py_2/P_2x_2+(\beta_{22}-V_2)(P-P_2)+P\delta_{12}y_1^2-D_{11}\{y_1^4P^3\}, \quad \ldots\ldots (\mathbf{2})$$

$$G_x^E=x_1\mu_1^E+x_2\mu_2^E, \quad \ldots\ldots\ldots\ldots\ldots\ldots (\mathbf{3})$$

where P_1 and P_2 are the vapour pressures of the pure components, V_1 and V_2 the liquid molar volumes, β_{11}, β_{22}, β_{12}, and D_{11} are coefficients in the equations of state for the pure and mixed vapours. δ_{12} is given by

$$\delta_{12}=2\beta_{12}-\beta_{11}-\beta_{22}.$$

The equation of state for the pure component vapours was taken as

$$V=RT/P+\beta_{jj}+D_{jj}P^2,$$

and that for the mixed vapour as

$$V_{12}=RT/P+\beta_{11}y_1^2+2\beta_{12}y_1y_2+\beta_{22}y_2^2+D_{11}y_1^4P^2.$$

The value of D_{22} for benzene was assumed to be zero and the values of the other coefficients were calculated from equations given by Kretschmer and Wiebe (1954) for *iso*propanol and by Allen, Everett, and Penney (1952) for benzene. The value of β_{12} was evaluated by the method given by Brown and Smith (1954).

The values of the coefficients at 45 °C were:

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2	D_{11}	D_{22}
—2·15	—1·23	—0·97	1·44	0·079	0·092	$-1\cdot195\times10^{-5}$	0

Units are l/mol except D_{11}, which is in l/mm² mole.

The values of the correction terms involving D_{11} in equations (1) and (2) were less than 1 cal/mol.

Values of the derived thermodynamic functions are given in Table 7 in calories per mole of mixture.

The excess free-energy data were fitted by the method of least squares to equation (4)

$$G_x^E=x_1x_2[a+b(x_1-x_2)+c(x_1-x_2)^2]. \quad \dots\dots\dots\dots \quad (4)$$

The values of the constants in this equation and the standard deviation σ of the fit were found to be, in cal/mol,

$$a=963\cdot7, \quad b=-173\cdot0, \quad c=134\cdot3, \quad \sigma=1\cdot7.$$

These values do not indicate separation into two liquid phases.

The excess free-energy data were shown to be thermodynamically consistent by comparing the areas above and below datum on a plot of $\mu_1^E-\mu_2^E$ against x_1; their ratio was 1·002.

The excess free energy of mixing for the systems containing 2,2,4-trimethylpentane, toluene, and methyl*cyclo*hexane was calculated from the experimental data of Kretschmer, Nowakovska, and Wiebe (1948) and Kretschmer and Wiebe (1949*a*, 1949*b*). The non-ideality of the vapours was allowed for by using the method of Brown and Smith (1954), values of β_{22} being calculated from the Berthelot equation. The values used were (l/mol)

2,2,4-Trimethylpentane 25 °C ..	—2·34
Toluene 35 °C	—1·75
Methyl*cyclo*hexane 35 °C	—1·90

The excess free-energy data for the system ethanol+benzene have been determined by Brown and Smith (1954).

VI. THERMODYNAMIC PROPERTIES

The excess free energy G_x^E, heat of mixing H_x^M, and excess entropy of mixing TS_x^E for the five alcohol systems were calculated at even mole fractions, at the temperature of measurement, from the data given in the earlier sections of the

Table 8

THERMODYNAMIC PROPERTIES
Ethanol + benzene 45 °C

x_1	G^E_x	H^M_x	TS^E_x
0·1	125	230	+105
0·2	202	294	+92
0·3	247	315	+68
0·4	267	312	+45
0·5	268	285	+17
0·6	250	241	−9
0·7	215	189	−26
0·8	160	132	−28
0·9	88	68	−20

Table 9

THERMODYNAMIC PROPERTIES
Ethanol + toluene 35 °C

x_1	G^E_x	H^M_x	TS^E_x
0·1	140	182	+42
0·2	213	231	+18
0·3	258	243	−15
0·4	286	235	−51
0·5	288	210	−78
0·6	267	178	−89
0·7	231	140	−91
0·8	172	97	−75
0·9	98	50	−48

Table 10

THERMODYNAMIC PROPERTIES
Ethanol + 2,2,4-trimethylpentane 25 °C

x_1	G^E_x	H^M_x	TS^E_x
0·1	158	123	−35
0·2	250	150	−100
0·3	304	162	−142
0·4	334	161	−173
0·5	340	152	−188
0·6	321	138	−183
0·7	284	119	−165
0·8	225	93	−132
0·9	136	57	−79

present paper. T °K$=t$ °C$+273 \cdot 16$, 1 cal$=4 \cdot 1840$ abs. joules. These data are given in cal/mol of mixture in Tables 8 to 12. For the systems containing toluene, methyl*cyclo*hexane, and 2,2,4-trimethylpentane Kretschmer, Nowakowska, and Wiebe (1948) and Kretschmer and Wiebe (1949*a*, 1949*b*) calculated heats of mixing from the excess free-energy data at two temperatures. Their values are approximately 30 per cent. higher and more symmetrical in mole fraction than the directly measured values given above.

TABLE 11

THERMODYNAMIC PROPERTIES

Ethanol+methyl*cyclo*hexane 35 °C

x_1	G^E_x	H^M_x	TS^E_x
0·1	165	121	— 44
0·2	254	158	— 96
0·3	306	168	—138
0·4	334	167	—167
0·5	339	159	—180
0·6	320	143	—177
0·7	280	122	—158
0·8	217	94	—123
0·9	126	59	— 67

TABLE 12

THERMODYNAMIC PROPERTIES

*iso*Propanol+benzene 45 °C

x_1	G^E_x	H^M_x	TS^E_x
0·1	110	251	141
0·2	177	350	173
0·3	219	397	178
0·4	240	408	168
0·5	241	393	152
0·6	225	357	132
0·7	193	299	106
0·8	145	222	77
0·9	80	123	43

VII. DISCUSSION

The results given here, together with the results of Scatchard and Ticknor (1952) for methanol+benzene and those of Barker, Brown, and Smith (1953) for ethanol+carbon tetrachloride, enable some interesting comparisons to be made.

If we compare the thermodynamic properties of the ethanol systems we find that those having non-aromatic components are similar, while those with aromatic components have more positive values of the excess entropy and heat of mixing. This indicates stronger interaction of alcohol molecules with aromatic than with non-aromatic molecules. This causes increased breaking of alcohol hydrogen bonds and this occurs at a higher concentration of alcohol in aromatic systems than in non-aromatic systems.

Comparison of the systems containing benzene with different alcohols shows that the heat and excess entropy of mixing become rapidly more positive as the hydrocarbon chain of the alcohol molecule becomes longer. More positive heats of mixing could be due either to a larger heat change on breaking an individual hydrogen bond or to the fact that more hydrogen bonds are broken in solutions of longer-chain alcohols. Increased heat of breaking individual hydrogen bonds would be expected to lead to more *negative* excess entropy of mixing. The second alternative, however, is consistent with the observed increase of both heat of mixing and excess entropy of mixing with alcohol chain-length. If more hydrogen bonds are broken at a given concentration in systems with longer-chain alcohols, this can only be because the entropy increase on breaking an individual hydrogen bond is larger in these systems. This is presumably associated with a larger gain in configurational freedom on breaking hydrogen bonds between longer-chain alcohol molecules. It is uncertain how far this increase continues as the size of the alcohol molecule increases, but the corresponding properties calculated from less reliable data listed in Appendix I for *n*-propanol+benzene and the four butanol+benzene systems suggest that the properties of the butanol systems are not very different from those of the *iso*propanol system.

VIII. ACKNOWLEDGMENTS

The authors wish to thank Mr. J. A. Barker and Mr. O. H. Rigby for their help with this work.

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APPENDIX I

n-Propanol + benzene 40 °C (Lee 1931)
*iso*Propanol + benzene 25 °C (Olsen and Washburn 1937)
n-Butanol + benzene 25 °C (Allen, Lingo, and Felsing 1939)
*iso*Butanol + benzene 25 °C (Allen, Lingo, and Felsing 1939)
sec.-Butanol + benzene 25 °C (Allen, Lingo, and Felsing 1939)
tert.-Butanol + benzene 25 °C (Allen, Lingo, and Felsing 1939)
n-Propanol + benzene 20 °C (Pahlke 1935)
*iso*Propanol + benzene 20 °C (Pahlke 1935)
tert.-Butanol + benzene 20 °C (Pahlke 1935)
n-Butanol + benzene 20 °C (Perrakis 1925; Pahlke 1935).

AUSTRALASIAN MEDICAL PUBLISHING CO. LTD.
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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 10, NUMBER 4, PAGES 417-422, 1957

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Reprinted from the Australian Journal of Chemistry, Volume 10, Number 4, pp. 417–422, 1957

HEATS OF MIXING

III. ACETONE AND ALCOHOL SOLUTIONS

By I. Brown* and W. Fock*

[*Manuscript received March* 26, 1957]

Summary

The heats of mixing at 45·00 °C have been measured at intervals over the whole concentration range for the following systems: acetone+benzene, acetone+carbon tetrachloride, acetone+acetonitrile, acetone+nitromethane, *n*-propanol+benzene, and *n*-butanol+benzene. The heats of mixing are discussed in the light of the authors' earlier results for similar systems.

I. Introduction

The heats of mixing of a number of systems containing polar components are being measured to permit the excess entropy of mixing to be calculated with greater accuracy than can be obtained from free energy data alone. References are given below for published heats of mixing for some of these systems at temperatures of 20 °C or below, but these are not suitable for the calculation of excess entropies from free energy data which were measured at 45 °C. The results given here form part of a programme to provide experimental thermodynamic data for testing statistical theories of polar non-electrolyte solutions.

II. Apparatus and Methods

The apparatus used was that described by Brown and Fock (1955) and the method of operation was that given by those authors (Brown and Fock 1956). With the techniques used no latent heat effects occur due to changes in vapour composition on mixing.

III. Components

Acetone was purified by the method of Thirion and Craven (1952) and the alcohols by careful fractional distillation at high reflux ratios in the column described by Brown and Ewald (1951). The other liquids were purified by the methods described by Brown and Smith (1954, 1955). The density and refractive index of each purified liquid were measured as criteria of purity; the values obtained are shown in Table 1.

IV. Results

The results obtained are given in Tables 2 to 7, where x_1 is the mole fraction of the first-mentioned component and H_x^M, expressed as J/mol of mixture, is the heat of mixing. A check was made of the experimental data by plotting

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TABLE 1

PHYSICAL PROPERTIES OF COMPONENT LIQUIDS

Liquid	$n_D^{25\cdot00}$	$d_4^{25\cdot00}$
Acetone	1·35598	0·78501
Acetonitrile	1·34153	0·77662
Nitromethane	1·37968	1·13062
Benzene	1·49800	0·87362
Carbon tetrachloride ..	1·45739	1·58452
n-Propanol	1·38314	0·79959
n-Butanol	1·39731	0·80577

H_x^M/x_1x_2 against x_1 as recommended by Korvezee, Ruiter, and Stuyts (1953), for all systems the points were on smooth curves. The experimental errors were estimated to be from 2 to 3 per cent.

TABLE 2

HEAT OF MIXING ACETONE+BENZENE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·157	116	0·594	152
0·279	147	0·602	148
0·488	159	0·604	145
0·493	158	0·788	108

For the system acetone+benzene heat of mixing data are given at 30 °C by Möbius (1955), who also gives one value at 20 °C. A value at one concentration at 20 °C is given by Timofiev (1905). No reliable estimates could be calculated from published free energy data.

TABLE 3

HEAT OF MIXING ACETONE+CARBON TETRACHLORIDE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·132	256	0·619	196
0·294	317	0·620	189
0·493	266	0·799	106
0·496	263	0·839	83
0·615	197		

For the system acetone+carbon tetrachloride the only value for the heat of mixing is a single measurement by Timofiev (1905). No reliable estimates of the heat of mixing for this system could be obtained from free energy data even using the comparatively accurate data of Severns *et al.* (1955) at 50 °C and

TABLE 4

HEAT OF MIXING ACETONE + ACETONITRILE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·083	—22	0·465	—106
0·155	—47	0·467	—108
0·192	—57	0·759	—81
0·366	—96	0·890	—41
0·373	—99		

TABLE 5

HEAT OF MIXING ACETONE + NITROMETHANE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·081	—27	0·465	—159
0·191	—71	0·467	—159
0·363	—134	0·681	—163
0·367	—136	0·848	—107
0·461	—154		

TABLE 6

HEAT OF MIXING *n*-PROPANOL + BENZENE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·100	921	0·596	1084
0·218	1264	0·611	1052
0·479	1247	0·822	537
0·483	1264		

TABLE 7

HEAT OF MIXING *n*-BUTANOL + BENZENE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·082	865	0·550	1235
0·190	1254	0·551	1241
0·438	1393	0·804	635
0·439	1383		

that of Brown and Smith (1957) at 45 °C as the estimated errors were of the same order as the heats of mixing themselves.

No information seems to be available for the systems of acetone + acetonitrile or acetone + nitromethane.

Published heats of mixing are given for the system *n*-propanol + benzene at 15 °C by Schmidt (1926), at 20 °C by Pahlke (1935), and a single value by Timofiev.

Data on the heat of mixing of the system *n*-butanol + benzene at 20 °C are given by Perrakis (1925) and Pahlke (1935).

V. Discussion

The data given here for mixtures of acetone with carbon tetrachloride and with benzene, together with those for the corresponding systems containing acetonitrile and nitromethane (Brown and Fock 1956), form two interesting series of measurements. The heats of mixing for the carbon tetrachloride systems are all more positive than those for the corresponding benzene systems. This is probably due to the polar molecules interacting more strongly with the π-electrons of the benzene molecules than with the electrons of the carbon tetrachloride molecules. Similar conclusions on the interactions of ethanol with benzene and with carbon tetrachloride were reached by Brown, Fock, and Smith (1956).

In the series of solutions with carbon tetrachloride the heat of mixing becomes less positive in the order: nitromethane, acetonitrile, acetone; the same sequence is found for the series of benzene solutions. This is not the order of their dipole moments, which are respectively 3·54, 3·96, and 2·87 D, neither is it in the order of the difference from unity of the "*g*" factor of Oster and Kirkwood (1943).

The negative heats of mixing for acetone with nitromethane and with acetonitrile show that the electrostatic interaction between pairs of the unlike molecules is stronger than that between the like molecules; part of this effect may be due to weak hydrogen bonds between the oxygen of acetone and the positive ends of the nitromethane and acetonitrile molecules. The heat of mixing for the system acetone + propionitrile at 20 °C is also negative (Thacker and Rowlinson 1954). For the binary system nitromethane + acetonitrile, where the dipole moments and molar volumes of the components are very similar, it was shown by Brown and Fock (1956) that both the heat and excess free energy of mixing are very close to zero.

For solutions in benzene of aliphatic alcohols the variation in H_x^M with the size of the alcohol molecule was discussed by Brown, Fock, and Smith (1956), who showed that the heat and excess entropy of mixing became rapidly more positive in the series of benzene solutions containing methanol, ethanol, and *iso*propanol. The new data given here, together with published values at lower temperatures (Perrakis 1925; Schmidt 1926; Pahlke 1935; Williams, Rosenberg, and Rothenberg 1948; Scatchard *et al.* 1952; Tsao 1953; Thacker and Rowlinson 1954) show more clearly the effect of the size of the alcohol molecule. These data are shown in Figure 1, where the maximum in the H_x^M curve is plotted against the number of carbon atoms in the alcohol molecule.

These maxima all occur at mole fractions of alcohol between 0·28 and 0·48. Values at 20 °C are shown as triangles and those at 45 °C as circles, open symbols are used for normal alcohols and closed for *iso*propanol. It can be seen that, while the size of the normal alcohol has only a small influence in the maximum value of H_x^M, the maxima for *iso*propanol solutions are considerably higher than those for *n*-propanol. Probably this means that more alcohol-alcohol hydrogen bonds are broken at a given concentration in *iso*propanol solutions than in *n*-propanol solutions (cf. Brown, Fock, and Smith 1956). It is intended to measure values of the excess free energy of mixing for the system *n*-propanol+benzene. It will then be possible to calculate the excess entropy of mixing which may help to explain the difference in behaviour between *n*-propanol and *iso*propanol in benzene solution.

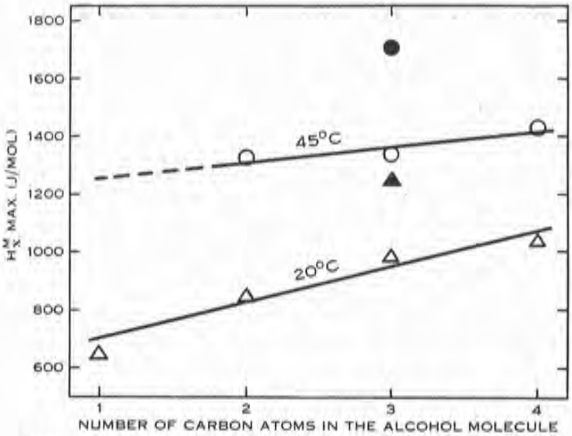

Fig. 1.—Heats of mixing, benzene+alcohol systems. ○ and △ Normal alcohols. ● and ▲ *iso*Propanol.

VI. ACKNOWLEDGMENTS

The authors wish to thank Mr. J. A. Barker for discussions of the results.

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AUSTRALASIAN MEDICAL PUBLISHING CO. LTD.
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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 14, NUMBER 3, PAGES 387–396, 1961

HEATS OF MIXING

IV. SYSTEMS OF n-ALCOHOLS WITH BENZENE AT 25, 35, AND 45°C

BY I. BROWN and W. FOCK

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HEATS OF MIXING

IV. SYSTEMS OF n-ALCOHOLS WITH BENZENE AT 25, 35, AND 45 °C

By I. BROWN* and W. FOCK*

[*Manuscript received February* 17, 1961]

Summary

A new apparatus has been made for the precise measurement of heats of mixing of liquids. With this apparatus measurements can be made in the absence of air, vapour, or mercury for systems which have volume changes on mixing of up to 1 ml per mol of mixture.

The apparatus has been used to measure the heats of mixing of ethanol, 1-propanol, and 1-butanol with benzene at 45 °C for comparison with previous measurements. New measurements have also been made over the concentration range for heats of mixing of ethanol, 1-propanol, and 1-butanol with benzene at 25 and 35 °C and for methanol, 1-hexanol, and 1-octanol with benzene and ethanol with toluene at 35 °C.

For these systems the heat of mixing per mol of mixture has a maximum at a mole fraction of alcohol from 0·30 to 0·35. The results show that the heats of mixing at a mole fraction of alcohol of 0·30 increase linearly with increase in temperature and at a given temperature they increase with the molecular weight of the alcohol but at a lower rate for the higher alcohols.

I. INTRODUCTION

A new cell has been designed to eliminate various undesirable features of the cell used previously (Brown and Fock 1955). This had one basic defect in design ; the heater was on the outside of the cell and the temperature measuring device was on the inside. This has been found to lead to errors in the measured values of heats of mixing due to uncertainty in the amount of heat exchange between the cell with its contents and the surroundings, particularly when appreciable changes in temperature occur during heating and mixing. It was also difficult to fill with the correct amount of liquid and the use of mercury as the separating medium was undesirable due to its possible catalytic effect on some mixtures and appreciable heat capacity.

The optimum design of such cells has been discussed in detail by McGlashan (1961), who showed that the ideal design is one in which there are no air or vapour spaces and no pressure changes due to volume changes on mixing.

In the design of a cell in which vapour or air spaces are not permissible it is necessary to allow for expansion of the liquids on heating from room temperature to the temperature of operation and for expansion due to changes in volume on mixing. In the new cell described below, thin corrugated diaphragms are used to reconcile these changes in volume with the minimum pressure change.

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II. APPARATUS

The cell, which has a total capacity of 30 ml, is shown diagrammatically in Figure 1. The brass body is in two parts *A* and *B* bolted together with six small bolts. The liquids in the two parts of the cell are separated by a 0·0005 in. brass diaphragm *C* held in place between two machined Teflon gaskets *D*. Side *A* contains a manganin heater *E* wound on a Teflon cylinder with leads soldered to glass-metal seals *F* fixed to the walls. The side *B* contains a strong coiled spring *G* held in compression by the catch *H* engaged on pin *I* which is triggered off by an external electromagnet that attracts the iron trigger *J*.

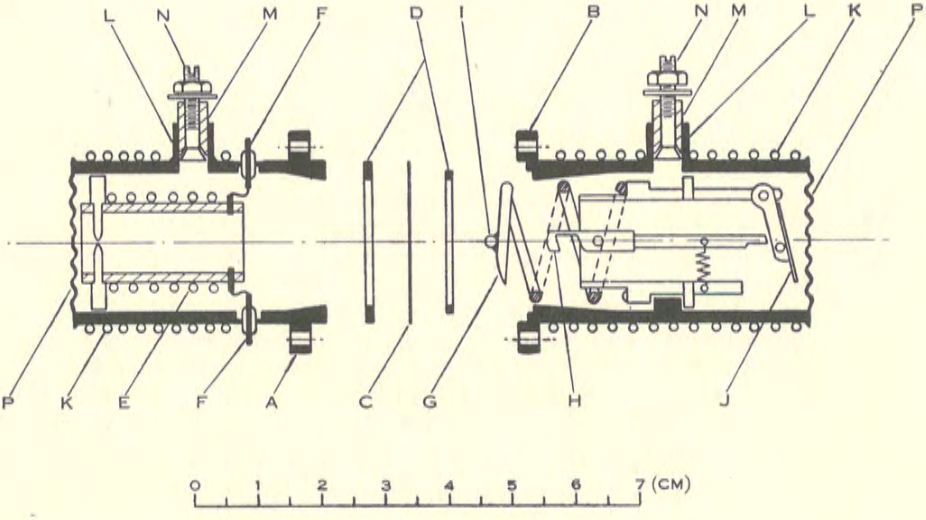

Fig. 1.—Heat of mixing cell.

A nickel resistance thermometer *K* of 140 Ω of 0·002 in. diameter wire is wound on both parts of the cell and insulated by a thin film of Araldite. Leads from the thermometer are connected to a Wheatstone bridge which automatically records the resistance–time curve. This recorder has a range of 150 Ω and a span of 1·00 Ω. An electrically driven decade box automatically changes the range as the pen reaches the top or bottom of the scale.

Each side has a filling opening *L* closed by a Teflon plug *M* which is expanded by a conical stainless steel bolt *N*. The assembled cell is mounted on a Polythene carriage in the vacuum box described previously by Brown and Fock (1955) and mixing is done by rocking the whole cell which contains a stainless-steel ball to help mixing.

The ends of the cell are corrugated diaphragms made from 0·003 in. beryllium-copper to allow for the expansion of the liquids on heating the cell to thermostat temperature and the volume change on mixing.

A microscope cover glass was also tried as the dividing diaphragm, but this required a modified breaking device and softer gaskets of Neoprene which adsorb some of the components used. The use of flexible metal bellows to allow for expansion leads to incomplete mixing in the convolutions and prevents the removal of trapped air bubbles on filling.

It was found that these diaphragms could be used repeatedly if the total volume change due to expansion on mixing and expansion on heating from the charging temperature of 20 °C to the operating temperature was less than 0·5 ml. The life of the diaphragms was limited when the mixing was carried out at 45 °C due to the volume change of about 1 ml on heating to the higher working temperature.

For the systems studied here, the heats of mixing were high and the error due to leaving an air space of 0·5 ml in each side of the cell was only about 0·1%. Measurements at 25 °C were done with the cell completely filled but those at 35 and 45 °C were made with an air space adjusted to give 0·5 ml on each side of the cell at thermostat temperature.

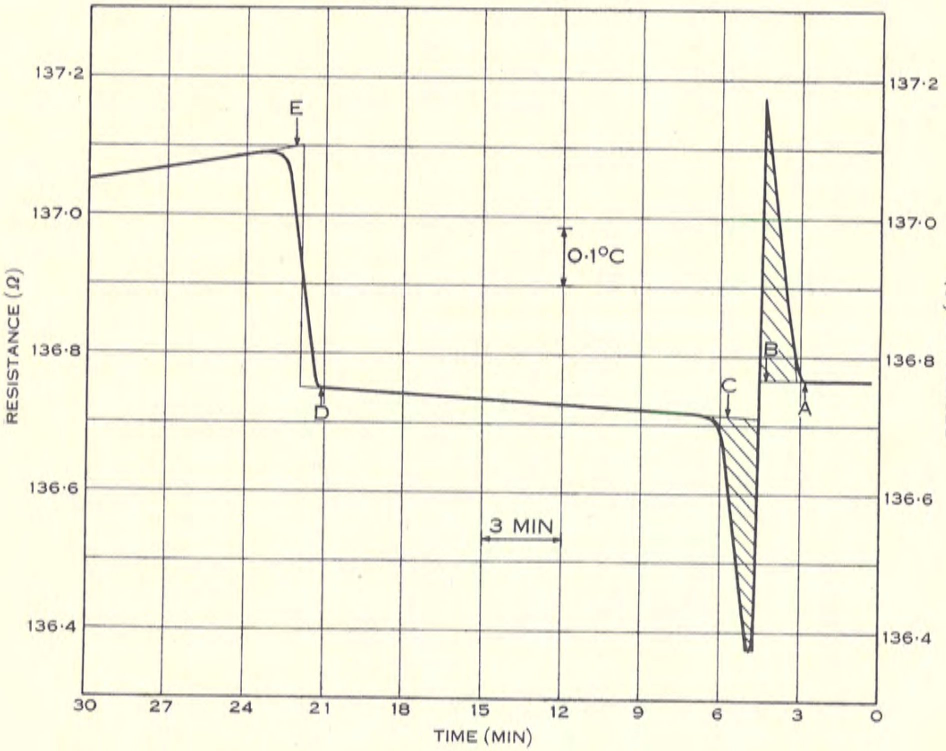

Fig. 2.—Typical resistance–time curve.

III. Experimental Procedure

The spring was cocked and the cell assembled with its brass diaphragm, each side was completely filled, and the closed cell weighed to ±1 mg after each filling. The electrical leads were soldered on and the cell mounted in the carriage in the vacuum box. After evacuation the cell was left overnight to reach thermostat temperature.

Mixtures with a mole fraction of alcohol x_1 from about 0·4 to 0·6 were obtained by mixing pure liquids, mixtures of higher or lower mole fraction were made with one side of the cell filled with a mixture whose heat of mixing was known from a previous run.

The measured heating of the cell was done at the same time as the mixing as described previously by Brown and Fock (1956). A typical recorder chart is reproduced in Figure 2. During the measured heating period *A* to *C* an amount of electrical energy approximately equal to the heat of mixing was dissipated in the heater. Mixing was made at time *B* chosen to make the shaded areas under the curve approximately equal. The second heating period from *D* to *E* provided a calibration for inexact compensation of the heat of mixing. Electrical energy measurements followed Brown and Fock's (1955) method. The changes in resistance recorded on the chart were proportional to the change in temperature of the resistance winding for the small range of temperature used. The heat of releasing the spring and breaking the diaphragm was found to be negligible (0·2 j).

Values of H^M, the heat of mixing per mol of mixture, were calculated using the methods described by Ruiter (1955) to allow for heat exchange between the cell with its contents and the surroundings.

The errors in x_1 and H^M due to errors in the measured quantities were calculated to be $\pm 0{\cdot}0008$ and 0·8% respectively for the primary mixtures and up to 0·0018 and 2% for mixtures of high or low mole fraction.

TABLE 1

THE PHYSICAL PROPERTIES OF THE COMPONENTS

Compound	$d_4^{25\cdot00}$	$n_D^{25\cdot00}$	Boiling Point (°C/760 mmHg)
Benzene	0·87365	1·49801	80·07
Toluene	0·86224	1·49406	110·60
Methanol	0·78683	1·32662	64·54
Ethanol	0·78511	1·35926	78·29
1-Propanol	0·79959	1·38314	97·08
1-Butanol	0·80578	1·39731	117·52
1-Hexanol	0·81531	1·41607	157·5
1-Octanol	0·82247	1·42741	195·2

IV. PURIFICATION AND PHYSICAL PROPERTIES OF COMPONENTS

Benzene, 1-propanol, and 1-butanol were purified by the methods of Brown and Smith (1959), ethanol by the method of Barker, Brown, and Smith (1953), and toluene by that of Brown, Fock, and Smith (1956). Methanol was distilled from sulphanilic acid, fractionally distilled and dried over magnesium. 1-Hexanol and 1-octanol were fractionally distilled and the fractions showing a single peak on a gas chromatogram were used. The physical properties of the components are given in Table 1.

V. Results

First, new measurements were made of the heats of mixing of ethanol, 1-propanol, and 1-butanol with benzene at 45 °C to test the performance of the cell and for comparison with those from the former cell. These results are presented in Tables 2(*c*), 3(*c*), and 4(*c*).

The present values obtained for ethanol+benzene are compared in Figure 3 with the recent results of Williamson and Scott (1960) measured at 45·0 °C in an apparatus similar to that described by Adcock and McGlashan (1954). The comparison is made between values of H^M/x_1x_2, where H^M is the heat of mixing in absolute joules per mole of mixture, x_1 is the mole fraction of ethanol, and x_2 that of benzene. The agreement is excellent.

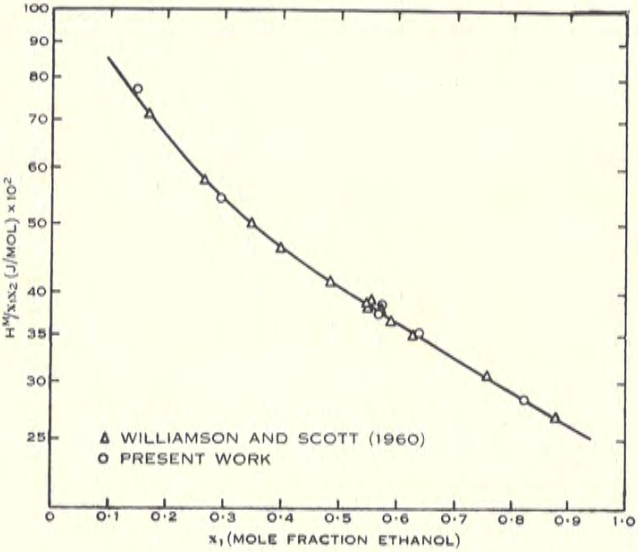

Fig. 3.—Heats of mixing ethanol+benzene 45·0 °C.

The heat of mixing data for this system at 45 °C obtained using Brown and Fock's (1955) cell were found to be about 13% higher than the new values given here. The old values were measured with the temperature changes due to mixing and measured heating taking place separately. This led to errors in the extrapolation of the temperature–time curves as well as those inherent in having an external heater and an internal temperature measuring device.

All subsequent measurements using the former cell (Brown and Fock 1956, 1957; Brown, Fock, and Smith 1956) were made with the mixing and heating done simultaneously to minimize temperature changes in the cell. The data obtained with this cell in 1957 for the systems 1-propanol+benzene and 1-butanol+benzene at 45 °C are approximately 2% and 1% respectively higher than the new values given in Tables 3 (*c*) and 4 (*c*). From these comparisons and those made with new measurements on other systems it appears that the measurements made with the 1955 cell with simultaneous heating and mixing are in agreement with values measured in the new cell for H^M below about 1000 j/mol and are about 2% high for values of H^M from about 1300 to 1400 j/mol.

Measurements were then made of a number of n-alcohol + benzene systems at 25 and 35 °C; the results are shown in Tables 2 to 5.

Table 2

HEATS OF MIXING ETHANOL + BENZENE

(a) 25·0 °C		(b) 35·0 °C		(c) 45·0 °C	
x_1	H^M (j/mol)	x_1	H^M (j/mol)	x_1	H^M (j/mol)
0·057	510*	0·162	905*	0·146	970
0·130	715*	0·164	880*	0·294	1130
0·130	725*	0·297	1005	0·567	925
0·269	845*	0·335	1005*	0·569	930
0·278	855*	0·343	995*	0·571	945
0·335	870	0·552	820*	0·637	815
0·541	710*	0·552	810*	0·822	420
0·560	690*	0·571	800		
0·596	635	0·636	705		
0·609	630	0·649	680*		
0·658	555*	0·859	295*		
0·660	540*				
0·865	220*				

* These measurements were made with the former cell.

Table 3

HEATS OF MIXING 1-PROPANOL + BENZENE

(a) 25·0 °C		(b) 35·0 °C		(c) 45·0 °C	
x_1	H^M (j/mol)	x_1	H^M (j/mol)	x_1	H^M (j/mol)
0·141	855	0·249	1145	0·326	1330
0·278	1035	0·250	1145	0·510	1205
0·289	1040	0·321	1180	0·585	1090
0·538	900	0·322	1175		
0·548	885	0·511	1070		
0·785	450	0·512	1060		
		0·575	955		
		0·577	955		
		0·783	540		

TABLE 4

HEATS OF MIXING 1-BUTANOL+BENZENE

(a) 25·0 °C		(b) 35·0 °C		(c) 45·0 °C	
x_1	H^M (j/mol)	x_1	H^M (j/mol)	x_1	H^M (j/mol)
0·118	830	0·213	1160	0·213	1270
0·239	1070	0·280	1245	0·243	1310
0·251	1090	0·453	1220	0·459	1350
0·487	1050	0·460	1215	0·461	1340
0·487	1030	0·488	1195	0·483	1340
0·496	1035	0·498	1180		
0·500	1035	0·526	1140		
0·740	600	0·528	1130		
		0·706	745		
		0·777	605		

TABLE 5

HEATS OF MIXING OF ALCOHOL SYSTEMS AT 35·0 °C

(a) Methanol+Benzene		(b) 1-Hexanol+Benzene		(c) 1-Octanol+Benzene		(d) Ethanol+Toluene	
x_1	H^M (j/mol)	x_1	H^M (j/mol)	x_1	H^M (j/mol)	x_1	H^M (j/mol)
0·381	800	0·089	835	0·158	1155	0·204	925
0·658	545	0·187	1150	0·353	1370	0·337	975
0·659	545	0·187	1145	0·356	1370	0·370	970
		0·410	1285			0·388	955
		0·422	1285			0·614	715
		0·688	855			0·614	720
						0·641	680
						0·654	650
						0·674	625

VI. DISCUSSION

The variation of the heats of mixing with temperature for mixtures of normal alcohols with benzene is shown in Figure 4 and the variation of H^M with the size of the alcohol molecule is shown in Figure 5. The values shown in these figures are for mixtures containing 0·30 mole fraction of alcohol and were estimated from the experimental data by interpolation on plots of H^M/x_1x_2 against x_1. It can be seen that the variation is linear with temperature. Our data for the methanol and ethanol systems are in excellent agreement with those of Williamson and Scott (1960). Figure 4 enables a comparison to be made between present data and published data measured at other temperatures.

For the system methanol+benzene the data at 25 °C of Thacker and Rowlinson (1954) are in good agreement with our data. The values of Tsao and Smith (1957) at 25 °C, Scatchard *et al.* (1952) at 20 °C, and Schmidt (1926) at 15 °C are slightly higher. The data of Pahlke (1935) at 20 °C are about 13% higher, and those of Williams, Rosenberg, and Rothenberg (1948) at 25 °C and of Washburn and Lightbody (1930) at 23 °C are about 7% lower than our values.

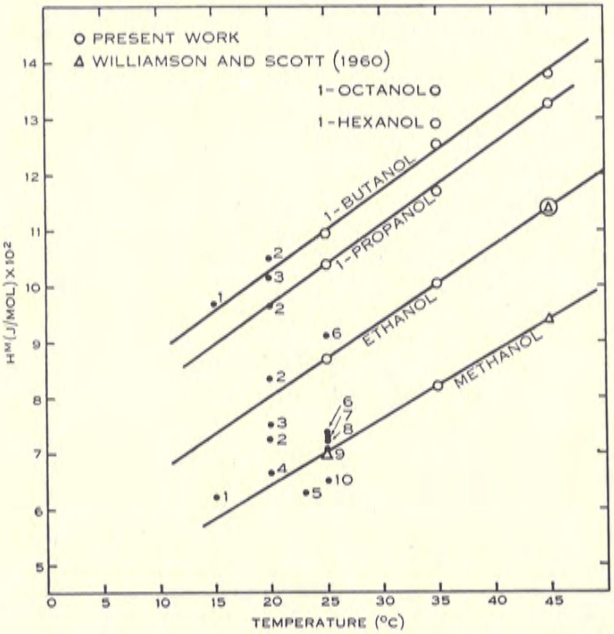

Fig. 4.—Heats of mixing of normal alcohols with benzene at $x_1=0\cdot30$. 1, Schmidt (1926); 2, Pahlke (1935); 3, Perrakis (1925); 4, Scatchard *et al.* (1952); 5, Washburn and Lightbody (1930); 6, Schnaible, Van Ness, and Smith (1957); 7, Tsao and Smith (1953); 8, Murti and van Winkle (1958); 9, Thacker and Rowlinson (1954); 10, Williams, Rosenberg, and Rothenberg (1948).

For the system ethanol+benzene the values of Schnaible, Van Ness,* and Smith (1953) at 25 °C and Pahlke (1935) at 20 °C are about 5% higher than our values and those of Perrakis (1925) at 20 °C about 6% lower. The data of Vialla (1914) at 20 °C and Winkelmann (1873) at 0, 5, and 15 °C are about 30% lower.

For the system 1-propanol+benzene the data of Pahlke (1935) at 20 °C are in agreement with our values, but the values of Schmidt (1926) at 15 °C are about 8% higher. For 1-butanol+benzene the values of Pahlke at 20 °C are slightly higher and those of Perrakis at 20 °C slightly lower than our data.

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* A recent personal communication has been received by the authors from Professor H. C. Van Ness, Rensselaer Polytechnic Institute, New York, giving heats of mixing data at 25, 35, and 45 °C for a number of the systems studied in this paper. His results are slightly higher but in substantial agreement with the present data.

The values of Chalela, Steinhauser, and Hougen (1957) for the system 1-pentanol+benzene at 20 °C appear to be appreciably low in comparison with our data on the other systems.

Values of heats of mixing for n-alcohol+benzene systems calculated from an extensive correlation of activity coefficients by Black (1959) give values which are about 6% higher than ours for methanol+benzene from 20 to 55 °C, but the values calculated at 55 °C for the systems containing ethanol to pentanol are too low by up to 50% and show a decrease with increase in molecular weight of the alcohol instead of an increase.

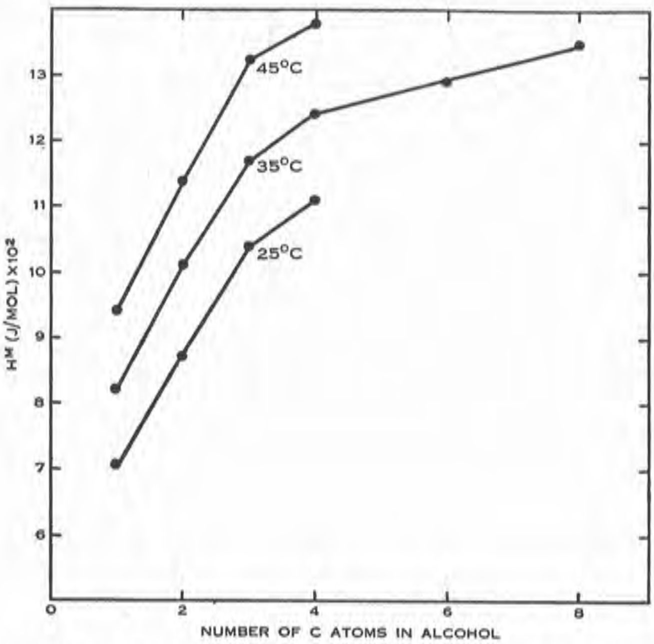

Fig. 5.—Heats of mixing of normal alcohols with benzene at $x_1=0\cdot30$.

The data given here show the changes in the values of H^M of benzene solutions of normal alcohols with changes in temperature and size of the alcohol molecule more accurately than those given previously by Brown and Fock (1957). A more detailed study of the behaviour of benzene solutions of alcohols will be possible when values of the excess free energies, heats of mixing, and volume changes on mixing for systems containing branched alcohols become available. These measurements are in progress.

VII. ACKNOWLEDGMENTS

The authors wish to thank Professor R. L. Scott and Dr. A. G. Williamson for sending their data before publication and for their valuable discussions; also Professor H. C. Van Ness for his data.

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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 17, NUMBER 10, PAGES 1106–18, OCTOBER 1964

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Reprinted for the
Commonwealth Scientific and Industrial Research Organization
Australia

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V.* SYSTEMS OF n-ALCOHOLS WITH n-HEXANE

By I. BROWN,† W. FOCK,† and F. SMITH†

[*Manuscript received April* 9, 1964]

Summary

Heats of mixing have been measured at 25°, 35°, and 45° for mixtures of ethanol, propan-1-ol, butan-1-ol, hexan-1-ol, and octan-1-ol with n-hexane and for methanol with n-hexane at 45°.

These heats of mixing were found to increase with an increase in temperature and to decrease with an increase in the size of the alcohol molecule. They showed anomalies for the systems containing methanol and ethanol. An explanation of these anomalies has been given.

The contribution of the hydroxyl groups to the enthalpy of any mixture of a n-alcohol with a n-alkane is defined as the enthalpy change on replacing the alcohol by its homomorphic alkane. The experimental results given here are consistent with the postulate that the contribution of the hydroxyl groups (per mole of alcohol) to the enthalpy depends only on the ratio of the number of hydroxyl groups to that of hydrocarbon units in the mixture. This postulate, if generally true, can be used for the prediction of the heats of mixing of any n-alcohol with a n-alkane and of the enthalpy difference between any n-alcohol and its liquid homomorphic alkane.

Other data support the conclusion that the postulate holds for all concentrations of alcohol, but show that the analogous postulate applied to free energies holds only for infinitely dilute solutions of alcohols. The interaction of the hydroxyl groups with the hydrocarbon units contribute $-7\cdot8$ and $-4\cdot5$ kJ/mole of alcohol to the enthalpies and free energies respectively of these infinitely dilute solutions.

The required values of the heats of mixing of the lower alkanes with n-hexane were estimated from the enthalpies of the alkanes using the principle of congruence; these were found to be appreciable and negative. They are in sign agreement with values extrapolated, from measured data at a higher temperature, using a principle of corresponding states for chain molecules.

INTRODUCTION

The authors have made extensive tests of the lattice theory of Barker[1] as applied to mixtures of n-alcohols with benzene. The data of Brown and Smith[2,3] for the excess free energies of mixing and those of Brown and Fock[4] for the heats of mixing were used to evaluate the parameters. A reasonable quantitative agreement between theory and experiment was obtained for individual systems, but no set of parameter values could be found which gives agreement for all the systems studied. The interactions of the alkyl groups with the solvent in these systems probably make

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* **Part IV**, *Aust. J. Chem.*, **1961, 14, 387.**

† Division of Physical Chemistry, CSIRO Chemical Research Laboratories, Melbourne.

[1] Barker, J. A., and Smith, F., *J. Chem. Phys.*, 1954, **22**, 375.

[2] Brown, I., and Smith, F., *Aust. J. Chem.*, 1954, **7**, 264.

[3] Brown, I., and Smith, F., *Aust. J. Chem.*, 1959, **12**, 407.

[4] Brown, I., and Fock, W., *Aust. J. Chem.*, 1961, **14**, 387.

Aust. J. Chem., 1964, **17**, **1106–18**

the major contribution to the heats of mixing, as the heats of mixing of n-alkanes with benzene are large.[5] To minimize this complicating factor in the study of mixtures involving hydrogen bonding, n-hexane was chosen as the solvent because heats of mixing of n-hexane with the higher alkanes are known to be small.[6,7] For mixtures of n-alcohols with this solvent it was found possible to obtain a correlation between the concentration of hydroxyl groups and their contribution to the heats of mixing.

TABLE 1

THE PHYSICAL PROPERTIES OF THE COMPONENTS

Compound	$d_4^{25\cdot00}$	$n_D^{25\cdot00}$	B.P. (760 mm)
n-Hexane	0·65481	1·37230	68·77
Methanol	0·78683	1·32662	64·54
Ethanol	0·78511	1·35926	78·29
Propan-1-ol	0·79959	1·38312	97·08
Butan-1-ol	0·80578	1·39731	117·52
Hexan-1-ol	0·81531	1·41607	157·5
Octan-1-ol	0·82247	1·42741	195·2

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus and experimental procedure were the same as those used previously by Brown and Fock.[4] The purification of the components was by the methods described previously.[3,4,8] Gas chromatography on squalane and polyethyleneglycol substrates was used together with the physical properties listed in Table 1 to check the purity of the components.

TABLE 2

HEATS OF MIXING: METHANOL+n-HEXANE AT 45·0°

x	H^M (J/mole)	x	H^M (J/mole)
0·1632	660	0·5352	749
0·1840	690	0·7559	606
0·2867	756	0·7709	594
0·3155	761	0·7712	594
0·5251	748	0·9047	359

RESULTS

The measured heats of mixing, H^M, in J/mole of mixture at x mole fraction of alcohol are given in Tables 2–7. Measurements on the methanol system were made only at 45° because of partial miscibility at the lower temperatures. The errors in x and H^M due to errors in the measured quantities were calculated to be ±0·0008

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[5] Schnaible, H. W., Van Ness, H. C., and Smith, J. M., *J. Amer. Inst. Chem. Engrs.*, 1957, **3**, 147.

[6] McGlashan, M. L., and Morcom, K. W., *Trans. Faraday Soc.*, 1961, **57**, 907.

[7] Van der Waals, J. H., *Rec. Trav. Chim. Pays-Bas*, 1951, **70**, 101.

[8] Brown, I., *Aust. J. Sci. Res.* A, 1952, **5**, 530.

and 0·8% respectively for the primary mixtures and up to 0·0018 and 2% respectively for mixtures of high and low mole fraction.

TABLE 3

HEATS OF MIXING: ETHANOL + n-HEXANE

25·0°		35·0°		45·0°	
x	H^M (J/mole)	x	H^M (J/mole)	x	H^M (J/mole)
0·1394	471	0·0738	475	0·1399	719
0·2392	545	0·1391	583	0·2369	813
0·2512	553	0·2540	676	0·2550	827
0·2546	552	0·4122	688	0·4133	833
0·4134	573	0·4391	683	0·4404	826
0·4274	572	0·6807	536	0·6820	629
0·4372	569	0·6826	533	0·7006	606
0·4396	569	0·7007	516	0·8646	337
0·6819	457	0·8647	296		
0·6842	453				
0·6984	445				
0·6986	448				
0·7009	443				
0·8685	253				

The results of Wolf, Pahlke, and Wehage[9] for these systems show fair agreement with our data for the ethanol + n-hexane system, but deviate increasingly for the systems with the higher alcohols, being approximately 20% lower than our values for the system hexan-1-ol + n-hexane. The correlation made by von Elbe[10] of his

TABLE 4

HEATS OF MIXING: PROPAN-1-OL + n-HEXANE

25·0°		35·0°		45·0°	
x	H^M (J/mole)	x	H^M (J/mole)	x	H^M (J/mole)
0·1925	556	0·1126	582	0·0966	678
0·2093	572	0·1898	680	0·1894	830
0·3600	611	0·2111	700	0·2115	858
0·3797	612	0·3571	746	0·3567	905
0·6301	474	0·3810	743	0·3815	906
0·6435	470	0·6410	567	0·6280	703
0·6448	464	0·6438	565	0·6467	683
0·8455	243	0·6463	561	0·6472	680
				0·8477	340

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[9] Wolf, J., Pahlke, K., and Wehage, K., *Z. phys. Chem.* B, 1935, **28**, 1.

[10] Von Elbe, G., *J. Chem. Phys.*, 1934, **2**, 73.

measurements for systems of n-alcohols with n-paraffins gives values of H^M which differ widely from our values and which increase with increasing carbon number of the alcohol, the reverse result of that found here and by Wolf *et al.*

TABLE 5

HEATS OF MIXING: BUTAN-1-OL + n-HEXANE

25·0°		35·0°		45·0°	
x	H^M (J/mole)	x	H^M (J/mole)	x	H^M (J/mole)
0·1634	500	0·0941	528	0·1581	746
0·1772	513	0·1602	614	0·1806	780
0·3151	572	0·1799	636	0·3108	848
0·3323	573	0·3113	700	0·3360	853
0·5817	452	0·3355	700	0·5785	695
0·5960	439	0·5790	571	0·5986	674
0·5971	439	0·5988	546	0·5994	673
0·8173	213	0·5989	543	0·8160	339
		0·8190	265		

The correlation developed in the next section allows a comparison of the data of Savini and Van Ness (personal communication) for ethanol + heptane at 25° with our data for ethanol + hexane; the striking agreement of these two sets of data is shown in Figure 2, p. **1111**.

TABLE 6

HEATS OF MIXING: HEXAN-1-OL + n-HEXANE

25·0°		35·0°		45·0°	
x	H^M (J/mole)	x	H^M (J/mole)	x	H^M (J/mole)
0·1245	417	0·0713	443	0·1227	625
0·1371	430	0·1170	519	0·1398	653
0·2523	489	0·1401	533	0·2490	716
0·2686	494	0·2366	598	0·2709	728
0·5046	475	0·2727	604	0·5026	663
0·5049	462	0·5033	553	0·5230	648
0·5055	456	0·5210	540	0·5230	652
0·5215	454	0·5270	541	0·7689	353
0·7586	253	0·7667	291		

The heats of mixing of each system increase with increasing temperature; values at $x = 0{\cdot}5$ are shown in Figure 1. For the systems of n-alcohol + n-hexane, graphs of H^M against x show interesting features by comparison with the corresponding plots for the systems of n-alcohol+benzene: the heats of mixing of the hexane systems are lower than those of the corresponding benzene systems (except in regions of high dilution of either component) and decrease as the carbon number of the alcohol, N_a, is increased from 3 to 8, whereas the heats of mixing of the benzene systems increase with increasing N_a. The latter effect is due to the large contribution of the interactions of alkyl groups with benzene. The measurements at 25° show the ethanol+hexane system to be anomalous, as its H^M versus x curve lies below that for the propan-1-ol system over the concentration range from about $x = 0{\cdot}1$ to $x = 0{\cdot}7$. This anomaly is more pronounced at 45° for the ethanol system, and even more so for the methanol system.

TABLE 7

HEATS OF MIXING: OCTAN-1-OL + n-HEXANE

25·0°		35·0°		45·0°	
x	H^M (J/mole)	x	H^M (J/mole)	x	H^M (J/mole)
0·1011	373	0·0561	402	0·1003	575
0·1137	381	0·1120	482	0·1132	593
0·2118	428	0·2252	539	0·2083	655
0·2262	434	0·4447	510	0·2270	660
0·4462	435	0·4639	507	0·4445	620
0·4479	433	0·7175	317	0·4642	613
0·4606	422	0·7178	313	0·4653	611
0·7027	288			0·7233	367

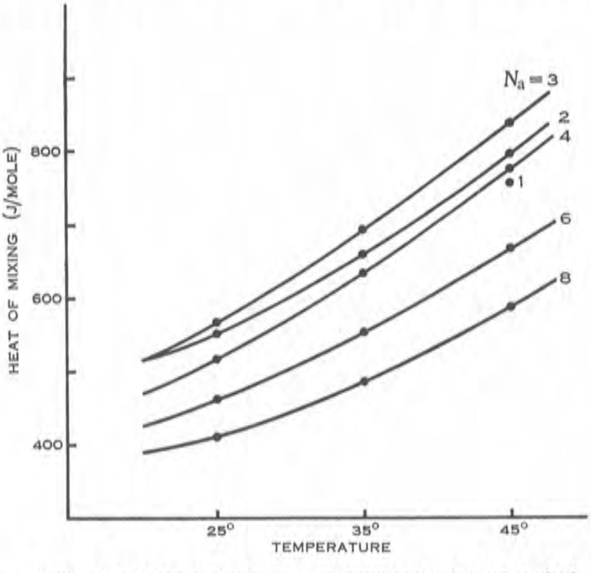

Fig. 1.—Heats of mixing n-alcohols + n-hexane at alcohol mole fraction $x = 0{\cdot}5$. Variation with temperature. N_a, carbon number of alcohol.

Discussion

(*a*) *General*

In a study of binary mixtures of n-alcohols with alkanes von Elbe[10] plotted the heats of mixing per mole of alcohol, at a fixed temperature, against volumetric concentration (moles per litre) of alcohol in the mixture and he found that his points all lay on one curve. This is not in agreement with our results, which when so plotted give a series of curves, one for each mixture, similar to those shown in Figure 2.

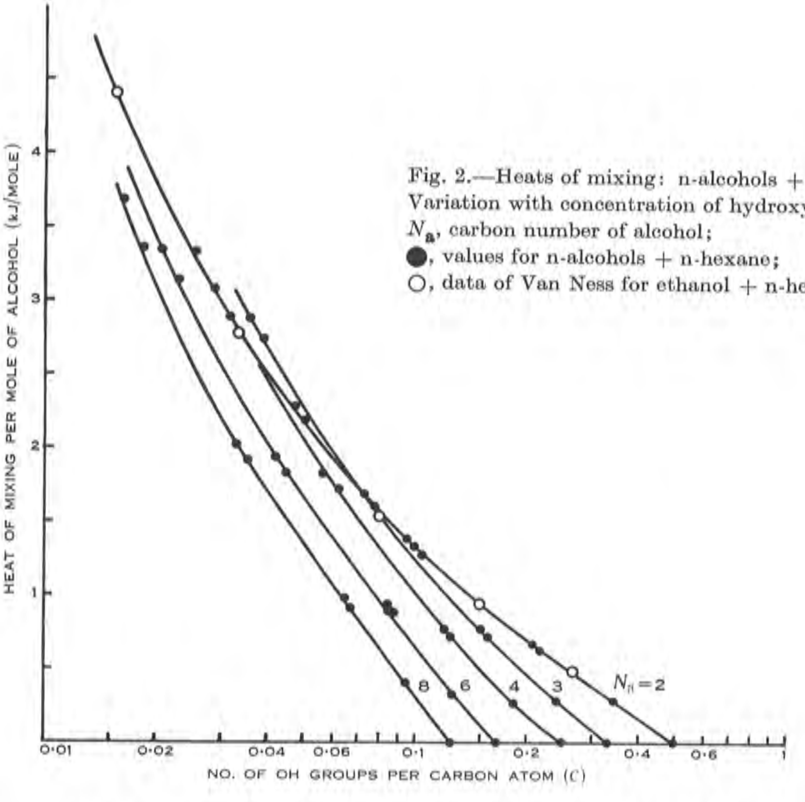

Fig. 2.—Heats of mixing: n-alcohols + n-hexane at 25°. Variation with concentration of hydroxyl groups.
N_a, carbon number of alcohol;
●, values for n-alcohols + n-hexane;
○, data of Van Ness for ethanol + n-heptane at 25°.

Instead of using volumetric concentration as the abscissa we express the alcohol concentration C as the ratio of the number of OH groups to the total number of carbon atoms in the mixture, that is

$$C = x/[xN_a + (1-x)\,N_p] = x/\bar{N}$$

where x is the mole fraction of alcohol in the mixture, N_a and N_p are the carbon numbers of the alcohol and paraffin respectively, and $\bar{N}$ is the average chain length in the mixture. For pure alcohols $C = 1/N_a$.

The heats of mixing per mole of alcohol, H^M/x, at 25° are plotted against C in Figure 2. The curves, with the exception of that for the ethanol system, are congruent, that is they can be made closely coincident by displacement in the direction of the ordinate. The use of volumetric concentration in place of C gives a similar set of curves which are less closely coincident on displacement.

If the curve for the ethanol system is ignored for the moment, Figure 2 suggests that only the contributions of the hydroxyl groups to the heats of mixing are important and that there is one parent curve of enthalpy difference from which the separate heat of mixing curves result owing to the different values of C for each pure alcohol.

The enthalpy contribution of the hydroxyl groups is taken to be the difference between the enthalpy of an alcohol+paraffin mixture and that of the corresponding mixture in which the alcohol is replaced by its homomorphic hydrocarbon. It is postulated that this difference is a function of the concentration C only (at any fixed temperature). The homomorphic hydrocarbons are chosen as those having the same number of carbon atoms in the molecule as the alcohols, as the molar volumes[11] of these homomorphic hydrocarbons at 25° differ by only about 1 ml from the partial molar volumes of the corresponding alcohols at infinite dilution in heptane.[12]

The function postulated is thus:

$$\phi(C) = (H_{\mathrm{ap}} - H_{\mathrm{hp}})/x \tag{1}$$

where H_{ap} is the enthalpy of the mixture of alcohol+paraffin and H_{hp} is that of the corresponding homomorphic mixture. The enthalpies of the liquids are all measured from the datum of ideal gas at 1 atm and 25°.

The heats of mixing are related to $\phi(C)$ by equation (2)

$$(H^{M}_{\mathrm{ap}} - H^{M}_{\mathrm{hp}})/x = \phi(C) - \phi(1/N_{\mathrm{a}}) \tag{2}$$

where $\phi(1/N_{\mathrm{a}})$ is the difference between the enthalpy of the pure alcohol and that of the homomorphic hydrocarbon, $(H_{\mathrm{a}} - H_{\mathrm{p}})$.

(*b*) *Test of Equation (2) at 1 atm*

If H^{M}_{hp} is negligible then a plot of H^{M}_{ap}/x against C for these systems should give a series of curves displaced from one another by the increments in $\phi(1/N_{\mathrm{a}})$. The experimental results of all but the ethanol and methanol systems do in fact form such a series of curves (see Fig. 2).

For solutions infinitely dilute in alcohol equation (2) becomes:

$$h^{\circ}_{\mathrm{ap}} - h^{\circ}_{\mathrm{hp}} = \phi(0) - \phi(1/N_{\mathrm{a}}) \tag{2a}$$

where h° denotes excess partial molar enthalpy at infinite dilution. If h°_{hp} and H^{M}_{hp} are negligible then $H^{\mathrm{M}}_{\mathrm{ap}}/x$ at any constant value of C should show the same variation with N_{a} as does h°_{ap}. Values of h°_{ap} were obtained from preliminary measurements of Van Ness (private communication). The total change in h°_{ap} as N_{a} increases from 3 to 8 agrees (within experimental errors) with the corresponding change in H^{M}_{ap}/x at constant C determined from the data of Figure 2; this implies that equation (2) holds down to infinite dilution.

Because the ethanol system is anomalous when the term H^{M}_{hp}/x is neglected, values of this term have been estimated; details are given in Section (*f*). It is necessary to

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[11] "Selected Values of Properties of Hydrocarbons and Related Compounds." American Petroleum Inst. Res. Proj. 44. (A. & M. College: Texas 1961.)

[12] Staveley, L. A. K., and Spice, B., *J. Chem. Soc.*, 1952, 406.

evaluate this term at 41·7 atm (the saturation pressure of ethane at 25°) so that all the homomorphic hydrocarbons are liquids.

(c) *Test of Equation (2) at 41·7 atm*

The change in H^M_{ap} with pressure from 1 to 41·7 atm was calculated for the ethanol+n-hexane system using equation (3)

$$(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P \tag{3}$$

and the data of Harms[13] on volume change of mixing and was found to be negligible. It is therefore assumed that the values of H^M_{ap} at 41·7 atm for all the alcohol+hexane systems are substantially the same as those at 1 atm.

Table 8
ENTHALPIES OF LIQUID n-PARAFFINS AND HEATS OF MIXING OF n-PARAFFIN + n-HEXANE
At 25·0° and 41·7 atm

Carbon Number	H_{p} (kJ/mole)*	H^M_{hp} (kJ/mole)	
		(3+6)	(2+6)
2	−9·47	—	0
3	−16·59	0	−1·65
4	−21·56	−0·05	−1·15
5	−26·50	−0·08	−0·63
6	−31·34	0	0
7	−36·20	—	—
8	−41·05	—	—

* Standard state: ideal gas at 25° and 1 atm.

Values of the left-hand side of equation (2) have been calculated for 25° and 41·7 atm using all the experimental data given in Tables 3–7, and have been plotted against C; these values form a good set of congruent curves, including that of the ethanol system. Thus the anomalous behaviour of the ethanol+hexane system (and presumably that of the methanol system) is due to the contribution of the term H^M_{hp}. This contribution is more negative at higher temperatures, leading to a larger anomaly at 45° than at 25°, in agreement with our data.

Since equation (1) applies to pure alcohols as well as mixtures, the parent curve of enthalpy difference can be determined from values of the enthalpies at 41·7 atm of pure alcohols and their homomorphic hydrocarbons, and compared with that obtained from heats of mixing data. However, values of H_{a} are not known for most alcohols to better than ±1·0 kJ/mole.

The parent curve obtainable from our set of congruent curves requires a datum. This can be obtained from enthalpy data for, say, $N = 3$. The value used for

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[13] Harms, H., *Z. phys. Chem.* B, 1942, **53**, 280.

propan-1-ol was calculated from the value[14] of H_a at 1 atm corrected to 41·7 atm by the use of equation (3) and volumetric data;[11] the value of H_h for propane at 41·7 atm was taken from Table 8. These give a value of $-30 \cdot 73$ kJ/mole for $(H_a - H_h)$ at $N = 3$.

Values of $\phi(C)$ calculated from our data of heats of mixing are shown in Figure 3. All points lie on a single curve with a scatter less than the estimated errors. The values of $\phi(C)$ calculated from the data of Savini and Van Ness for the ethanol+n-heptane system also lie on the curve.

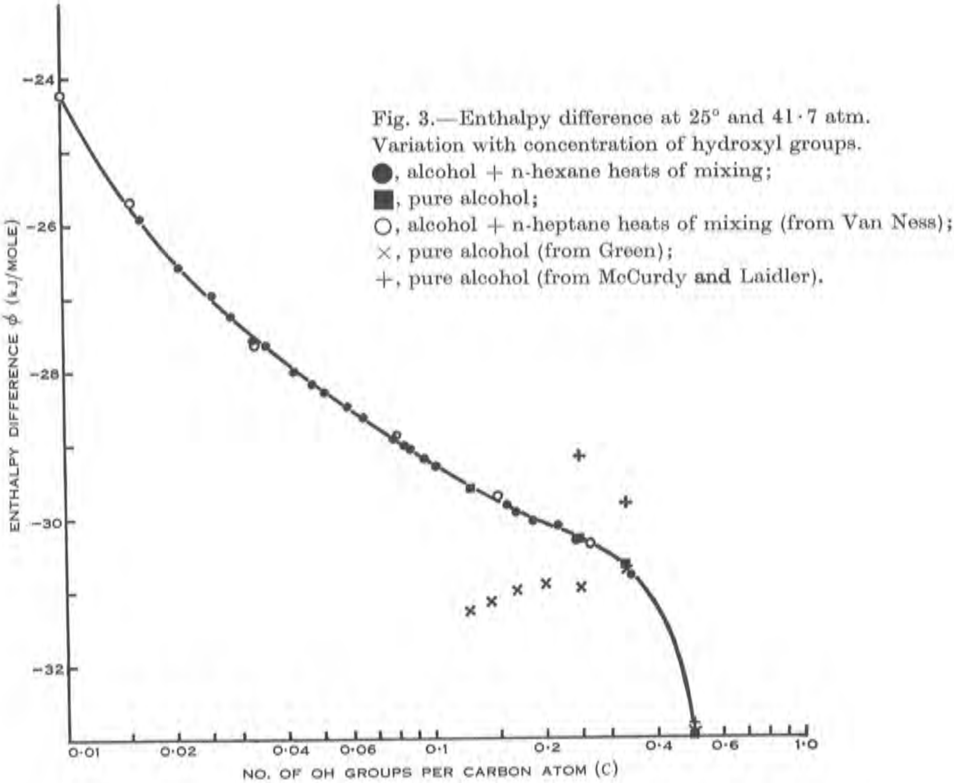

Fig. 3.—Enthalpy difference at 25° and 41·7 atm. Variation with concentration of hydroxyl groups.
●, alcohol + n-hexane heats of mixing;
■, pure alcohol;
○, alcohol + n-heptane heats of mixing (from Van Ness);
×, pure alcohol (from Green);
+, pure alcohol (from McCurdy and Laidler).

Values of $\phi(0)$ at 25° and 41·7 atm were calculated from equation (2a). The values of h_{ap}° were those determined at 1 atm for a number of solutions of alcohols in paraffins by Van Ness (personal communication), and were assumed to be independent of pressure. Values of h_{hp}° were estimated from a plot of H_p against N_p from the data of Table 8 and values of $\phi(1/N_a)$ were read from the graph of Figure 3. The results are given in Table 9, from which it can be seen that the calculated values of $\phi(0)$ are sensibly constant with an average value of $-7 \cdot 8$ kJ/mole of alcohol.

The value of $\phi(0)$ is a measure of the contribution of the interactions between hydroxyl groups and hydrocarbon units to the enthalpy change in the process of

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[14] Green, J. H. S., *J. Appl. Chem.*, 1961, **11**, 397.

taking one mole of alcohol from the ideal-gas state at 1 atm to infinite dilution in paraffin at 41·7 atm.

By analogy with equation (2a) the free energy contribution ΔG for the same process was calculated using the excess chemical potentials at infinite dilution of n-alcohols in n-hexane obtained from the correlation of Pierotti, Deal, and Derr.[15] The values found for ΔG are also shown in Table 9 and are substantially constant at an average value of $-4\cdot5$ kJ/mole. The equation for excess free energies analogous to equation (2) has been tested using limited unpublished data and appears to fail except for solutions infinitely dilute in alcohol, as shown above.

TABLE 9

VALUES OF FUNCTIONS AT INFINITE DILUTION

Carbon Number	$\phi(0)$* (kJ/mole)	ΔG* (kJ/mole)
2	$-7\cdot3$	$-4\cdot5$
3	$-7\cdot9$	$-4\cdot6$
4	$-8\cdot1$	$-4\cdot7$
5	—	$-4\cdot3$
6	$-7\cdot8$	$-4\cdot0$
7	—	$-4\cdot4$
8	$-7\cdot6$	$-4\cdot0$

* For definition see text.

From these estimates of $\phi(0)$ and ΔG the entropy contribution for this process is estimated to be $T\Delta S = -3\cdot3$ kJ/mole; this is presumably not a lattice configurational contribution.

(d) *Enthalpies of Pure Liquid Alcohols and their Mixtures*

If equation (1) is true and if the enthalpy of one alcohol is known accurately, the curve of Figure 3 can be used to calculate values of the enthalpies of other alcohols as those of the corresponding alkanes and the volumetric data required to calculate $(\partial H/\partial P)_T$ are available. Figure 3 also shows a comparison of our curve of $\phi(C)$ with values of $\phi(1/N_a)$ at 25° and 41·7 atm calculated from the values of H_a at 25° and 1 atm of Green[14] and of McCurdy and Laidler.[16] Our correlation lies between these two sets of values, just within the claimed limits of uncertainty of the former, but outside those of the latter.

Heats of mixing of methanol with a number of higher alcohols up to dodecan-1-ol have been measured by Diaz Peña and Martin[17] and it has been claimed (Diaz Peña, personal communication) that mixtures of alcohols obey the principle of congruence; if so, values of H_a for alcohols up to dodecanol can be determined provided that values for two alcohols are known. Values of H_a at $N = 3$ and 12 were obtained using the data of Figure 3 and the data of Diaz Peña and Martin were then used to evaluate H_a of the other alcohols, and hence $\phi(1/N_a)$, in the range $N_a = 2$ to 12. The

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[15] Pierotti, G. J., Deal, C. H., and Derr, E. L., *Ind. Engng. Chem.*, 1959, **51**, 95.

[16] McCurdy, K. G., and Laidler, K. J., *Canad. J. Chem.*, 1963, **41**, 1867.

[17] Diaz Peña, M., and Martin, F. F., *An. R. Soc. Esp. Fís. Quím.*, 1963, **59**, 323, 331.

values obtained for N_a between 3 and 12 are more negative than those shown in Figure 3 by up to 0·05 kJ/mole, and the value for $N_a = 2$ is more negative by 0·28 kJ/mole. This discrepancy suggests that equation (1) does not apply to mixtures of alcohols with alcohols where the hydroxyl groups are attached to two alkyl chains of different size in the one mixture.

(e) *Application of Lattice Theories to Alcohol Systems*

Extensive trials of the theory of Barker[1] have been made using the experimental results of this paper in conjunction with limited unpublished data on the excess free energies and volume changes of mixing. It was not found possible to obtain a single set of parameter values which gives adequate agreement between theoretical and experimental values for all these systems, even when the mixing process at constant volume was considered.

If the heats of mixing of paraffin systems at 41·7 atm do change sign in going from mixtures of long chains to those of short chains then agreement between data obtained at constant pressure and the results of a lattice theory is impossible. A study by McGlashan, Morcom, and Williamson[18] of mixtures of higher alkanes has already demonstrated this, and has shown further that the results obtained from a lattice theory compare best with those of a mixing process "at constant volume per element," but that in this case the mixing process "with zero volume change" is a good approximation. The volume per element of an alcohol is very different from that of an alkane, so that for mixtures of these, the process of "mixing with zero volume change" is not a good approximation to the process considered in lattice theories. This then may be the reason why no satisfactory agreement has been obtained between theory and experiment for the properties of systems of alcohols with hexane and with benzene.

(f) *Heats of Mixing of n-Alkane Mixtures*

The principle of congruence has been used as a basis for the calculation of values of H^M_{hp} for mixtures of ethane, propane, and n-butane with n-hexane. It is not possible to determine values of the heat of mixing of liquid methane with n-hexane at the temperature required as this is above the critical temperature of methane.

The heats of mixing of liquid alkanes with $N_p^{\cdot} > 5$ are positive and have been shown by McGlashan and Morcom[6] to be consistent with the principle of congruence. Barker and Linton[19] have applied the principle of congruence successfully to mixtures of alkanes at vapour densities; hence it might be reasonable to expect this principle to hold for mixtures of fluids near the critical region.

Values of H^M_{hp} at 41·7 atm and 25° for alkane+hexane mixtures were thus estimated from values of the enthalpies of the normal paraffins under these conditions using the principle of congruence. These values were calculated from the values of enthalpy at 1 atm or at saturation pressure, P_s, given in the A.P.I. tables[11] and

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[18] McGlashan, M. L., Morcom, K. W., and Williamson, A. G., *Trans. Faraday Soc.*, 1961, **57**, 601.

[19] Barker, J. A., and Linton, M., *J. Chem. Phys.*, 1963, **38**, 1853.

corrected to 41·7 atm by the use of equation (3). The required values of V and $(\partial V/\partial T)_p$ were obtained from the A.P.I. tables[11] and from the data of Sage, Webster, and Lacy[20] and values of P_s for propane and butane from data given by Jordan.[21] It was assumed that $(\partial H/\partial P)_T$ was independent of pressure in the range from 1 to 50 atm.

The positive values of the heats of mixing of liquid alkanes with $N_p > 5$ and the values of H_p at 41·7 atm and 25° given in Table 8 indicate a point of inflexion in the H_p versus N_p curve so that the principle of congruence indicates a change in sign of H^M_{hp} to negative values for mixtures of short chains. Values of H^M_{hp} for the systems (2+6) and (3+6), i.e. ethane and propane with hexane, at 41·7 atm calculated from these H_p values at mole fractions corresponding to $\bar{N} = 3$, 4, and 5 are also given in Table 8. These negative values are reasonable as the negative values of H^M for the (6+16) system at 76° reported by Friend *et al.*[22] seem consistent with negative values for shorter chains at 25°.

Holleman and Hijmans[23] have developed a corresponding states treatment applicable to the excess functions of alkane mixtures and they conclude that it indicates that H^M must have the same sign throughout the liquid region. However, we consider that their treatment only implies that the reduced H^M values for a system at one temperature will apply at another temperature to some other specific system irrespective of the sign of H^M involved. Applying their transformation to the negative H^M values for the (6+16) system at 76° thus indicates negative values of H^M at 25° for the hypothetical (4·2+8·5) system, in sign agreement with values estimated from the H_p data of Table 8.

The above treatment indicates that the point of inflexion in the curve of H_p against N_p will shift to higher N values at higher temperatures; this point occurs at about $N = 6$ at 25° and the predicted position at 96° is about $N = 12$. Thus an S-shaped curve of H^M against x is expected for the system (8+24) at 96° and this has indeed been found experimentally (Holleman, personal communication). Quantitative comparisons were not attempted as the H_p values at 25° given in Table 8 are at a pressure of 41·7 atm.

CONCLUSIONS

The experimental results of this work indicate that the heat of mixing of a n-alcohol with a n-alkane less that of the homomorphic mixture is the difference between two values of the one function of the concentration of hydroxyl groups; the value at the concentration in the mixture and that in the alcohol before dilution occurs. This relation can be obtained from the postulate that the function represents the contribution of the hydroxyl groups, per mole of alcohol, to the enthalpy of the mixture. This postulate is, however, not the only one from which the above relation can be obtained.

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ACKNOWLEDGMENTS

The authors wish to thank Dr. J. A. Barker of these Laboratories for suggesting that one parent curve of enthalpy difference could be the precursor of the set of heat-of-mixing curves. The authors are grateful to Professor H. C. Van Ness, Professor Th. Holleman, and Dr. M. Diaz Peña for supplying details of their results before publication.

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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 15, NUMBER 1, PAGES 1–8, 9–12 1962

VOLUME CHANGES ON MIXING

I. ALCOHOL + BENZENE SOLUTIONS

~~II. SYSTEMS CONTAINING ACETONE, ACETONITRILE, AND NITROMETHANE~~

By I. Brown and F. Smith

Reprinted for the
Commonwealth Scientific and Industrial Research Organization
Australia

VOLUME CHANGES ON MIXING

I. ALCOHOL+BENZENE SOLUTIONS

By I. Brown[*] and F. Smith[*]

[*Manuscript received October* 6, 1961]

Summary

Direct measurements have been made at 25, 35, and 45 °C of the volume changes on mixing of benzene with each of the following alcohols : methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 1-hexanol, and 1-octanol.

These systems have positive values of V^M, the volume change on mixing per mole of mixture, with maxima at mole fractions of alcohol from 0·15 to 0·35 for the normal alcohol systems and from 0·34 to 0·54 for the secondary and tertiary alcohol systems. The systems containing the three lower normal alcohols also show at 25 °C small negative values of V^M with minima at mole fractions of from 0·85 to 0·95.

Values of V^M increase with the molecular weight of the alcohol and with an increase in temperature. For a given alcohol molecular weight the values of V^M increase with alcohol type in the order primary, iso, secondary, tertiary.

I. Introduction

These measurements were made as part of a study of the thermodynamic properties of alcohol solutions.

The direct measurement of volume change on mixing is both quicker and more accurate than its determination from density measurements on the mixture and on pure components. The direct method requires fewer and less accurate weighings and errors due to evaporation are far smaller than those found using the density method, particularly at elevated temperatures. Apparatus for the direct measurement of V^M has been described by Keyes and Hildebrand (1917), Staveley and Spice (1952), and Desmyter and Van der Waals (1958). The apparatus described here is similar to that of Keyes and Hildebrand.

The only direct measurements on alcohol solutions are those of Staveley and Spice (1952) but these were confined to 20 °C and mole fractions of alcohol below 0·04. Values of V^M for a number of the systems studied by us were calculated from density data taken from the literature but considerable variation was found between values of V^M determined for some systems from the data of different authors.

II. Experimental

(*a*) *Apparatus and Technique*

The mixing cell used for these measurements had a total capacity of 14 ml ; it is shown diagrammatically in Figure 1. It differed from the cell of Keyes and Hildebrand (1917) in having only one precision bore capillary of 1·4 mm

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i.d. (0·001767 ml/mm at 25 °C) the other side being closed by a well-ground stopper. The cell required only one set of liquid level measurements and tests showed that no significant errors resulted from immersion of the stopper in the water-bath.

Mercury (3 to 4 ml) was first placed in the cell to separate the liquids and the previously degassed first component was added to the stoppered side and the cell reweighed. The second component was then added to the other chamber using a hypodermic needle.

The full cell was mounted in a water thermostat (±0·01 °C) and allowed to reach temperature equilibrium. Air bubbles due to degassing of the second component rose to the surface, the level was adjusted to a suitable position relative to the reference mark on the capillary, and the upper walls of the capillary were dried by a small current of dry air. The cell contents were thoroughly mixed by repeated rocking of the cell about a horizontal axis through about 90°. The change in liquid level in the capillary, read to ±0·01 mm by a travelling microscope, gave the volume change on mixing and the final weighing of the cell gave the amount of the second component.

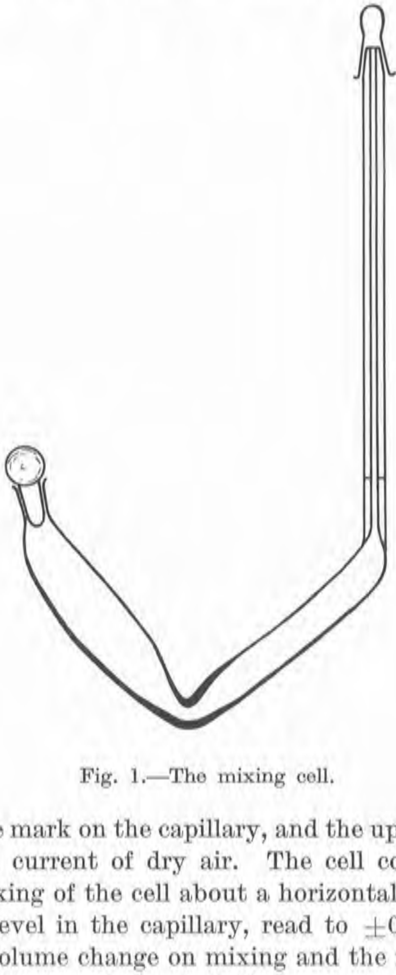

Fig. 1.—The mixing cell.

Two mixing cells were used, one with both chambers of 5 ml each and the other with capacities of 7 and 3 ml. Using both cells direct measurements could be made of mixtures having a mole fraction of alcohol from 0·3 to 0·7.

For components with appreciably different molar volumes or for measurements at high or low mole fraction it was necessary to mix one pure component with a mixture of known volume change.

(b) *Purification and Physical Properties of Components*

Benzene and the normal alcohols were purified by the methods described by Brown and Fock (1961) and 2-propanol by the method of Brown, Fock, and Smith (1956). The branched butanols were fractionally distilled using the column described by Brown and Ewald (1951) and fractions which gave a single peak when gas chromatographed on Apiezon L at 100 °C were used. The 2-methyl-2-propanol was then fractionally frozen three times and redistilled. The density of this alcohol after the first fractional distillation was $d_4^{27\cdot0}=0\cdot77845$ and after freezing and redistillation was 0·77838. This value was consistent with the value of $d_4^{25}=0\cdot78043$ of Simonsen and Washburn (1946), the value $d_4^{25}=0\cdot78052$ of Kenttämaa, Tommila, and Martti (1959), and the value of $d_4^{20}=0\cdot78581$ of Dreisbach and Martin (1949). However, a plot of density against temperature of data by four authors given by Timmermans (1950) indicates the much higher value $d_4^{27}=0\cdot77934$. The physical properties of the components are given in Table 1.

TABLE 1
THE PHYSICAL PROPERTIES OF THE COMPONENTS

	$d_4^{25\cdot00}$	$n_D^{25\cdot00}$	Boiling Point (°C/760 mmHg)
Methanol	0·78683	1·32662	64·54
Ethanol	0·78511	1·35926	78·29
1-Propanol	0·79959	1·38314	97·08
2-Propanol	0·78100	1·37497	82·23
1-Butanol	0·80578	1·39731	117·52
2-Methyl-1-propanol	0·79779	1·39384	107·75
2-Butanol	0·80251	1·39525	99·41
2-Methyl 2-propanol	0·77838*	1·38401*	82·32
1-Hexanol	0·81531	1·41607	157·5
1-Octanol	0·82247	1·42741	195·2
Benzene	0·87365	1·49801	80·07

* 27·00 °C.

III. RESULTS

Direct measurement of volume changes using the mixing cell was the method employed for most of the determinations. Some of the values at 25 and 45 °C for the lower alcohols were calculated from density measurements made using single stemmed pyknometers as described by Brown and Ewald (1950). The errors in V^M due to errors in the measured quantities at 25 °C were estimated to be ±0·007 ml/mole for the values calculated from density measurements and ±0·003 ml/mole for the direct measurements using the cell. At 45 °C evaporation during the measurements led to larger errors which were estimated to be ±0·02 ml/mole for those calculated from densities and ±0·004 for the direct measurements.

A comparison of the two methods for the system 2-propanol+benzene showed agreement within 0·005 ml/mole at 25·0 °C (V^M=0·30 ml/mole) and to within 0·023 at 45·0 °C (V^M=0·41 ml/mole).

The measurements of V^M for the system 2-methyl-2-propanol+benzene were made at 27·0 °C as this alcohol has a melting point of 25·66 °C.

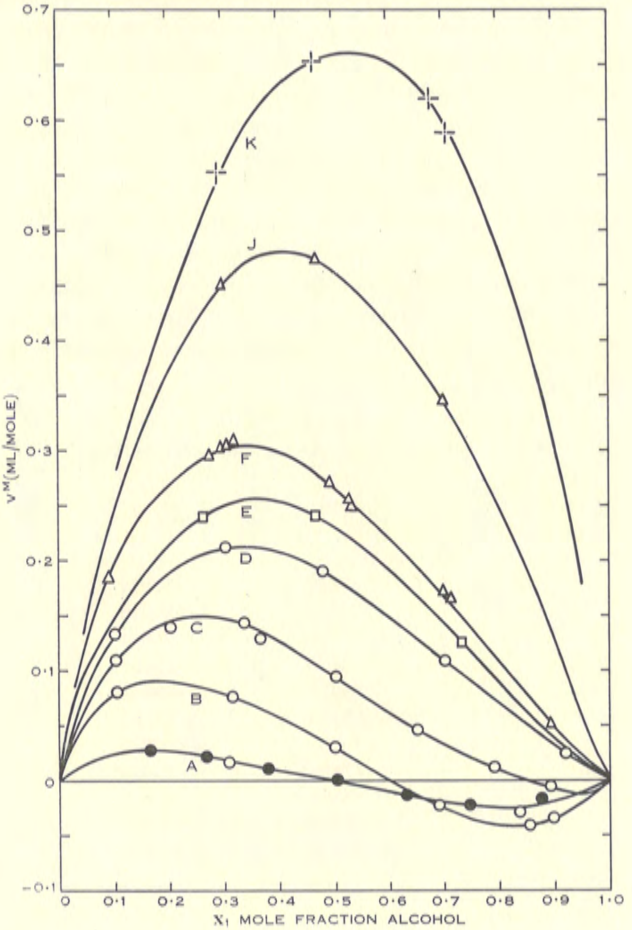

Fig. 2.—Volume change on mixing at 25·0 °C for alcohol+benzene mixtures as a function of composition.

A, Methanol ● Results of Scatchard, Wood, and Mochel (1946) ; *B* ethanol ; *C*, 1-propanol ; *D*, 1-butanol ; *E*, 2-methyl-1-propanol ; *F*, 2-propanol ; *J*, 2-butanol ; *K*, 2-methyl-2-propanol, this latter set of results is at 27·0 °C.

The values of V^M at 25·0 °C as a function of composition for the systems are shown in Figure 2. These data show that the values of V^M are positive except for the three lower normal alcohols at high alcohol mole fraction. The maximum values of V^M become rapidly more positive as the size of the alcohol molecule is increased and as the number of alkyl groups on the alpha carbon is increased ;

a smaller increase in V^M results from branching of the alkyl group. Figure 3 shows the variation of V^M with temperature from 25 to 45 °C at an alcohol mole fraction of 0·300. The volume change on mixing increases with increase in temperature at a similar rate for the systems containing ethanol, the propanols, and the butanols but this effect becomes small for the hexanol system and a slight decrease is shown for the octanol system.

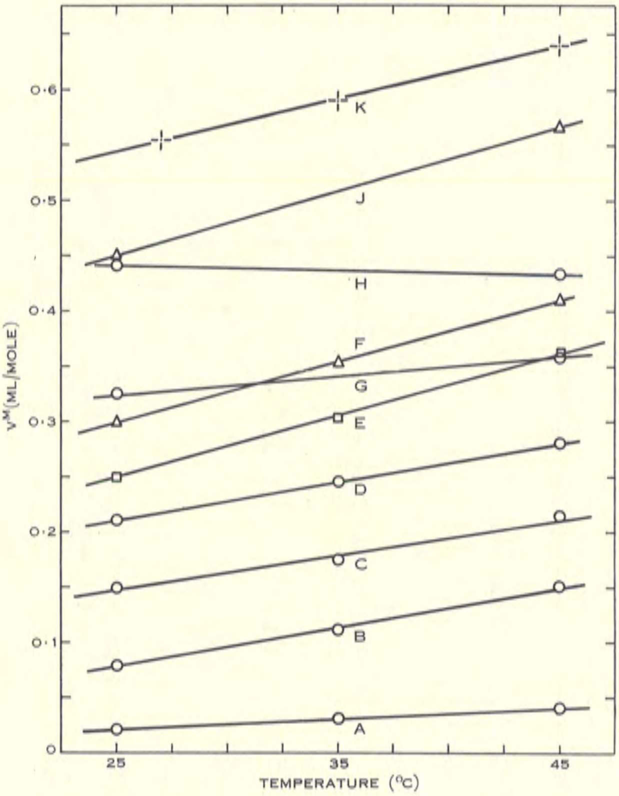

Fig. 3.—Volume change on mixing for alcohol+benzene mixtures at composition 0·300 mole fraction alcohol as a function of temperature.
A, Methanol; *B*, ethanol; *C*, 1-propanol; *D*, 1-butanol; *E*, 2-methyl-1-propanol; *F*, 2-propanol; *G*, 1-hexanol; *H*, 1-octanol; *J*, 2-butanol; *K*, 2-methyl-2-propanol.

Figure 4 shows the relation between the molecular weight and type of alcohol and V^M of alcohol+benzene systems at 25·0 °C at an alcohol mole fraction of 0·300.

IV. Discussion

The only published direct measurements of volume changes on mixing for alcohol solutions are those of Staveley and Spice (1952), but these could not be compared with our measurements as they were made at 20 °C and confined to mole fractions of alcohol below 0·04.

Values of V^M for many of the systems studied were calculated from published density data and considerable variation was found between the values for a given system calculated from data of different authors. However, values calculated from the data of Harms (1942) for a number of these systems are in good agreement with our values. The directly measured values are probably more accurate than those calculated from density measurements. A comparison of values is given below.

Methanol+Benzene: The values of Scatchard, Wood, and Mochel (1946) and Scatchard and Ticknor (1952) at 25 °C are in close agreement with our measurements, and those of Harms (1942) at 6 and 30 °C were about 0·02 ml/mole lower. The values of Pesce and Evdokimoff (1940) at 25 °C have about the correct magnitude but the wrong concentration dependence. The values of Starobinets, Starobinets, and Ryzhilnova (1951) at 25 °C, Fischler (1913) at 25 °C, Perrakis (1925) at 25 °C, and Teitelbaum (1950) at 25 °C scatter badly mostly far below the other values.

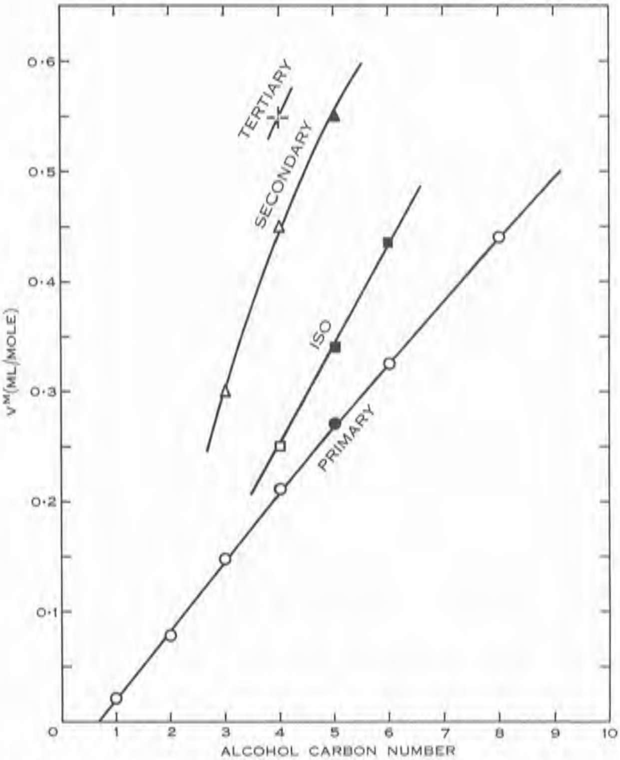

Fig. 4.—Volume change on mixing as a function of alcohol carbon number for alcohol+benzene mixtures at composition 0·300 mole fraction alcohol. Solid symbols are values calculated from density measurements by other authors (see text).

Ethanol+Benzene: The volume changes derived from the data of Harms (1942) at 6 and 30 °C and Klapproth (1940) at 22 °C and Heyman and Graffunder (1931) at 56·7 °C agree well with our values. Those of Goss (1940) at 20 °C and Kowalski and Modzelewski (1901) at 18 °C and Barbaudy (1926) at 25 °C are in fair agreement, while those of Perrakis (1925) at 20 °C, Burwinkel (1914) at 17 °C, Starobinets, Starobinets, and Ryzhilnova (1951) at 25 °C and Ramsay and Ashton (1902) at 10, 46, and 78 °C scatter far from the other values.

1-Propanol+Benzene: The values of Harms (1942) at 22 °C and Spells (1936) at 22 °C agree with our values, while those of Racewicz and Zubkowski (1933) at 20 °C and Perrakis (1925) at 20 °C are about 0·03 ml/mole higher and lower than our values respectively.

For 2-propanol+benzene the values derived from the data of Poltz (1936) at 22 °C agree well with ours, but those of Olsen and Washburn (1938) at 25 °C and Perrakis (1925) at 20 °C are well below these values.

For 1-butanol+benzene values of V^M calculated from the data of Jones *et al.* (1948) at 25 °C and Harms (1943) at 22 °C are within 0·005 ml/mole of our values. The data of Smyth and Stoops (1929) at 10, 20, 30, 40, 50, and 60 °C show the same variation with temperature as our results but are consistently about 0·03 ml/mole higher. The data of Klapproth (1940) and Huyskens and Cracco (1960) are in disagreement with our values, being too low and too high respectively.

For 2-methyl-1-propanol+benzene the data of Harms (1942) at 22 °C are in agreement with our values. For the system 2-butanol+benzene the values derived from the data of Klapproth (1940) at 22 °C are very much lower than our values.

For 2-methyl-2-propanol+benzene the data of Spells (1936) at 25 °C are 13% higher than our value.

For 1-hexanol+benzene the data of Harms (1942) are 0·03 ml/mole higher than ours, while those of Jones *et al.* (1948) at 25 °C are considerably lower. Figure 4 shows that values of V^M at 25 °C for four additional systems are in reasonable agreement with our data. These values were estimated from density data on the following alcohol+benzene systems: 1-pentanol at 25 °C by Jones *et al.* (1948), " iso " pentanol (probably a mixture of 2-methyl-1-butanol and 3-methyl-1-butanol) and 3-pentanol at 20 °C by Spells (1936), and 2-methyl-1-pentanol at 22 °C by Harms (1942).

Values of V^M calculated from density data for the systems 2-octanol+benzene by Coppock and Goss (1939) and for 2-methyl-3-heptanol by Smyth and Stoops (1929) appear to be lower than would be expected from the data shown in Figure 4.

To summarize, the values of V^M for the benzene+alcohol systems are known with reasonable accuracy over the temperature range 20 to 50 °C for normal alcohols up to C_8 and the systems with the branched alcohols up to C_4 from 25 to 45 °C.

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THERMODYNAMIC PROPERTIES OF ALCOHOL SOLUTIONS

Summary and Discussion of Results

(With additional unpublished data)

Alcohols are strongly associated by hydrogen bonding between the hydroxyl groups on adjacent molecules and also to a smaller extent by interaction between hydroxyl groups and alkyl groups.

An estimate was made of the contributions to the energy and entropy of liquid normal alcohols due to hydrogen bonding. In these calculations the energy and entropy changes on taking a mole of alcohol from the ideal gas state at one atmosphere to liquid at 25°C and at its saturation pressure were determined and from these were subtracted the corresponding changes for the homomorphic n-alkane on going from ideal gas to liquid at the same density as that of the alcohol. The homomorphic alkanes were those having the same number of carbon atoms as the alcohols. The resultant energy contribution was found to be substantially constant for alcohols from ethanol to octanol at $\Delta E = -28 \pm 1.5$ Kj per mole, close to the estimate of the hydrogen bond strength made by Badger & Bauer.[1] The values of the corresponding contributions to the entropy of liquid alcohols was also found to be substantially constant for this range of alcohols. Expressed as the temperature entropy product it was found to be $T\Delta S = -16 \pm 2$ Kj/mole.

In solution, the changes in the thermodynamic properties which take place on dilution of an alcohol with a non-polar solvent are partly due to the number and strength of the hydrogen bonds broken. The magnitude of the changes depend on the alcohol, the solvent, the concentration and the temperature and are governed by the balance of the intermolecular interactions between hydroxyl-hydroxyl and hydroxyl-alkyl groups in the alcohol and hydroxyl-solvent and alkyl-solvent interactions between alcohol and solvent. It is difficult to estimate accurately the separate contributions due to each of these factors.

A. Solutions of Normal Alcohols

The detailed data on the thermodynamic properties of solutions of normal alcohols given in the preceding papers is supplemented by unpublished data on the excess free energy and volume changes on mixing for the system n-propanol + n-hexane given in the attached tables 4 and 5 of the appendix to this section.

The properties of solutions of normal alcohols in n-hexane and in benzene can be briefly summarised by the values of the excess free energy (G^E), the heat of mixing (H^M), the excess entropy of mixing (S^E) and the volume change on mixing (V^M) at 25°C and a mole fraction of alcohol $x_1 = 0.5$, given in tables 1 and 2.

1. Variation with temperature

For solutions of an alcohol in benzene and in n-hexane at a fixed mole fraction the heat of mixing and excess entropy of mixing both become more positive with a rise in temperature, but the contribution of these changes to the change in the excess free energy of mixing almost

Table 1. n-Alcohols + n-Hexane 25° $x = 0.5$

Alcohol	G^E	H^M	TS^E	V^M
	j/mole			ml/mole
methanol	(1650)	(490)	(-1160)	-
ethanol	1405	555	-850	+0.41
1-propanol	1245	565	-680	+0.18
1-butanol	1140	510	-630	+0.08
1-hexanol	(980)	465	(-515)	-0.16
1-octanol	(845)	415	(-430)	-0.35

Table 2. n-Alcohols + Benzene 25° $x = 0.5$

Alcohol	G^E	H^M	TS^E	V^M
	j/mole			ml/mole
methanol	1260	615	-645	+0.0
ethanol	1110	755	-355	+0.03
1-propanol	1000	940	-60	+0.10
1-butanol	925	1025	+100	+0.18
1-hexanol	(805)	1060	(+225)	+0.31
1-octanol	(740)	1130	(+390)	+0.42

(Values in brackets are extrapolated)

cancel giving a slight decrease in G^E with a rise in temperature for the benzene solutions and a slight increase for the n-hexane solutions. For the benzene solutions the variation of G^E, H^M and TS^E with temperature at even values of mole fraction are given in tables 6 to 9 (see appendix). The volume changes on mixing of the lower alcohols in benzene at $x = 0.5$ also become more positive with an increase in temperature. For the 1-hexanol system this change is small and for the 1-octanol system a slight decrease was found.

The increases in H^M, S^E and V^M found on increasing the temperature are largely due to the breaking of more hydrogen bonds caused by increased thermal agitation.

2. Variation with the size of the alcohol molecule

In mixtures of a n-alcohol with a n-paraffin the contribution of the hydroxyl groups to the enthalpy of the mixture per mole of alcohol, at a fixed temperature was found to be a function only of the concentration of hydroxyl groups in the mixture. The heat of mixing of a given mixture less that of the homomorphic mixture was found to be equal to the difference between the value of this function at the concentration in the mixture and that in the alcohol before dilution occurred.

In n-hexane solution at $x_1 = 0.5$ and 25°C, H^M is positive and falls slowly as the carbon number of the alcohol, Na, is increased from 3 to 8. This is the result of the contribution of the hydroxyl groups to the enthalpy per mole of alcohol in the mixture falling off less rapidly than the contribution in the pure alcohol as Na is increased. When Na is decreased below 3 the value of H^M falls due to the additional negative contribution from the interaction between alkyl group and solvent.

In benzene solution under the same conditions H^M is more positive than in hexane solution and continues to rise as Na is increased from 1 to 8 due to additional large positive contribution from the interaction between the alkyl groups and the solvent as is shown by the large positive values of H^M for paraffin + benzene systems. This contribution increases as Na is increased.

The excess entropy of mixing in these alcohol solutions is negative at high alcohol concentrations due to the fact that most of the hydrogen bonds remain unbroken and there is thus a restriction of translation of the alcohol molecules. A larger positive change in entropy occurs in forming the ideal solution than in forming the actual solution. At sufficiently low alcohol concentration the restriction of translation vanishes as all hydrogen bonds are broken and the gain of freedom of orientation leads to a positive excess entropy of mixing. This effect occurs at a higher alcohol concentration in benzene solution than in hexane solution because of the increased breaking of hydrogen bonds due to the larger interaction between hydroxyl groups and solvent in the former solution.

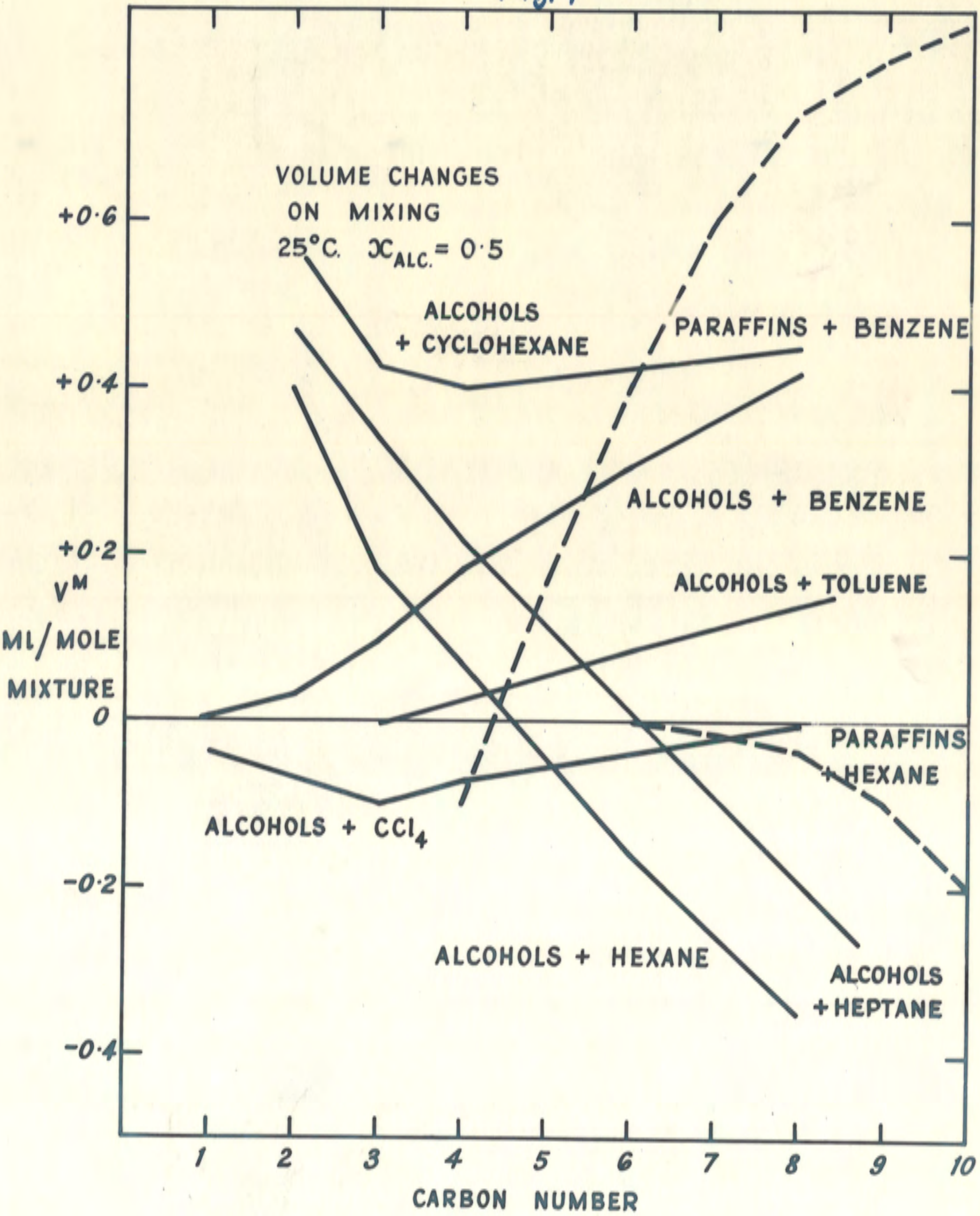
The excess entropy of mixing at $x = 0.5$ and 25°C for both these series of solutions becomes more positive as Na is increased. This is the result of more hydrogen bonds being broken at a given mole fraction in the solution of longer chain alcohols than in the mixtures containing the shorter chain alcohols due to a larger alkyl group to solvent interaction in the former. This may be also the result of a larger gain in configurational freedom on breaking an hydrogen bond between the longer chain alcohol molecules than between the shorter chain molecules.

The volume changes on mixing at 25°C and $x = 0.5$ for the hexane solutions are positive for the systems containing the lower alcohols and become negative as Na is increased, while those in benzene solution are positive and increase as Na is increased. These effects are due to two causes: the first is the volume change due to breaking hydrogen bonds; this is larger for a given alcohol in benzene solution than in hexane solution as more hydrogen bonds are broken at $x = 0.5$ in the former solvent. The second cause is the appreciable contributions from the interaction between alkyl groups and solvent which become more positive in benzene solution and more negative in hexane solution as Na is increased as is shown by the values of V^M for the paraffin + solvent systems given in figure 1.

3. Variation with the solvent

The variation of the thermodynamic properties of alcohol solutions with change in solvent is due to changes in the interactions between both the hydroxyl and the alkyl groups of the alcohol with the solvent molecules. These variations have been discussed in some detail for hexane and benzene solutions. This behaviour is further illustrated in figure 1 where the variation of V^M with the carbon number of the alcohol is shown for a number of solvents. A similar pattern of behaviour was found for the heats of mixing.

Fig. 1


VOLUME CHANGES
ON MIXING
25°C. $x_{ALC.} = 0{\cdot}5$
ALCOHOLS
+ CYCLOHEXANE
PARAFFINS + BENZENE
ALCOHOLS + BENZENE
ALCOHOLS + TOLUENE
PARAFFINS
+ HEXANE
ALCOHOLS + CCl$_4$
ALCOHOLS + HEXANE
ALCOHOLS
+ HEPTANE
+0·6
+0·4
+0·2
0
-0·2
-0·4
V^M
Ml/MOLE
MIXTURE
1
2
3
4
5
6
7
8
9
10
CARBON NUMBER

B. Branched Alcohols

The thermodynamic properties of branched, secondary and tertiary alcohols were also investigated for 2-propanol and the butanols in both n-hexane and benzene solution. The volume changes on mixing in benzene solution have been summarised in figure 4 of paper No. 12. Similar results were found from a limited number of measurements of V^M made in n-hexane solution.

Unpublished data on systems containing branched alcohols are given in the appendix. Tables 10 to 13 show the variation of G^E, H^M and TS^E with temperature for the benzene solutions at even values of mole fraction. The measured values of H^M of branched alcohols in n-hexane are given in tables 14 to 16 and those in benzene in tables 17 to 19. Tables 20 to 22 give the measured values of the excess chemical potentials and excess free energy of mixing for systems of the branched alcohols in benzene.

The heats of mixing, excess entropies and volume changes on mixing at a given concentration, temperature and value of Na become in general more positive in the order: normal, iso, secondary, tertiary as shown for example in table 3. The order in which the solution properties of these different types of alcohol occur appears, from a study of the heat of mixing data, to be due to differences in the effective strength of the hydrogen bonds.

The heat of mixing data at 45°C are summarised in Figure 2. The heats of mixing at a mole fraction of 0.5 increase at approximately the same rate with a rise in temperature for all the systems studied except for the tertiary butanol systems where the rise is less pronounced.

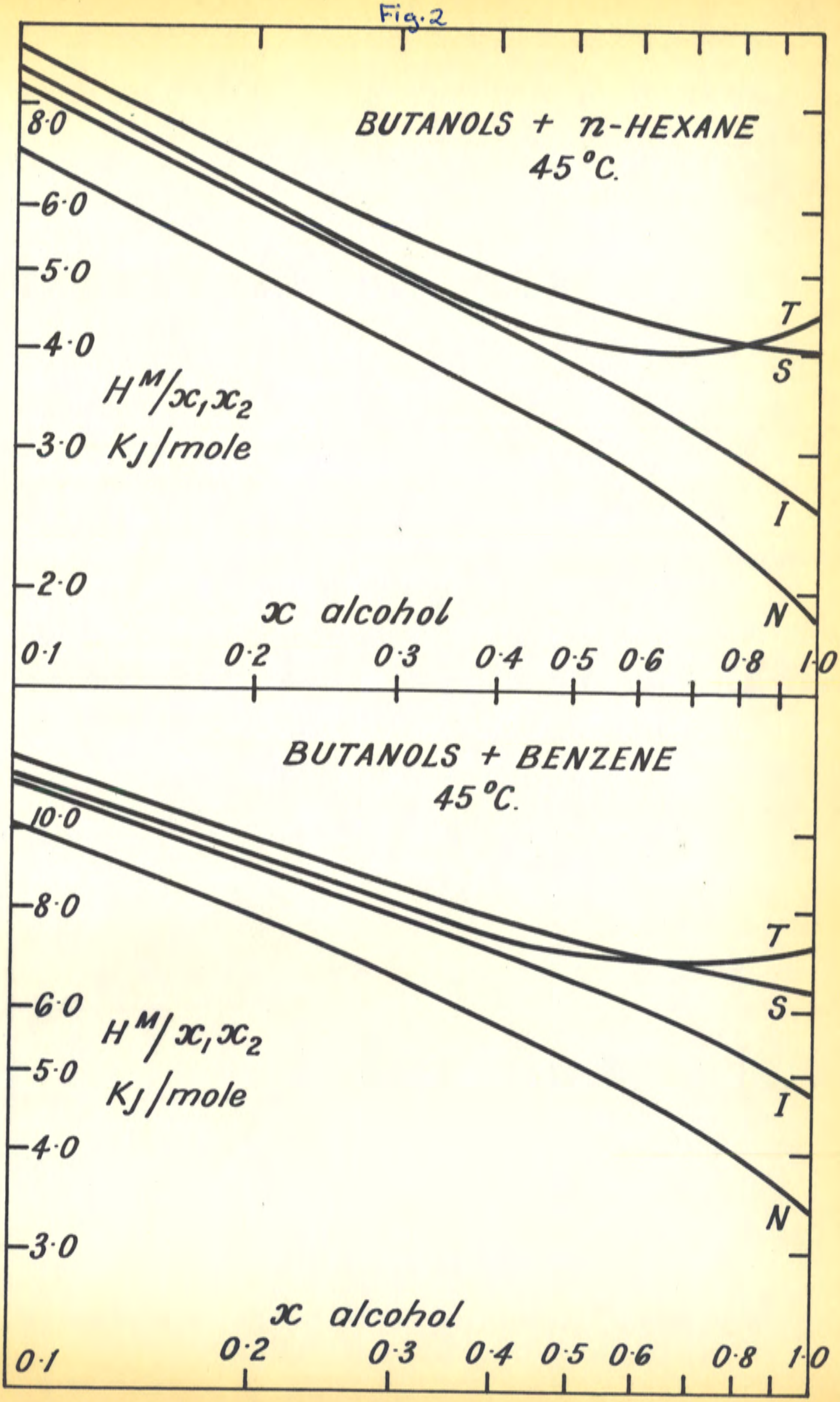
Table 3. Branched Alcohols + Benzene 25° $x = 0.5$

Alcohol	G^E	H^M	TS^E	V^M
	j/mole			ml/mole
n-propanol	1000	940	-60	0.10
iso-propanol	1035	1290	+265	0.27
n-butanol	925	1025	100	0.18
iso-butanol	970	1315	345	0.23
sec-butanol	915	1590	675	0.46
tert-butanol	890	1675	785	0.66

This leads to a reversal of the order of H^M at $x = 0.5$ for the systems containing secondary and tertiary butanol at a temperature of about 35° for the benzene solutions and at about 20° for the hexane solutions. This can be seen by comparing the data of table 3 with that of figure 2. For solutions of the branched butanols in benzene H^M is more positive than the corresponding values in n-hexane as was found for the systems of the normal alcohols in these solvents.

The heats of vapourisation of the butanols decrease rapidly in the order: normal, iso, secondary, tertiary, and it is possible that the contribution to the energy of these liquid alcohols due to hydrogen bonding also decreases in this order, but to a lesser extent. However, estimated values of this contribution were not sufficiently accurate to confirm this.

Fig.2


BUTANOLS + n-HEXANE
45 °C.
8·0
6·0
5·0
4·0
3·0
2·0
H^M/x_1x_2
KJ/mole
T
S
I
N
x alcohol
0·1
0·2
0·3
0·4
0·5
0·6
0·8
1·0
BUTANOLS + BENZENE
45 °C.
10·0
8·0
6·0
5·0
4·0
3·0
H^M/x_1x_2
KJ/mole
T
S
I
N
x alcohol
0·1
0·2
0·3
0·4
0·5
0·6
0·8
1·0

It has been found by Geiseler, Fruwert & Stockel[2] that the highly branched octanols have less of the higher alcohol polymers at a given concentration in carbon tetrachloride than the less branched isomers. It is thus probable that the branched butanols have slightly weaker hydrogen bonds than those in n-butanol. This could lead to the breaking of more hydrogen bonds at a given mole fraction on dilution of the branched alcohol than with the normal alcohol as the number of bonds broken can increase more rapidly than the heat of breaking one bond decreases, provided the strength of the hydrogen bonds is high enough. (See Barker and Smith[3]). This may be the reason why the heat of mixing of the branched butanols with both benzene and hexane become more positive in the order shown in Table 3 and figure 2. The dip in the H^M curve for the tertiary butanol systems at 45°C as x_1 is decreased from 1.0 is probably due to the same cause as that found for the H^M of methanol and ethanol in hexane solution; that is, a negative contribution (more pronounced at 45° than at 25°) due to alkyl group to solvent interaction. The heat of mixing of the homomorphic system neopentane + n-hexane is probably negative by anology with the system 3,3-diethyl pentane + n-octane which has a H^M of -90 j/mole at 50°C and $x = 0.5$.

These results indicate that the branched alcohol solutions in hexane will not follow the same enthalpy difference correlation found for the normal alcohols solutions.

C. Comparison With Theory

The lattice theory of Barker and Smith[3] and the association theories of the type proposed by Kretschmer &

Wiebe[4] have both been found inadequate to explain quantitatively the complex changes in the thermodynamic properties which have been found to take place on solution of alcohols in nonpolar solvents. These two theories cannot lead to the prediction of volume changes on mixing.

The use of the homomorph approach for solutions of alcohols in n-paraffins gave only a correlation of heats of mixing. An estimate was made of the volume changes on mixing from the volume change on breaking of hydrogen bonds together with that calculated for the mixture of n-hexane with the homomorphic hydrocarbon. This method did not yield the large negative values of V^M found for the solutions of the higher alcohols in n-hexane.

A more complex model is required to fit in with all the experimental data. Perhaps a model in which the alcohol "polymers" are in the form of spherical micelles with a number of alcohol units hydrogen bonded together near the centre and with their alkyl chains radiating outwards. It would however be very difficult to calculate the thermodynamic properties of solutions based on such a complex model.

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2. Geiseler, G., Fruwert, J. and Stockel, E., Z. Phys. Chem. 1962, 32 : 330.
3. Barker, J. A., and Smith, F., J. Chem. Phys. 1954, 22 : 375.
4. Kretschmer, C. B., and Wiebe, R., J. Chem. Phys., 1954, 22 : 1697.

Appendix

Tables 4 to 22 give details of unpublished measurements of the thermodynamic properties of alcohol solutions.

The symbol x_1 refers to the mole fraction of alcohol in the liquid and y_1 to that in the vapour. P is the pressure, μ_1^E and μ_2^E are the excess chemical potentials of the alcohol and solvent respectively and G^E, H^M, S^E and V^M are the changes on mixing in excess free energy, heat, excess entropy and volume. G^E, H^M and TS^E are given in joules per mole of mixture. (In some tables, however, units of calories are used to simplify typing in the limited page width available).

Table 4. 1-Propanol + n-Hexane Excess Free Energies 45.0°C

x_1	y_1	P	μ_1^E	μ_2^E	G^E
		mm.Hg	cal/mole		
0.0		337.71			
0.2847	0.1361	360.85	563	161	275
0.4447	0.1489	349.36	317	291	303
0.5289	0.1566	345.24	235	382	305
0.5410	0.1584	344.19	223	396	302
0.7440	0.1926	306.79	73	668	225
1.0		69.35			

Table 5. 1-Propanol + n-Hexane
Volume Changes on Mixing 25.0°C (ml/mole)

x_1	V^M	x_1	V^M
0.0453	0.105	0.3987	0.218
0.1075	0.185	0.5073	0.179
0.1976	0.225	0.5929	0.121
0.2967	0.234	0.7061	0.082

Table 6. Methanol + Benzene (cal/mole)

x_1	G^E			H^M			TS^E		
	25°	35°	45°	25°	35°	45°	25°	35°	45°
0.1	141	140	140	135	144	163	−6	+4	+23
0.2	226	228	229	160	191	212	−58	−28	−8
0.3	277	280	282	168	197	224	−101	−75	−50
0.4	300	304	307	162	190	219	−138	−114	−88
0.5	302	306	310	147	173	201	−155	−133	−109
0.6	284	289	293	124	147	173	−160	−142	−120
0.7	245	250	254	97	116	138	−149	−134	−116
0.8	186	190	194	67	80	96	−120	−111	−99
0.9	106	108	110	35	41	49	−71	−67	−61

Table 7. Ethanol + Benzene (cal/mole)

x_1	G^E			H^M			TS^E		
	25°	35°	45°	25°	35°	45°	25°	35°	45°
0.1	128	127	125	153	174	192	+25	+47	+67
0.2	203	202	201	196	228	254	−7	+26	+53
0.3	246	246	246	208	240	272	−38	−6	+26
0.4	265	267	268	201	232	267	−64	−35	−1
0.5	265	267	268	180	212	246	−85	−55	−22
0.6	246	248	250	151	180	211	−95	−68	−39
0.7	209	212	214	116	141	166	−92	−71	−48
0.8	155	158	159	77	96	113	−78	−62	−46
0.9	86	87	88	38	48	57	−48	−39	−31

Table 8. n-Propanol + Benzene (cal/mole)

x_1	G^E			H^M			TS^E		
	25°	35°	45°	25°	35°	45°	25°	35°	45°
0.1	118	116	113	172	191	221	+54	+75	107
0.2	186	184	181	233	260	294	+48	+77	113
0.3	224	223	221	249	280	317	+25	+57	96
0.4	241	240	239	245	277	313	+4	+37	74
0.5	239	239	238	225	256	292	−14	+17	54
0.6	220	220	220	192	220	255	−42	0	35
0.7	185	186	186	148	174	205	−37	−12	19
0.8	136	136	137	99	119	144	−37	−18	7
0.9	74	74	75	49	60	76	−25	−14	1

Table 9. n-Butanol + Benzene (cal/mole)

x_1	G^E			H^M			TS^E		
	25°	35°	45°	25°	35°	45°	25°	35°	45°
0.1	111	109	106	181	191	199	70	82	93
0.2	176	173	169	244	277	291	69	99	122
0.3	210	208	205	260	300	327	50	92	123
0.4	224	222	219	264	299	329	40	77	110
0.5	221	220	217	245	280	311	24	61	94
0.6	201	200	198	210	241	272	9	41	74
0.7	167	166	165	164	190	217	−3	24	52
0.8	121	121	120	111	131	152	−10	10	32
0.9	65	65	65	55	66	78	−10	1	13

Table 10. iso-Propanol + Benzene (cal/mole)

x_1	G^E			H^M			TS^E		
	25°	35°	45°	25°	35°	45°	25°	35°	45°
0.1	115	113	110	176	196	215	61	83	106
0.2	185	182	178	268	297	330	83	115	152
0.3	227	224	220	309	341	375	82	117	156
0.4	247	244	240	321	355	391	74	111	151
0.5	248	245	241	308	343	378	61	98	137
0.6	231	229	226	277	309	342	46	81	116
0.7	197	196	194	228	257	284	31	61	91
0.8	147	146	145	166	187	207	19	41	63
0.9	82	81	80	90	102	113	9	21	33

Table 11. iso-Butanol + Benzene (cal/mole)

x_1	G^E			H^M			TS^E		
	25°	35°	45°	25°	35°	45°	25°	35°	45°
0.1	113	109	106	206	230	243	93	121	137
0.2	177	173	168	288	316	348	111	143	180
0.3	217	213	208	321	359	390	104	156	182
0.4	233	229	224	330	371	404	97	142	180
0.5	232	229	224	314	354	390	82	125	166
0.6	214	211	207	279	315	348	65	104	141
0.7	182	180	177	227	257	286	45	77	109
0.8	135	133	132	161	183	204	26	50	72
0.9	75	75	74	84	96	108	9	21	34

Table 12. sec-Butanol + Benzene (cal/mole)

x_1	G^E			H^M			TS^E		
	25°	35°	45°	25°	35°	45°	25°	35°	45°
0.1	105	101	96	227	243	264	122	142	168
0.2	166	161	155	318	340	374	152	179	219
0.3	202	196	189	368	395	429	166	199	240
0.4	219	212	205	387	418	449	168	206	244
0.5	219	213	207	380	411	440	161	198	234
0.6	203	198	192	347	377	404	144	179	212
0.7	174	169	164	295	319	342	121	150	178
0.8	129	126	122	219	237	254	90	111	132
0.9	72	70	68	121	131	140	49	61	72

Table 13. tert-Butanol + Benzene (cal/mole)

x_1	G^E			H^M			TS^E		
	25°	35°	45°	25°	35°	45°	25°	35°	45°
0.1	102	97	92	231	240	245	129	143	153
0.2	160	154	148	321	333	353	161	179	205
0.3	193	187	181	374	385	410	181	198	229
0.4	212	206	199	400	411	431	188	205	232
0.5	212	205	199	400	411	426	188	206	229
0.6	198	192	185	377	388	398	179	196	213
0.7	170	164	158	331	339	345	161	175	187
0.8	128	123	119	255	260	265	127	137	146
0.9	71	69	66	146	149	152	75	80	86

The data at 25° are extrapolated.

Table 14. Heats of Mixing iso-Butanol + n-Hexane (j/mole)

25.0°				45.0°			
x_1	H^M	x_1	H^M	x_1	H^M	x_1	H^M
0.0047	106	0.176	612	0.040	522	0.308	1023
0.0097	180	0.309	707	0.047	568	0.331	1026
0.020	267	0.329	714	0.080	696	0.575	882
0.040	362	0.576	589	0.092	737	0.594	853
0.080	467	0.594	571	0.159	879	0.596	846
0.092	484	0.594	572	0.177	906	0.816	439
0.159	590	0.816	285				

Table 15. Heats of Mixing sec-Butanol + n-Hexane (j/mole)

25.0°				45.0°			
x_1	H^M	x_1	H^M	x_1	H^M	x_1	H^M
0.0047	100	0.177	722	0.048	617	0.333	1197
0.0097	186	0.311	855	0.093	823	0.580	1112
0.020	289	0.332	866	0.161	998	0.594	1088
0.040	407	0.579	813	0.177	1029	0.598	1088
0.080	539	0.596	791	0.332	1184	0.817	615
0.093	569	0.597	798				
0.160	693	0.818	504				

Table 16. Heats of Mixing tert-Butanol + n-Hexane (j/mole)

27.0°				45.0°			
x_1	H^M	x_1	H^M	x_1	H^M	x_1	H^M
0.038	400	0.324	807	0.040	541	0.325	1057
0.077	527	0.569	838	0.080	740	0.577	979
0.155	662	0.572	837	0.160	925	0.588	971
0.172	691	0.587	845	0.172	952	0.806	649
0.303	790	0.800	609	0.309	1046		

Table 17. Heats of Mixing iso-Butanol + Benzene (j/mole)

25.0°		35.0°		45.0°	
x_1	H^M	x_1	H^M	x_1	H^M
0.115	940	0.115	1030	0.114	1116
0.128	981	0.124	1073	0.128	1180
0.234	1268	0.236	1403	0.234	1533
0.252	1287	0.248	1428	0.252	1569
0.482	1334	0.484	1501	0.481	1651
0.484	1346	0.484	1512	0.484	1643
0.500	1313	0.496	1480	0.500	1627
0.735	857	0.743	948	0.737	1076

Table 18. Heats of Mixing sec-Butanol + Benzene (j/mole)

25.0°		35.0°		45.0°	
x_1	H^M	x_1	H^M	x_1	H^M
0.114	1018	0.116	1092	0.115	1208
0.128	1076	0.126	1146	0.126	1240
0.234	1413	0.237	1526	0.236	1679
0.252	1453	0.249	1560	0.250	1689
0.483	1608	0.485	1730	0.483	1850
0.484	1608	0.486	1724	0.486	1843
0.501	1590	0.498	1724	0.500	1860
0.736	1131	0.738	1216	0.736	1309

Table 19. Heats of Mixing tert-Butanol + Benzene (j/mole)

27.0°		35.0°		45.0°	
x_1	H^M	x_1	H^M	x_1	H^M
0.110	1006	0.112	1046	0.111	1100
0.113	1050	0.121	1098	0.112	1099
0.227	1413	0.228	1470	0.230	1562
0.230	1441	0.242	1513	0.232	1575
0.474	1686	0.471	1733	0.473	1748
0.476	1684	0.479	1730	0.477	1749
0.493	1679	0.488	1731	0.477	1805
0.731	1323	0.737	1313	0.730	1356

Table 20. iso-Butanol + Benzene Excess Free Energy 45.0°C

x_1	y_1	P	μ_1^E	μ_2^E	G^E
		mm.Hg	cal/mole		
0	0	223.33	-	0	0
0.0464	0.0451	225.12	1064	6	55
0.1007	0.0689	223.91	838	24	106
0.2162	0.0944	218.43	537	78	177
0.2964	0.1072	213.74	404	124	207
0.4333	0.1275	203.28	242	215	227
0.5096	0.1405	195.60	176	273	224
0.5879	0.1568	185.55	122	338	211
0.7004	0.1910	168.28	63	441	177
0.7989	0.2445	139.14	28	542	132
0.8716	0.3269	110.94	15	611	91
1.0	1.0	40.34	0	-	0

Table 21. sec-Butanol + Benzene Excess Free Energy 45.0°C

x_1	y_1	P	μ_1^E	μ_2^E	G^E
		mm.Hg	cal/mole		
0	0	223.33	-	0	0
0.0607	0.0687	228.66	912	9	64
0.1018	0.0915	228.54	765	22	97
0.2093	0.1275	224.60	507	66	158
0.3052	0.1507	219.38	359	116	190
0.3933	0.1714	213.13	261	169	205
0.5081	0.2003	202.76	166	248	206
0.6046	0.2299	190.44	103	323	190
0.7030	0.2738	173.16	59	408	162
0.7997	0.3436	149.30	28	501	122
0.8943	0.4791	116.00	9	601	71
1.0	1.0	60.88	0	-	0

Table 22. tert-Butanol + Benzene Excess Free Energy 45.0°C

x_1	y_1	P	μ_1^E	μ_2^E	G^E
		mm.Hg	cal/mole		
0	0	223.33	-	0	0
0.0475	0.1154	242.62	929	5	49
0.1012	0.1751	251.46	735	20	92
0.1788	0.2251	256.54	545	50	139
0.2924	0.2749	257.39	362	105	178
0.4027	0.3170	255.39	244	170	200
0.5136	0.3609	249.28	156	243	198
0.6147	0.4082	240.26	97	319	183
0.6993	0.4582	229.31	59	391	159
0.7945	0.5388	211.03	29	479	121
0.9060	0.6975	178.82	5	605	62
0.9514	0.8126	160.13	2	651	34
1.0	1.0	135.92	0	-	0

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AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 7, NUMBER 3, PAGES 269-272, 1954

LIQUID–VAPOUR EQUILIBRIA

V. THE SYSTEM CARBON TETRACHLORIDE + ACETONITRILE AT 45 °C

By I. Brown and F. Smith

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Reprinted from the Australian Journal of Chemistry, Volume 7, Number 3, pp. 269–272, 1954

LIQUID-VAPOUR EQUILIBRIA

V. THE SYSTEM CARBON TETRACHLORIDE + ACETONITRILE AT 45 °C

By I. BROWN* and F. SMITH*

[*Manuscript received March* 31, 1954]

Summary

Liquid-vapour equilibrium data are given for the system carbon tetrachloride + acetonitrile at 45·00 °C. These data are used to calculate the excess free energy of mixing for this system.

I. INTRODUCTION

The liquid-vapour equilibrium data for this system have not been recorded in the literature. The present measurements were made to provide isothermal values of the excess free energy of mixing required for an investigation of the thermodynamic properties of solutions of polar liquids.

II. EXPERIMENTAL

(*a*) *Apparatus*

The liquid-vapour equilibrium data and vapour pressure measurements were made by the methods used by Brown and Smith (1954). The analysis was by density measurements as used by Brown and Ewald (1950).

(*b*) *Purification and Properties of Components*

The carbon tetrachloride was purified by the method used by Barker, Brown, and Smith (1953). The acetonitrile was dried over anhydrous calcium chloride and carefully fractionated, using the column described by Brown and Ewald (1951), retaining fractions boiling over a range of 0·02 °C and having a constant density. The physical properties of the components are shown in Table 1.

TABLE 1

PHYSICAL PROPERTIES OF COMPONENTS

Property	Carbon Tetrachloride	Acetonitrile
B.p./760 mm Hg (°C) ..	76·65	81·57
$d_4^{25\cdot00}$	1·58435	0·77656
$n_D^{25\cdot00}$	1·45734	1·34154
n_D^{20}	1·4607	1·3443
Vapour pressure 45·00 °C ..	258·84	208·35

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The vapour pressure of acetonitrile was measured using the equilibrium still and the data are given in Table 2. These data were fitted by the method of Willingham *et al.* (1945) to the Antoine equation

$$\log_{10}P = A - B/(C+t),$$

where P is in standard mm Hg and t in °C. The values of the constants found and the standard deviation σ of the fit are given in Table 2.

TABLE 2

THE VAPOUR PRESSURE OF ACETONITRILE

t (°C)	P (mm Hg)	Antoine Equation Constants
29·97	110·54	$A = 7\cdot28034$
37·42	152·71	$B = 1420\cdot20$
44·95	207·88	$C = 241\cdot241$
45·01	208·47	$\sigma = 0\cdot10$ mm Hg
47·04	226·03	
47·06	226·16	
54·52	301·04	
67·28	475·37	
71·32	545·39	
$81\cdot54_6$	759·39	
$81\cdot55_7$	759·69	
$81\cdot56_4$	759·83	

(c) *Analytical Method*

The liquid and vapour samples were analysed by density measurements; 11 mixtures were made by weighing. The density-composition data are given in Table 3, where x_1 is the mole fraction of carbon tetrachloride in the mixture and n_D^{20} are refractive indices of the mixtures at 20 °C.

TABLE 3

DENSITY-COMPOSITION DATA

x_1	$d_4^{25\cdot00}$	Δ	n_D^{20}
0·0839	0·89338	+0·00258	1·3609
0·0933	0·90544	+0·00255	1·3627
0·1913	1·02234	+0·00093	1·3793
0·2857	1·12054	−0·00068	1·3933
0·4113	1·23264	−0·00155	1·4096
0·5088	1·30823	−0·00092	1·4204
0·6142	1·38045	+0·00039	1·4310
0·6972	1·43147	+0·00130	1·4385
0·8126	1·49523	+0·00191	1·4477
0·9174	1·54680	+0·00336	1·4550
0·9535	1·56343	+0·00047	1·4577

In order to use the data in Table 3 for analysis a method analogous to that used by Brown and Smith (1954) was employed. Values of the residuals Δ in equation (**1**) were calculated from the density-composition data and graphed against density. The composition of samples was then calculated from the measured density using equation (**1**) and values of Δ from the graph.

$$\Delta = d - d_2 + x_1(d_2 - d_1) + (d - d_1)(d - d_2)[0 \cdot 75 + 0 \cdot 3045(2d - d_1 - d_2)], \quad \ldots \quad (\mathbf{1})$$

where d, d_1, and d_2 are the measured densities of the mixture, pure carbon tetrachloride and pure acetonitrile respectively.

III. LIQUID-VAPOUR EQUILIBRIUM DATA

The liquid-vapour equilibrium data are shown in Table 4, where x_1 and y_1 are the mole fractions of carbon tetrachloride in the liquid and vapour respectively, P is the total pressure in standard mm Hg, and α is the relative volatility given by $\alpha = (y_1 x_2)/(y_2 x_1)$.

TABLE 4

CARBON TETRACHLORIDE + ACETONITRILE AT 45·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0347	0·1801	247·96	6·112	1032	1·9	37·6
0·0892	0·3309	291·58	5·051	916·8	9·3	90·2
0·1914	0·4603	335·99	3·604	727·0	35·7	168·0
0·2887	0·5129	355·85	2·595	569·6	87·8	226·9
0·3752	0·5429	364·57	1·978	453·9	145·1	261·0
0·4567	0·5633	368·82	1·535	359·5	212·3	279·5
0·4790	0·5684	369·62	1·432	336·2	232·9	282·4
0·5060	0·5740	370·23	1·315	308·6	259·5	284·3
0·6049	0·5936	371·09	0·9542	217·7	373·3	279·2
0·7164	0·6181	368·95	0·6406	131·9	541·4	248·0
0·8069	0·6470	362·78	0·4386	74·3	726·0	200·1
0·8959	0·7004	346·97	0·2716	29·3	989·1	129·2
0·9609	0·8001	314·43	0·1629	6·2	1298	56·7

These data show that an azeotrope is formed at 45·00 °C having a mole fraction of carbon tetrachloride of 0·590 and at a total pressure of 371·2 mm Hg.

IV. DERIVED THERMODYNAMIC FUNCTIONS

The excess chemical potentials μ_1^E and μ_2^E and the excess free energy of mixing G_x^E were calculated from the equilibrium data using equations (**2**), (**3**), and (**4**) of Brown and Smith (1954). The values obtained (cal/g-mol) are shown in Table 4. Values of the liquid molar volumes and second virial coefficients at 45 °C in the equation of state for the vapours used in these calculations were obtained by the methods described by Brown and Smith (1954), they are :

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−1·235	−4·500	−1·174	+3·40	0·097	0·053

The excess free energy data at 45·00 °C were fitted by the method of least squares to equation (2)

$$G^E_x = x_1x_2[a+b(x_1-x_2)+c(x_1-x_2)^2+d(x_1-x_2)^3]. \quad \ldots\ldots \quad (2)$$

The values of the constants and the standard deviation σ of the fit were (in cal/g-mol):

	a	b	c	d	σ
Four constant equation	$+1134 \cdot 3$	$+118 \cdot 9$	$+162 \cdot 2$	$+99 \cdot 5$	$1 \cdot 1$

Values of the second derivative of the total free energy of mixing with respect to x_1 were also calculated and these gave no change of sign, showing that equation (2) with the above values of the constants does not indicate separation into two liquid phases.

The method of Herington (1947) and Redlich and Kister (1948) was used to test the thermodynamic consistency of the results which was shown to be satisfactory as the ratio of the areas above and below datum in a plot of $\mu^E_1-\mu^E_2$ against x_1 was 1·032.

The errors in G^E_x due to the errors in the measured quantities were estimated to be of the order of 2·2 cal/mole of which approximately half is due to uncertainty in the estimated value of the virial coefficients of the vapours and their mixture.

V. CONCLUSIONS

Thermodynamically consistent values are given for the liquid-vapour equilibrium and excess free energy of mixing for the system carbon tetrachloride+acetonitrile at 45·00 °C. These data will be used to calculate the excess entropy of mixing for this system as soon as heat of mixing measurements have been completed. This system forms an azeotrope at 45·00 °C having a mole fraction of carbon tetrachloride of 0·590 and a total pressure of 371·2 mm Hg.

VI. ACKNOWLEDGMENT

The authors thank Mr. O. H. Rigby for his help in the purification of the components.

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Reprinted from the

AUSTRALIAN JOURNAL OF CHEMISTRY

VOLUME 8, NUMBER 1, PAGES 62-67, 1955

LIQUID–VAPOUR EQUILIBRIA

VI. THE SYSTEMS ACETONITRILE + BENZENE AT 45 °C AND ACETONITRILE + NITROMETHANE AT 60 °C

By I. Brown and F. Smith

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LIQUID–VAPOUR EQUILIBRIA

VI. THE SYSTEMS ACETONITRILE+BENZENE AT 45 °C AND ACETONITRILE+NITROMETHANE AT 60 °C

By I. Brown* and F. Smith*

[*Manuscript received October* 11, 1954]

Summary

Liquid-vapour equilibrium data are given for the systems acetonitrile+benzene at 45·00 °C and acetonitrile+nitromethane at 60·00 °C. These data are used to calculate the excess free energy of mixing for these systems.

I. Introduction

The liquid-vapour equilibrium data for these systems have not been recorded in the literature. The present measurements were made to provide isothermal values of the excess free energy of mixing required for an investigation of the thermodynamic properties of solutions of polar liquids.

II. Experimental

(*a*) *Apparatus*

The liquid-vapour equilibrium and vapour pressure measurements were made by the methods used by Brown and Smith (1954*a*). The acetonitrile+benzene system was analysed by refractive index measurements using a Hilger-Chance precision refractometer maintained at 25·00±0·01 °C. The acetonitrile+nitromethane system was analysed by density measurements as used by Brown and Ewald (1950).

(*b*) *Purification and Properties of Components*

The acetonitrile was purified by the method used by Brown and Smith (1954*b*) and the benzene by the method of Brown and Ewald (1951). The nitromethane was purified by careful fractional distillation through a column 76 cm long, 13 mm in diameter, packed with 1·6 mm Dixon packing, and operated at a reflux ratio of 10 : 1 at a head pressure of 104 mm Hg. The middle fractions boiling at a constant temperature (±0·01 °C) and having a constant density were retained and used immediately. The physical properties of the components are shown in Table 1.

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TABLE 1

PHYSICAL PROPERTIES OF COMPONENTS

Property	Acetonitrile	Benzene	Nitromethane
B.p./760 mm Hg (°C)	81·57	80·07	101·07
$d_4^{25\cdot00}$	0·776~~56~~62	0·87369	1·13107
$n_D^{25\cdot00}$	1·34154	1·49803	1·37971
Vapour pressure			
45·00 °C	208·35	223·66	—
60·00 °C	368·00	—	178·18

The vapour pressure of nitromethane was measured using the equilibrium still and the data are given in Table 2. These data were fitted by the method of Willingham *et al.* (1945) to the Antoine equation

$$\log_{10} P = A - \frac{B}{c+t},$$

where P is in standard mm Hg and t in °C. The values of the constants found and the standard deviation σ of the fit are given in Table 2.

TABLE 2

THE VAPOUR PRESSURE OF NITROMETHANE

t (°C)	P (mm Hg)	Antoine Equation Constants
101·36	767·09	
101·04	759·63	
100·30	742·34	$A=7\cdot15311$
95·85	645·36	$B=1365\cdot312$
89·34	522·24	$C=218\cdot508$
83·96	435·50	$\sigma=0\cdot16$ mm Hg
74·31	309·37	
64·33	211·86	
60·55	182·25	
55·00	144·83	
49·88	116·38	

Recent vapour pressure measurements by McCullough *et al.* (1954) gave 101·19 °C for the normal boiling point of nitromethane and a pressure of 178·06 mm Hg at 60·00 °C compared with our values of 101·07 °C and 178·18 mm Hg.

(*c*) *Analytical Methods*

The liquid and vapour samples from the system acetonitrile + benzene were analysed by refractive index measurements. The refractive index-composition data obtained on mixtures prepared by weighing are given in Table 3. The method of Brown and Smith (1954*a*) was employed to calculate the composition using equation (**1**) and a graph of the residuals Δ plotted against refractive index. Values of the residual were given by

$$\Delta = n - n_1 - x_2(n_1 - n_2) + 3\cdot087(n - n_1)(n - n_2), \quad \ldots\ldots \ (\mathbf{1})$$

where x_1 is the mole fraction of acetonitrile, x_2 is the mole fraction of benzene and n, n_1, and n_2 are the refractive indices of the mixture, pure acetonitrile and pure benzene respectively.

TABLE 3

ACETONITRILE + BENZENE

Refractive index-composition data

x_1	$n_D^{25\cdot00}$	Δ
0·0604	1·49233	+0·00111
0·1005	1·48826	+0·00154
0·1998	1·47758	+0·00223
0·3050	1·46506	+0·00219
0·4011	1·45244	+0·00157
0·5070	1·43721	+0·00056
0·5130	1·43635	+0·00055
0·5959	1·42316	—0·00047
0·7038	1·40446	—0·00159
0·8059	1·38490	—0·00215
0·8992	1·36510	—0·00188
0·9493	1·35366	—0·00121

The samples from the system acetonitrile + nitromethane were analysed by density measurements. The density-composition data obtained on mixtures prepared by weighing are given in Table 4. The method of Brown and Smith (1954*b*) was employed to calculate the composition using equation (**2**) and a

TABLE 4

ACETONITRILE + NITROMETHANE

Density-composition data

x_1	$d_4^{25\cdot00}$	Δ′
0·0572	1·11163	~~+0·00003~~
0·1051	1·09527	~~+0·00007~~
0·2058	1·06070	~~+0·00014~~
0·3055	1·02612	~~+0·00013~~
0·4018	0·99237	~~+0·00007~~
0·5010	0·95730	~~—0·00003~~
0·5068	0·95523	~~—0·00002~~
0·5578	0·93708	~~—0·00006~~
0·5948	0·923~~89~~91	~~—0·00007~~
0·6985	0·886~~68~~70	~~—0·00009~~
0·7996	0·8500~~0~~4	~~—0·00013~~
0·8391	0·8356~~2~~6	~~—0·00011~~
0·9033	0·8121~~2~~8	~~—0·00013~~
0·9459	0·7965~~1~~6	~~—0·00007~~

graph of the residuals Δ' plotted against density. Values of the residual for the system were given by

~~$\Delta'=d-d_2+x_1(d_2-d_1)+0\cdot1229(d-d_1)(d-d_2)$, ... (2)~~

where x_1 is the mole fraction of acetonitrile and d, d_1, and d_2 are the densities of the mixture, pure acetonitrile and pure nitromethane respectively.

III. LIQUID-VAPOUR EQUILIBRIUM DATA

The liquid-vapour equilibrium data are shown in Tables 5 and 6, where x_1 and y_1 are the mole fractions of acetonitrile in the liquid and vapour respectively, P is the total pressure in standard mm Hg, and α is the relative volatility given by $\alpha=y_1x_2/y_2x_1$.

TABLE 5

ACETONITRILE+BENZENE AT 45·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0455	0·1056	239·70	2·477	637·1	2·3	31·4
0·0940	0·1818	251·67	2·142	548·4	9·9	60·5
0·1829	0·2783	264·66	1·723	423·4	28·4	100·6
0·2909	0·3607	273·45	1·376	310·5	63·3	135·2
0·3980	0·4274	277·49	1·129	226·0	107·9	154·9
0·5069	0·4885	278·03	0·9294	156·8	165·6	161·1
0·5458	0·5098	277·36	0·8658	134·9	189·8	159·8
0·5946	0·5375	275·86	0·7924	110·2	222·3	155·6
0·7206	0·6157	268·46	0·6211	56·3	326·1	131·7
0·8145	0·6913	257·81	0·5099	26·5	423·7	100·2
0·8972	0·7869	242·50	0·4230	9·3	527·5	62·6
0·9573	0·8916	225·30	0·3668	2·3	612·9	28·4

TABLE 6

ACETONITRILE+NITROMETHANE AT 60·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0951	0·1741	195·50	2·006	+0·3	−0·4	−0·3
0·1940	0·3255	213·70	2·005	+0·5	−0·4	−0·2
0·2930	0·4539	232·24	2·006	−0·2	+0·2	+0·1
0·3939	0·5658	251·20	2·005	−0·4	+0·7	+0·3
0·4614	0·6325	264·24	2·009	+0·8	+0·8	+0·8
0·5001	0·6674	271·45	2·006	+0·1	+1·5	+0·8
0·6051	0·7548	291·64	2·009	+0·7	+1·6	+1·0
0·8055	0·8925	329·97	2·005	−0·2	+3·2	+0·5
0·9025	0·9488	349·17	2·002	+0·4	+5·1	+0·9
0·9486	0·9737	358·27	2·006	+0·6	+4·2	+0·8

These data show that an azeotrope is formed at 45·00 °C having a mole fraction of 0·457 acetonitrile at a total pressure of 278·1 mm Hg.

IV. DERIVED THERMODYNAMIC FUNCTIONS

The excess chemical potentials μ_1^E and μ_2^E and the excess free energy of mixing G_x^E were calculated from the equilibrium data using equations (2), (3), and (4) of Brown and Smith (1954*a*). The values obtained (cal/g-mol) are shown in Tables 5 and 6.

The values of the liquid molar volumes V_1 and V_2 and the second virial coefficient in the equation of state for the mixed vapours, β_{12}, were obtained by the methods given by Brown and Smith (1954*a*).

Values of the second virial coefficient for acetonitrile β_{11} were obtained by extrapolation from the experimental values of Lambert *et al.* (1949). The values for benzene were obtained from the equation given by Allen, Everett, and Penney (1952) and the values for nitromethane from the equation given by Douslin (1954) which is based on the experimental data of McCullough (1954).

The values of the second virial coefficients and molar volumes (l/mol) used for the system acetonitrile+benzene at 45 °C were :

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−4·500	−1·236	−1·173	+3·39	0·053	0·092

For the system acetonitrile+nitromethane δ_{12} was assumed to be zero as the system is substantially ideal. The values used for this system at 60·00 °C were :

β_{11}	β_{22}	V_1	V_2
−3·350	−2·500	0·056	0·056

V. DISCUSSION

For the system acetonitrile+benzene at 45·00 °C the excess free energy data were fitted by the method of least squares to equation (3).

$$G_x^E = x_1x_2[a+b(x_1-x_2)+c(x_1-x_2)^2]. \quad \dots\dots\dots\dots \quad (3)$$

The values (cal/g-mol) of the constants and the standard deviation of the fit σ were :

a	b	c	σ
+643·3	−8·1	+70·1	0·53

These values do not indicate separation into two liquid phases. The thermodynamic consistency of the results was tested by the method used previously, the ratio of areas above and below datum in a plot of $\mu_1^E-\mu_2^E$ against x_1 was 1·006.

The error in G_x^E due to errors in the directly measured quantities was estimated to be of the order of 2·5 cal/mole.

For the system acetonitrile+nitromethane the errors in G_x^E were estimated to be just less than 2 cal/g-mol. The data given in Table 6 show that the excess free energy of mixing is zero within the experimental error over the whole concentration range when the deviations of the vapours from ideal gas behaviour are allowed for. At 60·00 °C the relative volatility of this system was found to be 2·006 over the whole concentration range.

The excess entropy for these systems will be calculated when heats of mixing have been measured.

VI. Acknowledgment

The authors thank Mr. O. H. Rigby for his help in the purification of the components.

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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 8, NUMBER 4, PAGES 501-505, 1955

LIQUID–VAPOUR EQUILIBRIA

VII. THE SYSTEMS NITROMETHANE + BENZENE AND NITROMETHANE + CARBON TETRACHLORIDE AT 45° C

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VII. THE SYSTEMS NITROMETHANE + BENZENE AND NITROMETHANE + CARBON TETRACHLORIDE AT 45 °C

By I. Brown* and F. Smith*

[*Manuscript received June 14, 1955*]

Summary

The liquid-vapour equilibrium data are given for the systems nitromethane + benzene and nitromethane + carbon tetrachloride at 45·00 °C. These data are used to calculate the excess free energy of mixing for these systems.

I. Introduction

The liquid-vapour equilibria for the system nitromethane + benzene have been determined at atmospheric pressure by Weck and Hunt (1954). The present measurements were made to provide isothermal values of the excess free energy of mixing required for an investigation of the thermodynamic properties of solutions of polar liquids.

II. Experimental

(*a*) *Apparatus*

The liquid-vapour equilibrium and vapour pressure measurements were made by Brown and Smith's (1954*a*) methods. The nitromethane + benzene system was analysed by refractive index measurements using a Hilger-Chance precision refractometer maintained at 25·00 ± 0·01 °C. The nitromethane + carbon tetrachloride system was analysed by density measurements as used by Brown and Ewald (1950).

Table 1

PHYSICAL PROPERTIES OF COMPONENTS

Property	Nitro-methane	Benzene	Carbon Tetrachloride
Boiling point/760 mm Hg (°C)	101·07	80·05	76·65
$d_4^{25\cdot00}$	1·13105	0·087366	1·58439
$n_D^{25\cdot00}$	1·37965	1·49792	1·45739
Vapour pressure 45·00 °C ..	93·72	223·74	258·84

(*b*) *Purification and Properties of Components*

The nitromethane was purified by the method used by Brown and Smith (1955), the benzene by the method described by Brown and Ewald (1951) and the carbon tetrachloride by the Barker, Brown, and Smith's (1953) method. The physical properties of the components are shown in Table 1.

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(c) *Analytical Methods*

Liquid and vapour samples from the system nitromethane+benzene were analysed by refractive index measurements. The refractive index-composition data obtained from mixtures prepared by weighing are given in Table 2, where x_1 is the mole fraction of nitromethane in the mixture. The method of Brown and Smith (1954*a*) was employed to calculate the composition of samples.

Table 2

NITROMETHANE+BENZENE

Refractive index ; composition data

x_1	$n_D^{25\cdot00}$	x_1	$n_D^{25\cdot00}$
0·0448	1·49430	0·5075	1·44934
0·1077	1·48906	0·6006	1·43828
0·2037	1·48050	0·6993	1·42563
0·2897	1·47238	0·8033	1·41108
0·4083	1·46025	0·8992	1·39647
0·4878	1·45158	0·9506	1·38812

Liquid and vapour samples from the system nitromethane+carbon tetrachloride were analysed by density measurements. The density-composition data obtained on mixtures prepared by weighing are given in Table 3, where x_1 is the mole fraction of nitromethane in the mixture. The method of Brown and Smith (1954*b*) was employed to calculate the composition of samples.

Table 3

NITROMETHANE+CARBON TETRACHLORIDE

Density : composition data

x_1	$d_4^{25\cdot00}$	x_1	$d_4^{25\cdot00}$
0·0509	1·57004	0·5004	1·41904
0·1000	1·55612	0·5946	1·37782
0·2001	1·52628	0·7049	1·32326
0·2929	1·49638	0·8063	1·26601
0·3963	1·45997	0·8954	1·20870
0·4948	1·42138	0·9445	1·17373

III. Liquid-Vapour Equilibrium Data

The liquid-vapour equilibrium data are shown in Tables 4 and 5, where x_1 and y_1 are the mole fractions of nitromethane in the liquid and vapour respectively, P is the total pressure in standard mm Hg, and α is the relative volatility given by $\alpha=y_1x_2/y_2x_1$.

From graphs of the data in Table 4 it can be seen that at 45·00 °C this system forms an azeotrope with a mole fraction of 0·120 nitromethane at a total pressure of 228·0 mm Hg.

From graphs of the data in Table 5 it can be seen that this system forms an azeotrope with a mole fraction of 0·227 nitromethane at a total pressure of 303·0 mm Hg.

TABLE 4

NITROMETHANE + BENZENE AT 45·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0445	0·0548	226·43	1·245	698·5	0·7	31·4
0·0966	0·1026	227·83	1·069	598·4	7·2	64·3
0·1979	0·1694	226·92	0·8266	457·8	31·3	115·7
0·2927	0·2173	223·50	0·6709	357·2	64·1	149·9
0·3921	0·2602	218·27	0·5453	270·7	109·7	172·8
0·4737	0·2942	213·14	0·4631	213·4	156·6	183·5
0·5259	0·3166	208·62	0·4176	180·0	189·2	184·4
0·6180	0·3543	200·11	0·3392	122·7	264·0	176·7
0·7118	0·4023	188·14	0·2725	74·8	355·1	155·6
0·8102	0·4765	170·13	0·2132	36·8	473·1	119·6
0·9051	0·6144	142·18	0·1671	15·1	606·8	71·3
0·9601	0·7708	117·19	0·1398	0·5	705·6	28·6

IV. DERIVED THERMODYNAMIC FUNCTIONS

The excess chemical potentials μ_1^E and μ_2^E and the excess free energy of mixing G_x^E were calculated from the equilibrium data using equations (**2**), (**3**), and (**4**) of Brown and Smith (1954*a*). The values obtained (cal/g-mol) are shown in Tables 4 and 5.

TABLE 5

NITROMETHANE + CARBON TETRACHLORIDE AT 45·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0459	0·1296	287·42	3·095	1360	7·3	69·4
0·0918	0·1780	297·19	2·142	1141	23·3	125·9
0·1954	0·2217	302·91	1·173	812·4	77·5	221·1
0·2829	0·2368	302·56	0·7865	618·1	137·3	273·3
0·3656	0·2458	301·42	0·5655	477·9	205·0	304·8
0·4659	0·2532	298·86	0·3887	337·9	302·3	318·9
0·5366	0·2598	296·88	0·3031	260·5	382·5	317·0
0·6065	0·2657	293·27	0·2348	189·6	473·2	301·2
0·6835	0·2773	287·10	0·1777	127·7	587·7	273·3
0·8043	0·3138	264·65	0·1113	52·1	808·5	200·1
0·9039	0·4078	214·63	0·0732	13·3	1036	111·5
0·9488	0·5283	170·95	0·0604	4·5	1149	62·6

The values of the liquid molar volumes V_1 and V_2 and the second virial coefficient in the equation of state for the mixed vapours β_{12} were obtained by the methods given by Brown and Smith (1954*a*).

The value of the second virial coefficient for nitromethane was obtained from an equation given by Douslin (1954) which was based on the experimental data of McCullough *et al.* (1954). The value for benzene was obtained from the equation given by Allen, Everett, and Penney (1952) and that for carbon tetrachloride from the Berthelot equation.

The values of the second virial coefficients and molar volumes (l/mol) used for the system nitromethane+benzene at 45 °C were :

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−3·11	−1·23	−1·13	2·09	0·06	0·09

For the system nitromethane+carbon tetrachloride at 45 °C the values used were :

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−3·11	−1·24	−1·15	2·05	0·06	0·10

V. DISCUSSION

For the system nitromethane+benzene at 45·00 °C the excess free-energy data were fitted by the method of least squares to equation (**1**) :

$$G^E_x = x_1x_2[a+b(x_1-x_2)+c(x_1-x_2)^2]. \quad \ldots\ldots\ldots\ldots \quad (\mathbf{1})$$

The values (cal/g-mol) of the constants and the standard deviation of the fit σ were

a	*b*	*c*	σ
741·8	42·7	0	2·0

These values do not indicate separation into two liquid phases. The thermodynamic consistency of the results was tested by the method used previously, the ratio of the areas above and below datum on a plot of $\mu^E_1-\mu^E_2$ *against* x_1 was 1·04. The error in G^E_x due to errors in the directly measured quantities was estimated to be 2·5 cal/mole.

For the system nitromethane+carbon tetrachloride at 45·00 °C the constants obtained in fitting the excess free-energy data to equation (**1**) were

a	*b*	*c*	σ
1275·6	−111·8	175·4	1·6

The ratio of the areas in the test for thermodynamic consistency was 1·001 and the errors in G^E_x due to those in the measured quantities were estimated to be 3 cal/mole.

VI. ACKNOWLEDGMENT

The authors thank Mr. O. H. Rigby for his help in the purification of the components.

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AUSTRALASIAN MEDICAL PUBLISHING CO. LTD.
SEAMER AND ARUNDEL STS., GLEBE, SYDNEY

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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 10, NUMBER 4, PAGES 423-428, 1957

LIQUID–VAPOUR EQUILIBRIA

VIII. THE SYSTEMS ACETONE + BENZENE AND ACETONE + CARBON TETRACHLORIDE AT 45 °C

By I. Brown and F. Smith

Reprinted for
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VIII. THE SYSTEMS ACETONE+BENZENE AND ACETONE+CARBON TETRACHLORIDE AT 45 °C

By I. Brown* and F. Smith*

[*Manuscript received May* 13, 1957]

Summary

The liquid-vapour equilibrium data are given for the systems acetone+benzene and acetone+carbon tetrachloride at 45·00 °C. These data are used to calculate the excess free energy of mixing for these systems.

I. Introduction

The isothermal liquid-vapour equilibria for the system acetone+benzene have been determined at 25 and 35 °C by Litvinov (1940) and measurements at atmospheric pressure have been made by Soday and Bennett (1930), Reinders and De Minjer (1940), Othmer (1943), Tallmadge and Canjar (1954), Canjar, Horne, and Rothfus (1956), and Kranich *et al.* (1956). For acetone+carbon tetrachloride, liquid-vapour equilibrium data have been measured at 0 °C by Gerrits (1904), at 50 °C by Severns *et al.* (1955), and at 760 mm Hg by Acharya and Rao (1953) and at 300, 450, and 760 mm Hg by Bachman and Simmons (1952). The present measurements were made in order to obtain values of the isothermal excess free energy of mixing at 45 °C for comparison with values obtained previously at this temperature for other systems containing polar components.

II. Experimental

(*a*) *Apparatus*

The liquid-vapour equilibrium and vapour pressure measurements were made using the equilibrium still described by Brown (1952); pressure measurements were made by the methods of Brown and Ewald (1950). Temperatures were measured with a calibrated Myer type platinum resistance thermometer and a calibrated Mueller bridge. The emergent stem of the resistance thermometer was maintained within less than 1 °C of the temperature being measured by means of a small electrically-heated tube, fitted with a differential thermocouple connected to a galvanometer. Temperatures were measured to $\pm 0\cdot002$ °C and are recorded to 0·01 °C. Liquid and vapour samples were analysed by refractive index measurements using a Hilger-Chance precision refractometer maintained at $25\cdot00\pm0\cdot01$ °C.

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(*b*) *Purification and Properties of Components*

Benzene was purified by the method described by Brown and Ewald (1951) and carbon tetrachloride by that of Barker, Brown, and Smith (1953). Previously, distilled acetone was dried by a chemical method (Brown and Fock 1955, 1957), with a resulting density of d_4^{25} 0·78501. For the present work, acetone was purified and dried by careful fractional distillation at a reflux ratio of 75 : 1, in the column described by Brown and Ewald (1951), rejecting a small head and a large tail fraction. The density of the product was d_4^{25} 0·78424 which agrees with that obtained by Thirion and Craven (1952). Timmermans (1950) reports the values d_4^{25} 0·78501 and n_D^{25} 1·35662, both considerably higher than our values shown in Table 1. According to Glazunov (1914), a high refractive index is indicative of the presence of water. Therefore, it appears that careful fractional distillation in an efficient column is the safest method for drying acetone. Chemical methods have the weakness that water may be formed from acetone condensation reactions at a faster rate than it is removed by the dehydrating agent. These findings are in agreement with those of Riddick (1955).

TABLE 1

PHYSICAL PROPERTIES OF COMPONENTS

Property	Acetone	Benzene	Carbon Tetrachloride
B.p./760 mm Hg (°C) ..	56·06	80·01	76·65
$d_4^{25\cdot00}$	0·78424	0·87371	1·58452
$n_D^{25\cdot00}$	1·35598	1·49796	1·45736
Vapour pressure 45·00 °C	512·72	223·66	258·84

TABLE 2

VAPOUR PRESSURE OF ACETONE

t (°C)	P (mm Hg)	Antoine Equation Constants
37·68	388·19	$A=7\cdot19958$
41·58	450·99	$B=1254\cdot51$
44·96	512·08	$C=234\cdot42$
45·00	512·80	$\sigma=0\cdot11$ mm Hg
45·00	512·85	
47·01	552·07	
49·31	599·82	
51·91	658·01	
56·02	759·06	
56·06	760·00	
56·07	760·26	
56·08	760·33	

The physical properties of the liquids used are shown in Table 1. The vapour pressures of the benzene and carbon tetrachloride samples were checked at 45 °C and at the normal boiling point, using the equilibrium still, and found to be in good agreement with values previously obtained by us. The vapour pressures of acetone were measured over a range of temperatures and are given in Table 2. These values were fitted by the method of Willingham *et al.* (1945) to the Antoine equation

$$\log_{10} P = A - \frac{B}{C+t},$$

where P is in standard mm Hg and t in °C. The values of the constants found and σ, the standard deviation of the fit, are given in Table 2.

(c) *Analytical Methods*

A number of mixtures was prepared from weighed amounts of the components ; their compositions and refractive indices are given in Tables 3 and 4.

TABLE 3

ACETONE + BENZENE

Refractive index : composition data

x_1	$n_D^{25\cdot00}$	x_1	$n_D^{25\cdot00}$
0·0475	1·49222	0·4988	1·43308
0·0916	1·48680	0·6091	1·41723
0·1946	1·47394	0·6921	1·40485
0·3002	1·46018	0·7973	1·38870
0·3851	1·44887	0·8994	1·37248
0·4969	1·43337	0·9633	1·36207

TABLE 4

ACETONE + CARBON TETRACHLORIDE

Refractive index : composition data

x_1	$n_D^{25\cdot00}$	x_1	$n_D^{25\cdot00}$
0·0565	1·45285	0·4850	1·41555
0·0785	1·45111	0·4992	1·41422
0·2075	1·44061	0·5965	1·40428
0·3023	1·43244	0·7089	1·39208
0·3365	1·43171	0·7869	1·38308
0·3813	1·42533	0·8904	1·37036
0·4085	1·42284	0·9393	1·36412

The method of Brown and Smith (1954) was employed to calculate the compositions of the liquid and vapour samples from the refractive index measurements.

III. RESULTS

The liquid-vapour equilibrium data are presented in Tables 5 and 6 where x and y are the mole fractions of acetone in the liquid and the vapour respectively, P is the total pressure in standard mm Hg, and α is the relative volatility given by $\alpha = y_1 x_2 / y_2 x_1$.

TABLE 5

ACETONE + BENZENE 45·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0470	0·1444	250·73	3·422	277·6	3·1	16·0
0·0963	0·2574	275·02	3·253	244·4	4·9	28·0
0·2207	0·4417	324·25	2·794	162·0	21·3	52·4
0·2936	0·5204	348·40	2·611	131·0	32·6	61·5
0·4011	0·6139	379·88	2·374	88·3	54·6	68·1
0·4759	0·6697	399·73	2·233	66·0	72·6	69·5
0·6125	0·7614	432·95	2·019	35·8	108·9	64·1
0·7045	0·8201	453·99	1·912	22·7	132·2	55·1
0·8081	0·8805	475·39	1·750	8·8	176·6	41·0
0·9084	0·9418	495·32	1·632	2·1	216·1	21·7
0·9529	0·9699	503·96	1·593	0·8	231·8	11·7

TABLE 6

ACETONE + CARBON TETRACHLORIDE 45·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0556	0·2165	315·32	4·694	567·9	4·7	36·0
0·0903	0·2910	339·70	4·135	493·5	11·6	55·1
0·2152	0·4495	397·77	2·976	314·7	44·0	102·2
0·2929	0·5137	422·46	2·550	240·3	68·9	119·1
0·3970	0·5832	448·88	2·125	164·6	110·4	131·9
0·4769	0·6309	463·92	1·875	118·0	144·4	131·8
0·5300	0·6621	472·84	1·738	93·0	168·6	128·5
0·6047	0·7081	485·16	1·586	67·4	202·1	120·6
0·7128	0·7718	498·07	1·363	33·4	265·7	100·1
0·8088	0·8360	506·89	1·205	14·4	326·4	74·0
0·9090	0·9141	512·32	1·065	3·1	395·4	38·8
0·9636	0·9636	513·20	1·000	0·6	435·5	16·4

From graphs of the data shown in Table 6, it was concluded that the system acetone + carbon tetrachloride forms an azeotrope at 45·00 °C at a mole fraction of acetone of 0·964 and a pressure of 513·2 mm Hg.

IV. DERIVED THERMODYNAMIC FUNCTIONS

The excess chemical potentials μ_1^E and μ_2^E and the excess free energy G_x^E were calculated from the equilibrium data using equations (2), (3), and (4) of Brown and Smith (1954). The values obtained (cal/g-mol) are shown in Tables

5 and 6. For these calculations it is necessary to know the liquid molar volumes and the second virial coefficients of the vapours for each component. Liquid molar volumes V_1 and V_2 were obtained from densities given by Timmermans (1950); the value of the second virial coefficient for acetone was obtained from the data of Lambert (1949), that for benzene from equation (A5) of Allen, Everett, and Penney (1952), and the value for carbon tetrachloride was calculated from critical data using the Berthelot equation. The second virial coefficients (β_{12}) in the equation of state for the mixed vapours and the allied coefficients (δ_{12}) were calculated by the method given by Brown and Smith (1954). For the system acetone+benzene at 45·00 °C, the second virial coefficients and molar volumes (l/mol) were taken to be

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−1·66	−1·23	−1·03	+0·84	0·08	0·09

For acetone+carbon tetrachloride at 45·00 °C the values used were

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−1·66	−1·24	−1·05	+0·80	0·08	0·10

V. Discussion

The excess free energy data were fitted by the method of least squares to equation (1)

$$G_x^E = x_1x_2[a+b(x_1-x_2)+c(x_1-x_2)^2]. \quad \ldots\ldots\ldots\ (1)$$

For the system acetone+benzene at 45 °C the values of the constants (cal/g-mol) and the standard deviation of the fit (σ) were

a	b	c	σ
280·3	−37·3	0	1·0

These values do not indicate separation into two liquid phases. The thermodynamic consistency of the results was tested by the method used previously (Brown and Smith 1954), the ratio of areas above and below datum on a plot of $\mu_1^E-\mu_2^E$ against x, was 1·05. Errors in G_x^E due to errors in the directly measured quantities were estimated to be ±2·0 cal/mol. For comparison, values of G_x^E were calculated from the data of Litvinov (1940) at 25 and 35 °C, but they are higher than the values reported here and show too great a change with temperature.

For acetone+carbon tetrachloride at 45·00 °C the constants obtained by fitting the excess free energy data to equation (1) were

a	b	c	σ
523·1	−111·5	+65·3	0·6

In the test for thermodynamic consistency the ratio of the two areas was 1·005, and the errors in G_x^E due to those in the measured quantities were estimated to be ±4 cal/mol.

The values of G_x^E calculated from the results of Severns *et al.* (1955) at 50 °C are in reasonable agreement with our data for 45 °C. Values of G_x^E at 45 °C were also calculated from the three sets of isobaric data of Bachman and Simmons (1952), but the values obtained were 10 per cent. higher than those given here.

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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 13, NUMBER 1, PAGES 30–37, 1960

LIQUID-VAPOUR EQUILIBRIA

X. THE SYSTEMS ACETONE + NITROMETHANE AND ACETONE + ACETONITRILE AT 45°C

By I. Brown and F. Smith

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LIQUID-VAPOUR EQUILIBRIA

X. THE SYSTEMS ACETONE+NITROMETHANE AND ACETONE+ACETONITRILE AT 45 °C

By I. Brown* and F. Smith*

[*Manuscript received October 21, 1959*]

Summary

Liquid-vapour equilibrium data are given for the systems acetone+nitromethane and acetone+acetonitrile at 45·00 °C. The data are used to calculate the excess free energy of mixing for these systems. The former system has a negative value of the excess free energy of mixing and shows a change in sign of the deviation of the activity of nitromethane from the Raoults law value at a mole fraction of acetone of 0·35. A value of the virial coefficient β_{12} in the equation of state of the mixed vapours was estimated from the equilibrium data for this system. The excess free energy of mixing for the system acetone+acetonitrile is zero within the experimental error over the whole concentration range.

The Stockmayer potential was used to calculate values of β_{12} for the binary systems formed from acetone, nitromethane, and acetonitrile. For the system acetone+nitromethane the value estimated from our data is more negative than the value calculated using the Stockmayer potential, indicating a specific interaction, possibly hydrogen bonding, between the acetone and nitromethane molecules.

I. Introduction

The liquid-vapour equilibria of the system acetone+acetonitrile has been measured at 760 mm Hg by Pratt (1947). No liquid-vapour equilibrium measurements have been reported for the system acetone+nitromethane. The present measurements were made to obtain values of the excess free energy of mixing for these systems at 45 °C for comparison with values obtained previously for other systems containing one or more of the same components.

II. Experimental

(*a*) *Apparatus*

The liquid-vapour equilibrium and vapour pressure measurements were made using the methods described by Brown and Smith (1959) but with water at 2 °C supplied to the condensers to prevent loss of acetone. The liquid and vapour samples for the system acetone+nitromethane were analysed by density measurements using the methods of Brown and Ewald (1950). Those for the system acetone+acetonitrile were analysed by refractive index measurements using a Hilger-Chance precision refractometer maintained at 25·00 °C.

(*b*) *Purification and Physical Properties of Components*

The acetonitrile, acetone, and nitromethane were purified by the methods of Brown and Smith (1954, 1955, 1957 respectively). The physical properties

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TABLE 1

PHYSICAL PROPERTIES OF COMPONENTS

Properties	Acetone	Nitromethane	Acetonitrile
$d_4^{25\cdot00}$	0·78424	1·13080	0·77656
$n_D^{25\cdot00}$	1·35599	1·37964	1·34151
Boiling point (°C/760 mm Hg) ..	56·06	101·02	81·56
Vapour pressure (45·00 °C, mm Hg)	512·72	93·72	208·35

of the liquids used are shown in Table 1. The vapour pressures of the liquids were checked at 45 °C and at the normal boiling point and found to be in good agreement with the values previously obtained by us.

TABLE 2

ACETONE + NITROMETHANE

Density : composition data

x_1	$d_4^{25\cdot00}$	x_1	$d_4^{25\cdot00}$
0·0519	1·10750	0·5020	0·93286
0·1000	1·08652	0·5929	0·90277
0·2021	1·04400	0·6972	0·86996
0·3050	1·00367	0·8179	0·83422
0·4251	0·95960	0·9117	0·80789
0·4999	0·93346	0·9512	0·79720

TABLE 3

ACETONE + ACETONITRILE

Refractive index : composition data

x_1	$n_D^{25\cdot00}$	x_1	$n_D^{25\cdot00}$
0·060	1·34287	0·598	1·35184
0·105	1·34381	0·602	1·35192
0·210	1·34586	0·700	1·35311
0·297	1·34739	0·795	1·35410
0·389	1·34888	0·904	1·35516
0·486	1·35034	0·962	1·35568
0·521	1·35082		

(c) *Analytical Methods*

Mixtures were prepared from weighed amounts of the components, and their compositions were calculated allowing for air buoyancy and for the weight of air-vapour mixture of the first component displaced on adding the second; their compositions and refractive indices or densities are given in Tables 2 and 3. The method of Brown and Smith (1954) was used to calculate the composition of the liquid and vapour samples.

III. RESULTS

The liquid-vapour equilibrium data are given in Tables 4 and 5 where x_1 and y_1 are the mole fractions of acetone in the liquid and vapour respectively, P is the total pressure in standard mm Hg, and α is the relative volatility given by $\alpha = y_1x_2/y_2x_1$.

TABLE 4

ACETONE+NITROMETHANE 45 °C

Experimental results and derived thermodynamic functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0528	0·2190	114·44	5·030	−33·2	+ 1·7	− 0·1
0·0810	0·3048	125·28	4·974	−37·3	+ 2·5	− 0·7
0·1262	0·4165	142·75	4·942	−37·5	+ 3·5	− 1·7
0·2068	0·5607	173·81	4·896	−37·7	+ 3·8	− 4·8
0·3080	0·6846	213·24	4·877	−35·2	+ 1·8	− 9·6
0·4027	0·7677	251·17	4·902	−30·0	− 3·4	−14·1
0·4056	0·7701	252·35	4·909	−29·6	− 4·1	−14·4
0·4926	0·8272	288·40	4·931	−24·5	− 8·2	−16·2
0·5336	0·8503	305·56	4·965	−21·9	−13·0	−17·7
0·6134	0·8885	339·89	5·022	−16·5	−21·2	−18·3
0·7036	0·9235	379·48	5·085	−11·2	−30·9	−17·0
0·8017	0·9547	423·46	5·213	− 5·7	−48·8	−14·2
0·9037	0·9805	469·66	5·358	− 1·5	−70·3	− 8·1

TABLE 5

ACETONE+ACETONITRILE 45 °C

Experimental results and derived thermodynamic functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·052	0·120	225·3	2·48	+24	0	+ 1
0·095	0·206	239·9	2·47	+25	+ 2	+ 4
0·192	0·367	268·5	2·44	+14	− 2	+ 1
0·305	0·510	302·7	2·37	+ 3	+ 1	+ 2
0·403	0·611	331·7	2·33	− 3	+ 5	+ 2
0·481	0·682	355·2	2·31	− 3	+ 7	+ 2
0·606	0·781	393·2	2·31	− 2	+ 3	0
0·706	0·849	423·6	2·33	0	− 4	− 1
0·807	0·904	454·1	2·25	− 2	+15	+ 2
0·896	0·951	481·4	2·25	0	+13	+ 1

IV. DERIVED THERMODYNAMIC FUNCTIONS

The excess chemical potentials μ_1^E and μ_2^E and the excess free energy of mixing G_x^E were calculated from the equilibrium data using equations (1), (2), and (3). The values obtained (cal/g-mol) are given in Tables 4 and 5.

$$\mu_1^E = RT \ln (Py_1/P_1x_1) + (\beta_{11} - V_1)(P - P_1) + P\delta_{12}y_2^2, \quad \ldots\ldots \quad (1)$$

$$\mu_2^E = RT \ln (Py_2/P_2x_2) + (\beta_{22} - V_2)(P - P_2) + P\delta_{12}y_1^2, \quad \ldots\ldots \quad (2)$$

$$G_x^E = x_1\mu_1^E + x_2\mu_2^E, \quad \ldots\ldots \quad (3)$$

where P_1 and P_2 are the vapour pressures of the pure components, β_{11}, β_{22}, and β_{12} are the second virial coefficients in the equation of state for the mixed vapours,

$$PV/RT=1+(y_1^2\beta_{11}+2y_1y_2\beta_{12}+y_2^2\beta_{22})\frac{1}{V}+\ldots,$$

and where

$$\delta_{12}=2\beta_{12}-\beta_{11}-\beta_{22}.$$

The liquid molar volumes V_1 and V_2 required for these calculations were obtained from density data given by Timmermans (1950). The values of the second virial coefficient for acetone and acetonitrile were obtained from the data of Lambert *et al.* (1949) and that for nitromethane from the equation given by McCullough *et al.* (1954).

(*a*) *Acetone+Nitromethane*

For this system no measured values of β_{12} or δ_{12} were available so values were estimated in the following way. Preliminary values of μ_1^E and μ_2^E were first calculated using corrections for the deviations of the vapours but with $\delta_{12}=0$ and the values obtained were tested for thermodynamic consistency by measuring the areas above and below datum under a plot of $(\mu_1^E-\mu_2^E)$ against x_1. These were found to correspond to $+5\cdot6$ cal/mol and $-23\cdot8$ cal/mol which gives a value of $-18\cdot2$ cal/mol for the integral

$$\int_0^1(\mu_1^E-\mu_2^E)\mathrm{d}x.$$

It was also found that the maximum in the plot of μ_2^E against x_1 was not at the same mole fraction as the minimum in the corresponding plot of μ_1^E. This means that the preliminary calculated values of the excess chemical potentials are not thermodynamically consistent due either to non-equilibrium conditions in the still or to the neglect of the mixture virial coefficient corrections. Previous data, obtained with the equilibrium still used in this work, for a number of other systems have been found to be thermodynamically consistent when reasonably accurate, measured or estimated values for the virial coefficients of pure and mixed vapours were used. Some of these systems had relative volatilities considerably higher than the values found here. It is therefore probable that the inconsistency of the preliminary values of the excess chemical potentials is mainly due to the neglect of corrections for the mixture virial coefficients.

A value of δ_{12} was then found by trial and error that reduced the value of the above integral to zero. This value was found to be $-2\cdot90$ l/mol. The final values of μ_1^E and μ_2^E given in Table 4 were calculated using the following values of the liquid molar volumes and virial coefficients (l/mol):

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
$-1\cdot66$	$-3\cdot11$	$-3\cdot83$	$-2\cdot90$	$0\cdot076$	$0\cdot056$

These final values showed that the maximum in μ_2^E was at the same mole fraction as the minimum in μ_1^E. As a further check on the consistency of the measured

x, y, and P data, Barker's (1953) method was used to calculate values of μ_1^E, μ_2^E, and G_x^E from the x and P values alone using the listed values for the virial coefficients and molar volumes. This gave the following expression for G_x^E:

$$G_x^E = x_1x_2[-62\cdot5-36\cdot9(x_1-x_2)].$$

Values of P, μ_1^E, μ_2^E, G_x^E, and y calculated from this expression were compared with the experimental and derived values given in Table 4 and the agreement was found to be good. The standard deviations were, respectively: 0·09 mm Hg, 2·3, 2·9, 1·3 cal/mol, and 0·0014 in mole fraction.

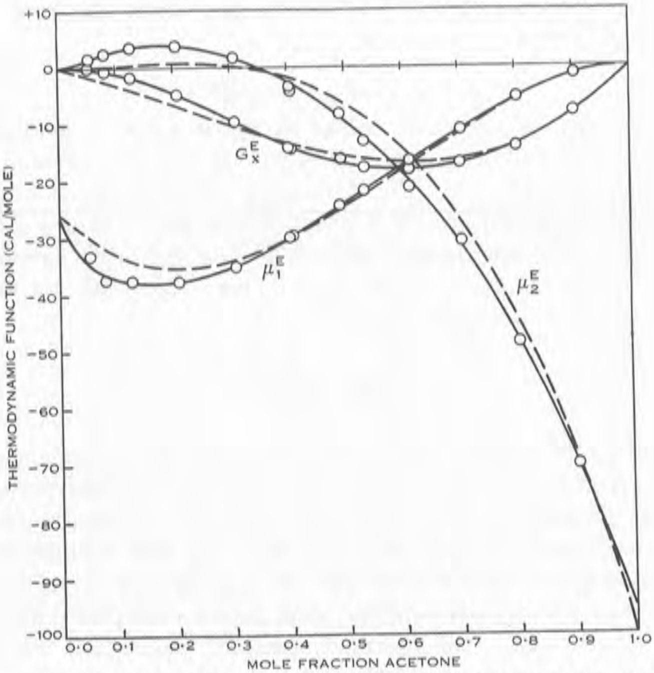

Fig. 1.—Thermodynamic functions: acetone+nitromethane 45 °C.
○—○ Experimental values from P, x, y data.
– – – Values from P, x data. $G_x^E = x_1x_2[-62\cdot5-36\cdot9(x_1-x_2)]$.

The errors in the value of G_x^E due to those in the measured quantities were estimated to be ±3 cal/mol. Graphs of the thermodynamic functions obtained by the two methods are shown in Figure 1.

This system shows an appreciable negative value of G_x^E and shows a change in sign of the deviation of the activity of nitromethane from the Raoult's law value at a mole fraction of acetone of about 0·35.

(b) *Acetone+Acetonitrile*

In the measurements on this system the accuracy of analysis of the liquid and vapour samples was reduced due to the small difference between the refractive indices (and other physical properties) of the components. Again no value of β_{12} or δ_{12} has been measured for this system and a correction for the vapour deviations was made assuming $\delta_{12}=0$. The values of the liquid molar volumes and second virial coefficients used in calculating values of the thermodynamic functions for this system were as follows:

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−1·66	−4·50	(−3·08)	0	0·076	0·050

The values of the derived thermodynamic functions are shown in Table 5. A plot of $(\mu_1^E-\mu_2^E)$ against x_1 showed the areas above and below datum to be approximately equal, but this test of thermodynamic consistency was not conclusive due to scatter of some of the points by about ±5 cal/mol.

The estimated maximum errors in the derived functions due almost entirely to errors in the compositions were found to be of the same order as the small values of the functions themselves. Thus the excess-free energy of mixing for this system is zero within the experimental error over the whole of the concentration range. This is in agreement with the results of Pratt (1947). A similar result was found by Brown and Smith (1955) for the system nitromethane+acetonitrile at 60 °C.

V. Discussion

For the system acetone+nitromethane our results indicate a change in sign of the deviation of the activity of nitromethane from the Raoult's law value at a mole fraction of acetone of 0·35 as is shown in Figure 1. The validity of this conclusion depends on the accuracy of our equilibrium data and on the reliability of the estimate that β_{12} has a value at 45 °C of −3·83 l/mol. Similar behaviour has been shown by McGlashan and Wingrove (1956) for the components of the mixture benzene+bromobenzene at 80 °C.

The value of the coefficient β_{12} estimated for this system, namely −3·83 l/mol, is more negative than either β_{11} or β_{22}. This kind of behaviour is not unique; it is shown, for example, by the systems diethyl ether+chloroform (Fox and Lambert 1951) and dioxane+chloroform (McGlashan and Rastogi 1958). Both of these systems resemble acetone+nitromethane in that they have negative heats of mixing.

It was suggested by Douslin (personal communication) that a value of the second virial coefficient for mixed vapours of polar molecules could be calculated using the Stockmayer potential (Stockmayer 1941) and employing suitable mixture rules.

The Stockmayer equation can be written in the form

$$\beta=b_0B^*(\tau,t),$$

where $b_0=\frac{2}{3}\pi\sigma^3$, $\tau=T/\theta$, $\theta=\varepsilon/k$, and $t=\mu^2/\varepsilon\sigma^3\sqrt{8}$, and where ε is the depth of the potential well, σ is the collision diameter, and μ is the dipole moment. Values of the function B^* have been tabulated by Hirschfelder, Curtiss, and Bird (1953) for values of t up to 1·5 and by Barker and Smith (1960) for t from 1·6 to 2·4.

For nitromethane values of the parameters θ, b_0, and t have been evaluated by Douslin and Waddington (1955) from the vapour pressure, vapour heat capacity, and heat of vaporization data of McCullough *et al.* (1954) and these lead to a calculated value of μ in good agreement with measured values.

TABLE 6
STOCKMAYER PARAMETER VALUES

Compound	Stockmayer Parameters			Second Virial Coefficients (45 °C l/mol)		Dipole Moment (D)	
	θ (°K)	t	b_0 (l/mol)	Calc.	Meas.	Calc.	Meas.
Acetone . .	479·0	0·8	0·06281	—1·57	—1·66	2·74	2·88
Nitromethane	290·4	1·6	0·09078	—3·11	—3·11	3·61	3·54
Acetonitrile	219·0	2·2	0·1060	—4·08	—4·50	3·98	3·96

For acetone, values of the parameters have been evaluated by Douslin (personal communication) from the second virial coefficient data of Lambert *et al.* (1949) and that of Pennington and Kobe (1957). For acetonitrile values have been evaluated by Barker (1959) from the second virial coefficient data of Lambert *et al.* (1949). These data are shown in Table 6 together with calculated and measured values of the dipole moments and the second virial coefficients at 45 °C for the pure component vapours.

TABLE 7
VALUES OF β_{12} AND δ_{12} CALCULATED FROM THE STOCKMAYER POTENTIAL

System	β_{12} (l/mol)	δ_{12} (l/mol)
Acetone+nitromethane . .	—2·00	+0·68
Acetone+acetonitrile	—4·10	+1·55
Acetonitrile+nitromethane . .	—3·48	+0·23

Values of the coefficient β_{12} were calculated from the Stockmayer parameter values listed in Table 6 using the following averaging rules.

$$b_{0_{12}}=[\tfrac{1}{2}(b_{0_{11}}{}^{\frac{1}{3}}+b_{0_{22}}{}^{\frac{1}{3}})]^3,$$
$$\theta_{12}=(\theta_{11}\cdot\theta_{22})^{\frac{1}{2}},$$
$$(b_0t\theta)_{12}=[(b_0t\theta)_{11}\cdot(b_0t\theta)_{22}]^{\frac{1}{2}}.$$

The first two are generally used in connection with the forces between non-polar molecules (see for example, Guggenheim 1952); and the third expresses the fact that the electrostatic interaction between two like or unlike molecules is proportional to the product of their dipole moments. The calculated values of β_{12} and the corresponding values of δ_{12} are shown in Table 7.

For the system acetone+nitromethane the value of $\delta_{12} \doteq +0 \cdot 68$ l/mol estimated using the Stockmayer potential is much more positive than the value $-2 \cdot 90$ l/mol estimated from our equilibrium data. If the latter value is correct, it indicates that there is a specific interaction in addition to the dipole-dipole interaction between acetone and nitromethane molecules. This may involve hydrogen bonding between oxygen of acetone and hydrogen of nitromethane. This is made more plausible by the negative values of the heat of mixing and volume change on mixing. $H^m = -163$ j/mol (Brown and Fock 1957). $V^m = -0 \cdot 255$ ml/mol (Brown and Smith, unpublished data). A similar interaction is indicated for the system acetone+acetonitrile.

The conclusions reached in this paper must, however, remain tentative until experimental values for δ_{12} for these systems have been measured.

VI. Acknowledgments

The authors wish to thank Dr. D. R. Douslin and Dr. J. P. McCullough of the U.S. Bureau of Mines, Bartlesville, Oklahoma, and Dr. J. A. Barker of the C.S.I.R.O. Chemical Research Laboratories, Melbourne, for their valuable help in the calculations of the mixture virial coefficient data using the Stockmayer equation.

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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 9, NUMBER 2, PAGES 180-183, 1956

HEATS OF MIXING

II. ACETONITRILE AND NITROMETHANE SYSTEMS

By I. Brown and W. Fock

Reprinted for
the Commonwealth Scientific and Industrial Research Organization, Australia

Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 9, NUMBER 2, PAGES 180-183, 1956

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By I. Brown* and W. Fock*

[*Manuscript received December* 1, 1955]

Summary

The heats of mixing at 45·00 °C have been measured at intervals over the whole composition range for the systems: acetonitrile+carbon tetrachloride, acetonitrile+benzene, acetonitrile+nitromethane, nitromethane+carbon tetrachloride, and nitromethane+benzene. These data, together with the excess free energy data of Brown and Smith (1954, 1955*a*, 1955*b*), have been used to calculate the excess entropy of mixing for these systems.

I. Introduction

The heats of mixing of a number of systems containing polar components are being measured to permit the excess entropy of mixing of such systems to be calculated with greater accuracy than can be obtained from free energy data alone. These measurements form part of a programme to provide experimental thermodynamic data for testing theories of polar non-electrolytic solutions.

II. Apparatus and Methods

The apparatus used was that described by Brown and Fock (1955). The only change in method was that the measured heating of the cell was done at the same time as the mixing, following the practice of Adcock and McGlashan (1954). The heater was switched on slightly before mixing so that approximately half the heat was introduced before mixing occurred. A second heating period 20 min after mixing provided a calibration for inexact compensation of the heat of mixing. This procedure reduces the errors due to extrapolation of the thermistor resistance-time curve.

Table 1

PHYSICAL PROPERTIES OF COMPONENT LIQUIDS

Liquid	$n_D^{25\cdot00}$	$d_4^{25\cdot00}$
Acetonitrile	1·34157	0·77662
Nitromethane	1·37966	1·13062
Carbon tetrachloride . .	1·45734	1·58444
Benzene	1·49795	0·87362

III. Components

The components were purified by the methods described by Brown and Smith (loc. cit.). The density and refractive index values are shown in Table 1.

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IV. RESULTS

The mole fraction x_1 of the first mentioned component and the heat of mixing in J/mol of mixture are given in Tables 2, 3, and 4. The experimental errors were estimated to be about $\pm 1 \cdot 5$ per cent. at $x_1 = 0 \cdot 5$ and 2 per cent. near the extremities of the concentration range. For the system acetonitrile + nitromethane, however, the errors are approximately ± 2 J/mol.

TABLE 2

HEAT OF MIXING OF ACETONITRILE SYSTEMS AT 45·00 °C

Acetonitrile + Carbon Tetrachloride		Acetonitrile + Benzene	
x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·179	737	0·150	249
0·369	930	0·311	398
0·581	867	0·507	501
0·585	834	0·584	496
0·593	868	0·592	489
0·682	755	0·666	475
0·683	750	0·669	467
0·872	416	0·867	287

TABLE 3

HEAT OF MIXING OF NITROMETHANE SYSTEMS AT 45·00 °C

Nitromethane + Carbon Tetrachloride		Nitromethane + Benzene	
x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·181	1017	0·173	428
0·211	1095	0·354	711
0·371	1367	0·579	824
0·436	1407	0·585	818
0·583	1377	0·666	775
0·595	1376	0·668	788
0·597	1346	0·865	463
0·687	1204		
0·844	773		

TABLE 4

HEAT OF MIXING ACETONITRILE+NITROMETHANE AT 45·00 °C

x_1	H_x^M (J/mol)
0·246	+9·5
0·247	+7·8
0·441	0·0
0·445	0·0
0·553	+0·5
0·556	—2·2
0·750	+5·7
0·751	+5·6

Estimated error in $H_x^M = \pm 2$ (J/mol).

V. THERMODYNAMIC PROPERTIES

The excess free energy of mixing at 45·00 °C for these systems has been determined from liquid-vapour equilibrium data by Brown and Smith (loc. cit.). These data, together with the reported heat of mixing data, have been used to determine graphically at even mole fractions the excess free energy, heat, and excess entropy of mixing of four of these systems at 45·00 °C. These data are given in cal/mol in Tables 5 and 6. The errors in TS_x^E shown in these tables have been estimated to be ±8 cal/mol for the nitromethane+carbon tetrachloride system and ±6 cal/mol for the other three.

TABLE 5

THERMODYNAMIC PROPERTIES AT 45·00 °C (CAL/MOL)

x_1	Acetonitrile+Carbon Tetrachloride			Acetonitrile+Benzene		
	G_x^E	H_x^M	TS_x^E	G_x^E	H_x^M	TS_x^E
0·1	127	121	—6	63	43	—20
0·2	207	186	—21	108	73	—35
0·3	255	215	—40	138	93	—45
0·4	279	223	—56	155	107	—48
0·5	284	215	—69	161	115	—46
0·6	267	198	—69	155	117	—38
0·7	232	174	—58	138	110	—28
0·8	176	137	—39	107	90	—17
0·9	97	82	—15	60	55	—5

1 cal=4·1840 J (abs.), T °K=t °C+273·16.

For the system acetonitrile+nitromethane at 60 °C the excess free energy of mixing is significantly zero over the whole concentration range. This indicates that the excess entropy of mixing (TS^E_x) for this system is not greater than $+2\cdot5$ cal/mol or less than $-1\cdot0$ cal/mol over the temperature range from 45 to 60 °C.

Table 6

thermodynamic properties at 45·00 °C (cal/mol)

x_1	Nitromethane+Carbon Tetrachloride			Nitromethane+Benzene		
	G^E_x	H^M_x	TS^E_x	G^E_x	H^M_x	TS^E_x
0·1	133	168	35	66	64	−2
0·2	225	256	31	116	115	−1
0·3	284	304	20	152	154	+2
0·4	313	332	19	174	181	+7
0·5	319	338	19	184	195	+11
0·6	302	321	19	179	195	+16
0·7	264	282	18	159	179	+20
0·8	204	219	15	124	145	+21
0·9	117	129	12	72	87	+15

VI. Discussion

It is interesting to note that the excess entropy values for the acetonitrile systems are negative, and those for the nitromethane systems are positive, while the values for the acetonitrile+nitromethane system are substantially zero. No simple explanation of this is obvious at present. Measurements are being made on the corresponding systems with acetone as the polar component.

VII. Acknowledgments

The authors thank Mr. F. Smith and Mr. O. H. Rigby for their help in the purification and measurement of the physical properties of the components.

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AUSTRALASIAN MEDICAL PUBLISHING CO. LTD.
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Reprinted from the
AUSTRALIAN JOURNAL OF CHEMISTRY
VOLUME 15, NUMBER 1, PAGES 1–8, 9–12 1962

VOLUME CHANGES ON MIXING

~~I. ALCOHOL + BENZENE SOLUTIONS~~

II. SYSTEMS CONTAINING ACETONE, ACETONITRILE, AND NITROMETHANE

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II. SYSTEMS CONTAINING ACETONE, ACETONITRILE, AND NITROMETHANE

By I. Brown* and F. Smith*

[*Manuscript received October* 11, 1961]

Summary

The volume changes on mixing have been measured at 25, 35, and 45 °C for the following binary systems: acetone+acetonitrile, acetone+nitromethane, acetonitrile+nitromethane and each of these polar components with benzene and with carbon tetrachloride.

The sign and concentration dependence of the volume changes on mixing of these systems follow closely the excess entropy changes on mixing calculated from the liquid–vapour equilibrium data and heats of mixing previously measured in these laboratories.

I. Introduction

These measurements were made as part of a study of the thermodynamic properties of binary mixtures containing polar components.

Most of the values at 25 °C were calculated from density measurements. The values at 35 and 45 °C and some at 25 °C were obtained by direct measurement of the volume change on mixing.

II. Experimental

The measurements were made using the apparatus and methods described by Brown and Smith (1962). Benzene was purified by the method of Brown and Ewald (1951), carbon tetrachloride by the method of Barker, Brown, and Smith (1953), and acetonitrile, nitromethane, and acetone by the methods of Brown and Smith (1954, 1955*a*, 1957 respectively). The nitromethane was dried by passing it through a short column packed with 4A Linde sieves.

The physical properties of the components used are shown in Table 1.

Table 1

PHYSICAL PROPERTIES OF THE COMPONENTS

	$d_4^{25\cdot00}$	$d_4^{35\cdot00}$	$d_4^{45\cdot00}$	$n_D^{25\cdot00}$
Benzene	0·87365	0·86295	0·8522	1·49801
Carbon tetrachloride	1·58433	1·56480	1·5442	1·45733
Acetone	0·78422	0·77265	0·7609	1·35599
Acetonitrile . .	0·77664	0·76575	0·7553	1·34152
Nitromethane . .	1·13063	1·11700	1·1033	1·37954

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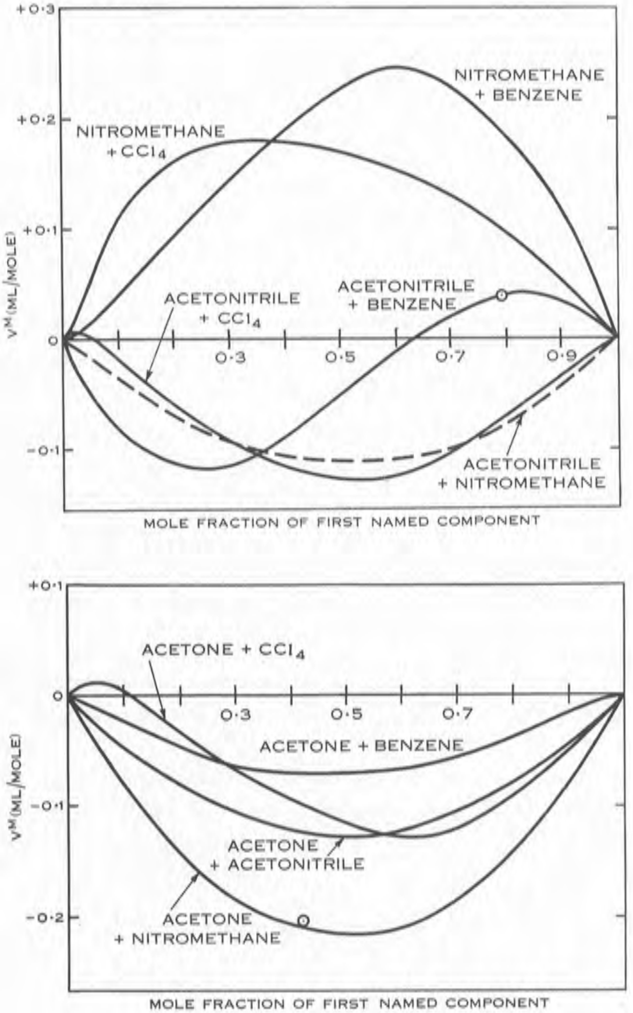
III. Results

The values at 25 °C of V^M, the volume change on mixing per mole of mixture, as a function of concentration are shown in Figures 1 and 2. The curves show values of V^M derived from density measurements; these have an uncertainty of $\pm 0 \cdot 007$ ml/mole. The open circles are directly measured values which have an uncertainty of $\pm 0 \cdot 003$ ml/mole.



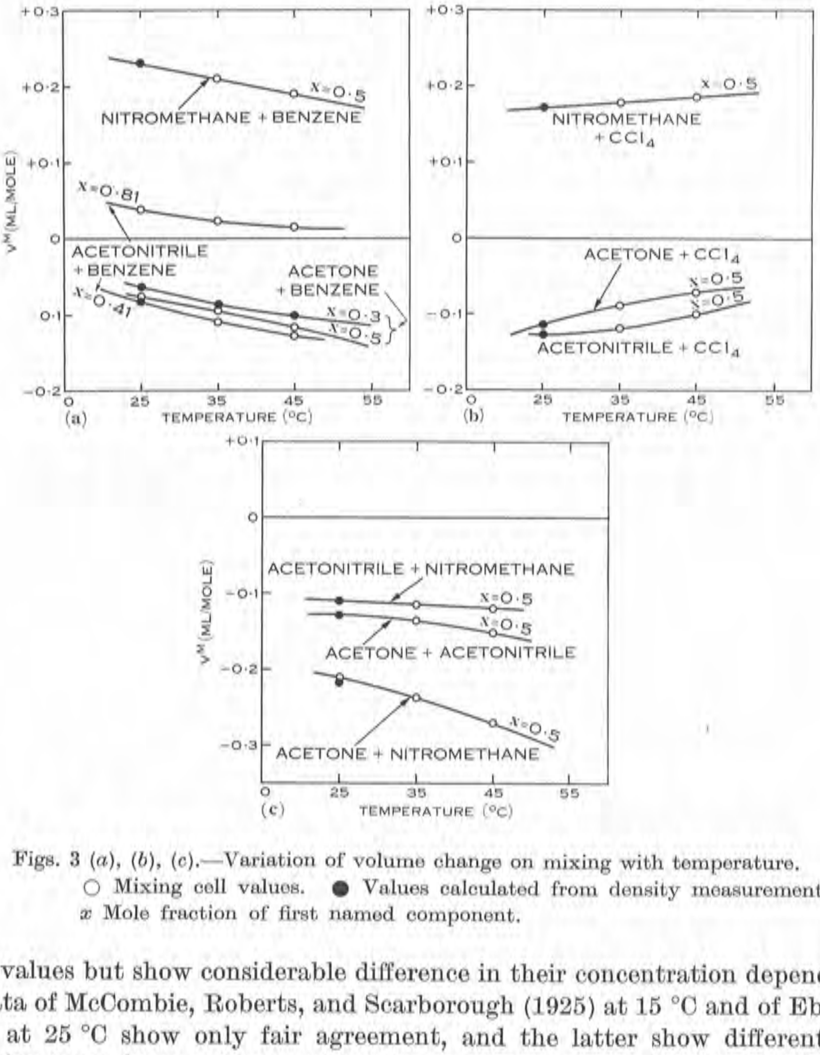
Figs. 1, 2.—Volume changes on mixing at 25 °C.
— Curves derived from density measurements.
○ Mixing cell values.

Figure 3 (*a*), (*b*), and (*c*) shows the variation of V^M with temperature over the range 25 to 45 °C. The values at 45 °C have an uncertainty of $\pm 0 \cdot 004$ ml/mole for the direct measurements and $\pm 0 \cdot 02$ ml/mole for the values derived from density measurements.

IV. Discussion

A literature survey revealed no direct measurements of V^M for any of these systems and density data on only three of them. Values of the volume changes on mixing calculated from these are compared below with our values.

For acetone+benzene the values from the data of Howard and Pike (1959) at 20, 25, 37·8, and 50 °C are only 0·005 ml/mole lower than our values. The data of Harms (1938) at 6 °C are in reasonable agreement with the magnitude of our values but show considerable difference in their concentration dependence. The data of McCombie, Roberts, and Scarborough (1925) at 15 °C and of Ebersole (1901) at 25 °C show only fair agreement, and the latter show different concentration dependence. The results of Barr and Bircumshaw (1921) and Bingham and Brown (1921) at 25 °C are in disagreement with our values.



Figs. 3 (*a*), (*b*), (*c*).—Variation of volume change on mixing with temperature.
○ Mixing cell values. ● Values calculated from density measurements.
x Mole fraction of first named component.

For acetone+carbon tetrachloride the values from the data of Bachman and Simmons (1952) at 25 °C agree well with our values. The values from the data of Earp and Glasstone (1935) at 20 °C are in reasonable agreement, but those of Krchma and Williams (1925) at 25 °C and Heyman and Graffunder (1931) at 25 °C are much lower.

For nitromethane+benzene the values from the data of Campbell and Hall (1951) at 25 °C are in good agreement with our values.

It is interesting to compare the volume changes on mixing of these systems with the heats of mixing, H^M, at 45 °C measured by Brown and Fock (1956, 1957) and the excess entropies of mixing, S^E, determined from the latter and the liquid–vapour equilibrium data of Brown and Smith (1954, 1955*a*, 1955*b*, 1957, 1960).

The system nitromethane+acetonitrile has an appreciable negative value of V^M although H^M and S^E are close to zero. In the systems acetone+nitromethane and acetone+acetonitrile, V^M, H^M, and S^E are all negative and symmetrical with concentration. This supports the suggestion of Brown and Smith (1960) from a study based on the contribution of vapour deviations to the liquid–vapour equilibrium that hydrogen bonding may take place between the oxygen of acetone and hydrogen of the nitromethane and acetonitrile.

The systems containing benzene and carbon tetrachloride have values of V^M, H^M, and S^E which become more positive on going from the acetone to the acetonitrile and to the nitromethane systems. In the benzene systems these thermodynamic properties are more positive at high mole fractions of the polar component while the reverse is found for the carbon tetrachloride systems. The carbon tetrachloride systems show an increase in V^M with a rise in temperature while all the others studied show a decrease.

The complex behaviour shown by these systems indicates that dipole interaction is not the only cause of the deviations and that the electron donor and acceptor properties of the components also play an important part.

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THERMODYNAMIC PROPERTIES — SOLUTIONS OF POLAR LIQUIDS

Summary and Discussion of Results

The first part of this study was devoted to solutions of alcohols in which the association is due largely to hydrogen bonding. In this second part, solutions of three polar liquids acetone, acetonitrile and nitromethane were chosen for study as these liquids are associated due to dipole-dipole interaction between their molecules.

It can be seen from the properties of these liquids given in Table 1, that nitromethane and acetonitrile are more strongly associated than is acetone.

Table 1. Properties of the Polar Liquids

	B.P.	H_{vap} @ B.P.	ϵ	μ	V	B
	°C/760 mm	K.cal/ mole		Debye	1/mole	45°C
Acetone	56.06	7.092	20.7	2.88	0.076	-1.66
Acetonitrile	81.57	7.127	37.5	3.96	0.050	-4.50
Nitromethane	101.07	8.225	35.9	3.54	0.056	-3.11

ϵ = dielectric constant, μ = dipole moment,
V = molar volume and B = second virial coefficient.

Thermodynamic Properties of Solutions

Liquid-vapour equilibria, calorimetric heats of mixing and volume changes on mixing were measured of the binary solutions of these liquids and solutions of each of them in benzene and in carbon tetrachloride. Details of these measurements and the values of G^E, H^M, TS^E and V^M calculated from these data are given in the preceding papers Nos. 14 to 20. A summary of the values of these properties at 45°C and at a mole fraction of 0.5 is given in Table 2. Figure 1 shows the variation of the thermodynamic properties with mole fraction for the nine systems studied.

These solutions form an interesting series of mixtures which show a wide variation in the values of their thermodynamic properties between the two extremes of their all being negative (acetone + nitromethane) to all being positive (nitromethane + carbon tetrachloride).

The data in Table 2 show that, in general, the four properties G^E, H^M, TS^E and V^M for all mixtures become more positive as the second component is varied in the order: acetone, acetonitrile, nitromethane, benzene, carbon tetrachloride. The main exceptions to this trend are the excess entropies of mixing for solutions containing acetone and acetonitrile, where this order is substantially reversed.

The thermodynamic properties of all these mixtures are the resultant of two contributions. Firstly the breakdown of clusters of the associated components on dilution with the solvent, leading to positive values of the excess properties; this contribution is predominant in the system

Table 2

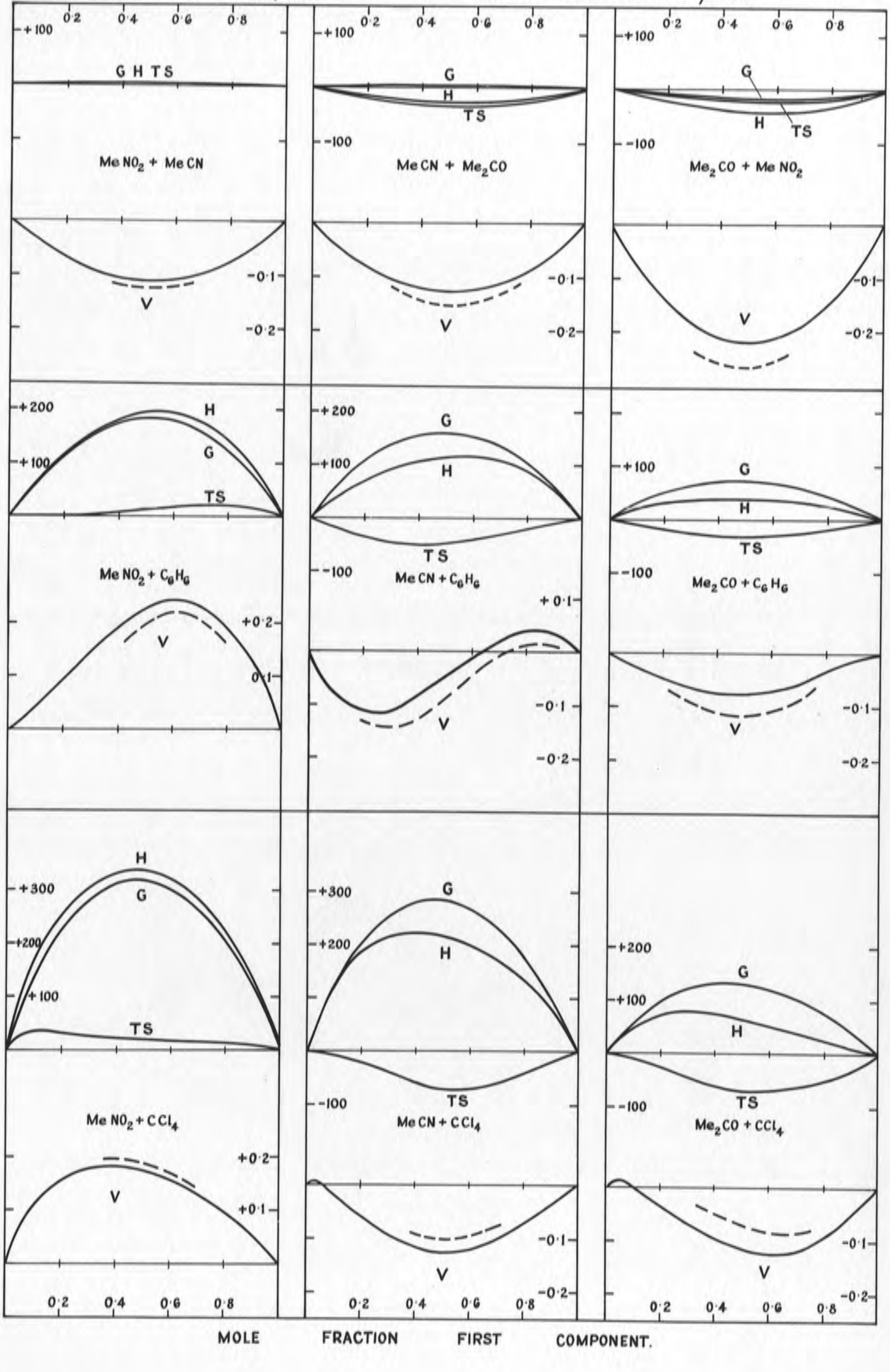
Thermodynamic Properties of Systems Containing Polar Liquids

45°C x = 0.5

System	G^E	H^M	TS^E	V^M
	J/mole			ml/mole
acetone + benzene	295	160	−135	−0.12
acetonitrile + benzene	675	480	−190	−0.08
nitromethane + benzene	775	815	+40	+0.19
acetone + CCl_4	545	260	−285	−0.07
acetonitrile + CCl_4	1185	900	−285	−0.10
nitromethane + CCl_4	1335	1415	+80	+0.19
acetone + nitromethane	−65	−160	−95	−0.27
acetone + acetonitrile	+10	−110	−115	−0.15
acetone + benzene	295	+160	−135	−0.12
acetone + CCl_4	545	+260	−285	−0.07
acetonitrile + acetone	+10	−110	−115	−0.15
acetonitrile + nitromethane	+3	0	−3	−0.12
acetonitrile + benzene	675	480	−190	−0.08
acetonitrile + CCl_4	1185	900	−285	−0.10
nitromethane + acetone	−65	−160	−95	−0.27
nitromethane + acetonitrile	+3	0	−3	−0.12
nitromethane + benzene	775	815	+40	+0.19
nitromethane + CCl_4	1135	1415	+80	+0.19

THERMODYNAMIC PROPERTIES OF SOLUTIONS OF POLAR LIQUIDS

G^E H^M TS^E 45°C. cal./mole V^M ——— 25°C. – – – – 45°C. ml./mole



nitromethane + carbon tetrachloride. Secondly the association between the solute and solvent due to electron donor-acceptor interactions, where these can occur, leading to negative values of the excess properties. This second factor predominates in the mixture acetone + nitromethane.

In the system nitromethane + acetonitrile, where the components have similar molar volumes and dipole moments, these two contributions almost cancel leading to values of G^E, H^M and TS^E very close to zero, although the value of V^M remains appreciably negative.

The thermodynamic properties of the systems containing carbon tetrachloride are similar to those of the alcohol + benzene systems; they have positive values (or a tendency to positive values) of H^M, TS^E and V^M at low mole fraction of the polar component and show an increase in V^M with an increase in temperature. The heats of mixing of the solutions containing carbon tetrachloride and benzene become more positive when the second component is changed in the order acetone acetonitrile, nitromethane which is in the same order as the heats of vapourisation of these polar components.

It is interesting to note that, while the value of V^M in the carbon tetrachloride solutions become more positive with an increase in temperature all the other six systems have values of V^M which become more negative with an increase in temperature. There does not seem to be any adequate explanation of this.

In the benzene solutions the values of the thermodynamic properties also become more positive as the polar component is varied in the order, acetone, acetonitrile, nitromethane, but the values are less positive than those in the corresponding solutions in carbon tetrachloride. This is due to the larger contributions from interactions of the polar molecules with the π electrons of benzene compared with those due to interactions between the polar molecules and molecules of carbon tetrachloride.

In the benzene solutions the thermodynamic properties have maxima or a tendency to be positive at high mole fractions of polar component in contrast to the carbon tetrachloride solutions. This is due to the interaction between the polar molecules and benzene having a larger effect at high benzene concentration and also possibly due to the breakdown of association of benzene at high mole fraction of the polar component.

In the solutions of nitromethane in both benzene and carbon tetrachloride the contribution to the properties due to the break-down of clusters of the polar molecules on dilution is predominant. The excess entropy of these systems is positive due to the expansion and the gain in rotational and translational freedom of the polar molecules which take place on solution in solvent.

In the corresponding solutions of acetonitrile and the less associated acetone, the values of the excess properties show the effect of some association between unlike molecules. For these systems the value of the excess entropy is negative due to the contraction and loss of rotational and translational freedom which takes place on mixing.

In the two solutions of acetone in acetonitrile and nitromethane the predominant contribution is the electron donor-acceptor interaction which occurs between the O of the acetone and the protonic alpha hydrogens of the other components.

Two interesting studies have been made by others on some of these systems. Kaulgud[1] has measured the ultrasonic velocity in solutions of the three polar liquids in both benzene and in carbon tetrachloride. He calculated the variation of adiabatic compressibility with concentration for these mixtures. The two nitromethane solutions showed negative velocity deviations and positive excess compressibility caused by the large expansion on mixing. The benzene solutions of acetone and acetonitrile showed a small positive velocity deviation and a negative excess compressibility which are in part due to the negative excess entropy. In the solutions of acetone and acetonitrile in carbon tetrachloride both the velocity deviation and the excess compressibility are negative.

The behaviour of the vapour mixtures of two of these systems has been studied by Bottomley and Spurling[2] who measured the second virial coefficients of the vapours for the systems nitromethane + acetone and nitromethane + benzene. They determined values of B_{11}, B_{22} and B_{12} at 50°C. From their results one can calculate δ_{12} which is twice the deviation of B_{12} from the arithmetic mean of B_{11} and B_{22} i.e. $\delta_{12} = 2B_{12} - B_{11} - B_{22}$ and also the volume change on mixing in the vapour $\Delta V = y_1 y_2 \delta_{12}$ where y_1 and y_2 are the mole fractions of components 1 and 2 in the vapour.

For the system nitromethane + acetone δ_{12} is negative and $\Delta V = -261$ ml/mole at $y = 0.5$ as compared with V^M at $x = 0.5$ in the liquid of -0.29 ml/mole. For the system nitromethane + benzene δ_{12} is positive and $\Delta V = +375$ ml/mole at $y = 0.5$ as compared with V^M at $x = 0.5$ in the liquid of $+0.19$ ml/mole. This shows that the balance of intermolecular forces which governs the properties of these liquid mixtures also determines the properties of the vapour mixtures.

For the system nitromethane + acetone these authors found that B_{12} and δ_{12} were considerably more negative than the values calculated from the Stockmyer potential but not as negative as was estimated in paper No. 18 by assuming thermodynamic consistency of the liquid-vapour equilibria.

The results described in this symmary illustrate well the complicated nature of the intermolecular interactions in solutions of polar liquids and the part played by the balance of these interactions in determining the thermodynamic properties of this type of solution. It is therefore not surprising that a theory of solution which can predict the properties of these mixtures, has yet to be developed.

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Reprinted from the
AUSTRALIAN JOURNAL OF APPLIED SCIENCE
VOLUME 10, NUMBER 3, PAGES 294–305, 1959

THE COMPOSITION OF A LURGI BROWN COAL TAR

I. PRELIMINARY SEPARATION OF CONSTITUENTS

By I. Brown

Reprinted for the
Commonwealth Scientific and Industrial Research Organization
Australia

THE COMPOSITION OF A LURGI BROWN COAL TAR

I. PRELIMINARY SEPARATION OF CONSTITUENTS

By I. Brown*

[*Manuscript received May* 19, 1959]

Summary

An investigation is being made of the compounds present in the light tar from the Lurgi gasification plant of The Gas and Fuel Corporation of Victoria at Morwell.

The conditions of formation of the tar and the methods employed to separate the various types of constituents are described.

The tar contains compounds which boil from 30°C to over 400°C. Eighty-three per cent. by weight of the tar boils below 380°C. This is made up of approximately 15 per cent. of phenols, 1·5 per cent. of pyridine and quinoline bases, 53 per cent. of aromatic hydrocarbons, 10 per cent. of olefinic hydrocarbons, and 3·5 per cent. of paraffinic hydrocarbons. Sulphur compounds, non-phenolic oxygen compounds, and non-basic nitrogen compounds are also present in small amounts.

I. Introduction

The Lurgi town-gas plant at Morwell was put into operation by The Gas and Fuel Corporation of Victoria in October 1956. The plant produces about 15 million ft^3/day of methane-rich town gas by the pressure gasification of 400 tons/day of Yallourn brown coal briquettes with steam and oxygen.

The composition of the raw material, Yallourn brown-coal briquettes, has been described by Reinbach (1953), Casamento and Ingles (1957), and Ingles (1957). An average composition taken from their data is given in Table 1. These data show that the coal has a higher percentage of oxygen and a lower percentage of nitrogen and sulphur than black coals usually employed in gas making.

Details of the plant and its operation have been given by Bennie (1957). The briquettes are gasified in the generators with steam and 95 per cent. oxygen under a pressure of 400 p.s.i.g. The temperature in the combustion zone is approximately 1200°C but the tar is formed in the upper zone of the generator where the temperature is about 600°C. The tar-laden gas leaves the generator at a temperature of 565°C and passes to the waste heat boiler where heavy tar and water are condensed. The gas under pressure and at a temperature of 150°C passes through three coolers in series and leaves at substantially the same pressure and at atmospheric temperature. The condensate from the three coolers goes to large gravity separating tanks from which the light tar and aqueous liquor pass to storage tanks.

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The by-products from the plant are: heavy tar from the waste heat boilers (approximately 1120 gal/day), light tar from the gas coolers (approximately 1740 gal/day), and aqueous liquor (approximately 125,000 gal/day). A secondary gas benzol (approximately 800 gal/day) is produced by stripping the wash oil from the gas scrubbers.

TABLE 1

TYPICAL COMPOSITION OF YALLOURN BROWN-COAL BRIQUETTES

Proximate (wt. %)	Moisture	Volatile	Fixed carbon	Ash		
	15·0	43·8	39·6	1·6		
Ultimate (wt. %	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur*	Ash
dry basis)	66·10	4·71	25·60	0·51	0·31	2·10

* Total sulphur.

Little has been published on the composition of brown coal tars; the bulk of these tars is produced in Germany and it has been the practice to hydrogenate a large proportion to produce diesel oil (see Rhodes 1949; Deadman and Fuidge 1950).

TABLE 2

PROPERTIES OF THE LIGHT TAR

Properties		Composition (wt. %)	
Density d_4^{25}	0·950	Carbon	85·7
Refractive index n_D^{25}	1·572	Hydrogen	8·9
Viscosity (cP/25°C)	3·24	Oxygen	5·4
		Nitrogen	0·4
Boiling range (°C/760 mm Hg)	30–420	Sulphur	0·5

This work is concerned with the composition of the light tar obtained from the gas coolers of the Lurgi plant. The light tar is a dark mobile liquid with a phenolic odour. The physical properties of the tar are given in Table 2 and its Engler-type distillation curve in Figure 3. A sample of 16 kg was taken from the plant in May 1957, and stored under nitrogen in a sealed container.

The methods used for the separation of the tar constituents were chosen to reduce to a minimum any changes in the labile constituents during processing. An outline of the preliminary separation of the tar into various types of compounds is given in Figure 1, where yields are given as parts per 10,000 calculated on a no-loss basis.

The tar was first separated into five broad fractions by isothermal distillation at temperatures close to 100°C in an atmosphere of oxygen-free nitrogen. Phenols and bases were put aside for further investigation after extraction from four of these fractions using sodium hydroxide and sulphuric acid respectively. The remaining neutral oils were then roughly fractionated under reduced pressure with a minimum of thermal hazard into nine fractions of closer boiling ranges than those from the isothermal distillation. The approximate quantities of the main types of hydrocarbons present in the lower boiling fractions were determined by absorption on silica gel and the distribution of oxygen, nitrogen, and sulphur was determined by microanalysis of the fractions.

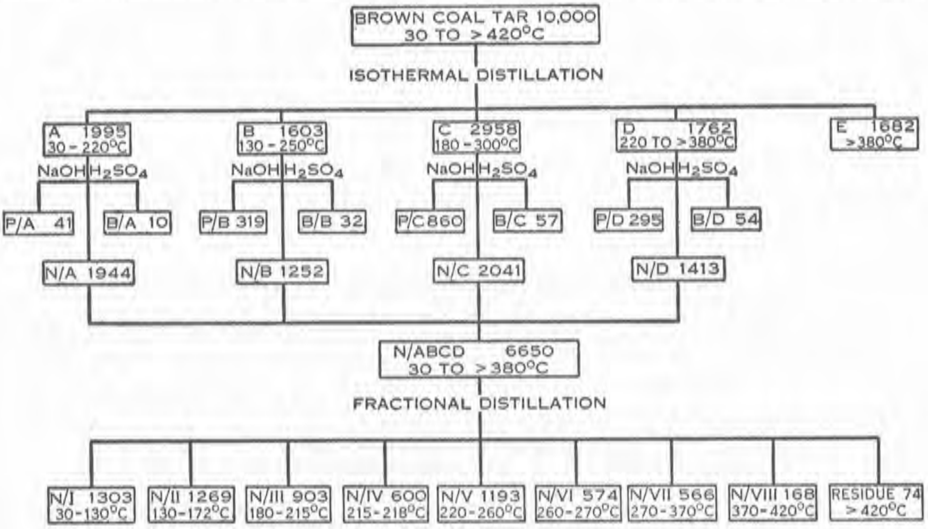

Fig. 1.—Preliminary separation of the tar.
Numbers = grams per 10,000 g of tar; temperatures, b.p. (°C/760 mm Hg); P, phenols; B, bases; N, neutrals.

Subsequent papers will give further details of the particular methods used for separating the constituents of each type, for the identification of the compounds present, and for the determination of the percentage of each in the tar.

II. Separation of the Tar into Fractions

(a) *Isothermal Distillation*

The tar was separated into a small number of broad fractions of different boiling range to reduce interference from low boiling compounds when processing the higher boiling material and to separate the high molecular weight substances which promote the formation of emulsions in the extraction of phenols and bases from the lower boiling material. Low temperature isothermal distillation was chosen for this preliminary separation as it has been shown by Thompson *et al.* (1955) to give minimum decomposition of labile materials in the separation of petroleum products. In the present work a form of spinning-band evaporator was used and the liquid was exposed to a temperature of 100°C for only about 30 sec during each distillation.

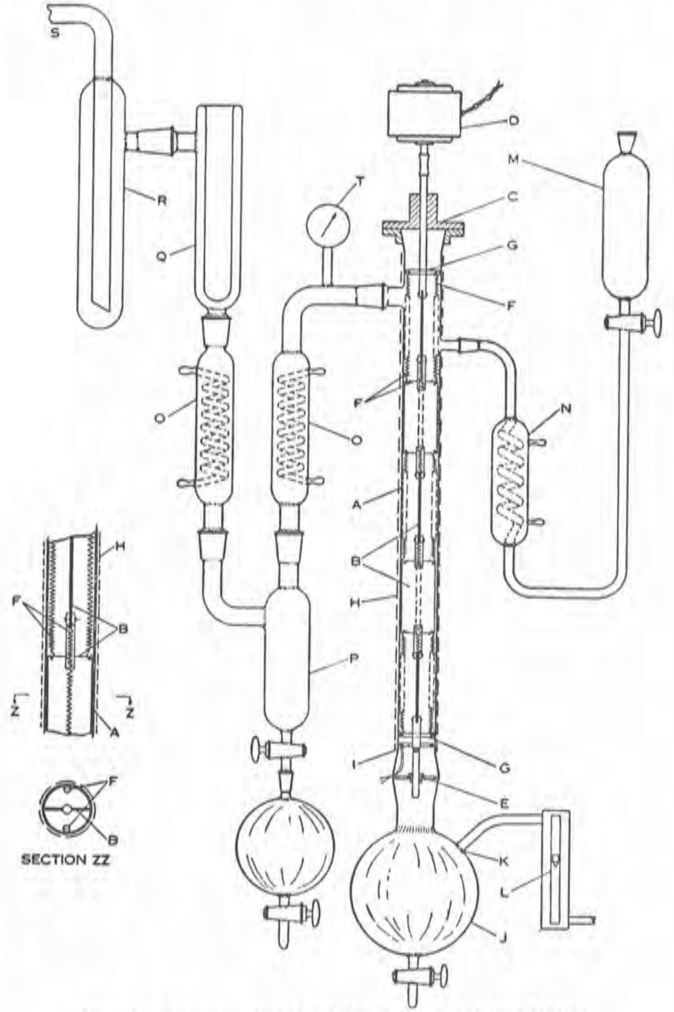

Fig. 2.—Evaporator used for isothermal distillation.

(i) *Apparatus*.—The evaporator is shown diagrammatically in Figure 2. The evaporator tube *A* was made from a 4 ft length of 1½-in. industrial glass pipe. It contains a spinning band made from four stainless steel blades *B*, 9·75 in. long by 1·4 in. wide. (In Figure 2, five blades are shown to illustrate better the relative position of the blades and wipers.) The blades are similar to the rotor (type *C*) described by Murray (1951), who has employed successfully spring-type wipers

TABLE 3

ISOTHERMAL DISTILLATION OF TAR*

Run No.	Pressure (mm Hg)	Film Temp. (°C)	Feed Rate (l/hr)	Nitrogen Flow Rate (l/min)		Vapour Temp. (°C)	Distillate		
				At 20°C 760 mm Hg	At Column Temp. and Pressure		Code	Yield (g)	Engler Boiling Range (°C/760 mm Hg)
1	760	100	1·5	5·0	6·8	90	A	3173	70–200 (96%)†
2	85	100	2·0	1·7	20	95	B	2547	138–230 (96%)
3	2	78	3·0	0·3	150	78	C_a	1835	188–275 (95%)
4	2	80	3·0	0·3	150	80	C_b	1897	
5	2	103	3·0	0·3	160	95	C_c	968	
6	2	140	2·0	0·2	115	135	D	2794	228–360 (92%)

* Starting material 16,345 g tar; final residue (code E) 2665 g, loss 466 g.

† Per cent. distilled at end-point.

in a spinning-band distillation column (Murray, unpublished data). The blades are joined by short lengths of slotted 0·25 in. diameter stainless steel rod loosely riveted to the blades, each blade being set at right angles to the adjacent ones. The blades are driven by a shaft passing through a Geco oil seal and ball bearing mounted in the flange *C* and driven at 700 r.p.m. by the ¼ h.p. motor *D*. The bottom blade is centred by a spigot fitting into a Teflon bearing, held in the spider *E*. Pairs of flexible Nichrome spring wipers *F* are stretched between small holes in the ends of alternate blades and touch the walls of the tube where they maintain a thin, turbulent film of liquid. Rods *G* are provided on the shaft above the top and below the bottom blades for the attachment of the upper and lower pairs of springs. The evaporator tube is heated by windings of Nichrome ribbon, one lagged winding below the feed inlet *H* and a smaller bare one above. The upper section can be operated at a lower temperature to provide some reflux to the column. A copper-constantan thermocouple mounted on a shim brass strip sprung onto the inner wall of the column just below the band is used to measure the film temperature. A residue flask *J* is attached to the lower end of the column and is provided with a nitrogen inlet *K* which is connected to a nitrogen flowmeter *L*. An additional bottom section equipped with blades, wipers, and a cooling jacket can be attached for rapid cooling of very labile residues.

In operation the voltage applied to the tube heaters is adjusted by Variac transformers to give the required film temperature and the nitrogen flow is started. Liquid is fed from the reservoir *M* by gravity or by a pump at about 1 to 3 l/hr through the steam-jacketed feed-heater *N* and into the column. The vapour as it is formed is swept by the nitrogen from the column through the spiral condensers *O* which are cooled with ice-water and the distillate is collected in the product receiver *P*. Any uncondensed product is trapped by the dry-ice trap *Q* and, if necessary, in the trap *R*, cooled in liquid air. The outlet *S* is vented to atmosphere or connected to a vacuum pump of adequate capacity. The operating pressure is measured by a vacuum gauge *T*. When operating at reduced pressure, provision is made for emptying the product and residue vessels without interrupting the operation of the unit.

With a feed liquid of a wide boiling range such as the brown-coal tar, it is necessary to run the unit at atmospheric pressure to remove the volatile constituents and then to re-run the residue at a number of lower pressures. This method, with the choice of suitable pressures, ensures the evaporation of a reasonable sized fraction of the liquid at each pressure without appreciable loss due to inadequate condensation of the more volatile constituents.

(ii) *Results*.—The first run made at atmospheric pressure and with a film temperature of 100°C gave 3·2 kg of low boiling distillate. The conditions of operation and yields of distillates from this and subsequent runs are shown in Table 3. The distillates A, B, C, D ranged from pale yellow to orange-red in colour, and the residue E was a black solid with a softening range of about 30 to 40°C. The boiling ranges of the distillates are shown as Engler-type distillation curves in Figure 3. The handling losses which occurred in each stage were approximately 2·5 per cent. of the feed, and the yields of fractions shown in Figure 1 include these losses.

(*b*) *Separation of Phenols and Bases from Neutral Oil*

The fractions A, B, C, and D were separated into acids, phenols, bases, and neutrals by extraction with aqueous solutions of 5 per cent. sodium bicarbonate, 20 per cent. sodium hydroxide, and 20 per cent. sulphuric acid respectively. The extractions were carried out in 5 l. separating funnels in which the phases were vigorously mixed with a vibromixer for 10 min, allowed to separate, and the aqueous layer run off and stripped of small amounts of neutral oil by washing with a small volume of ether. During the extractions the liquids were blanketed with nitrogen to reduce oxidation. Repeated extractions were made with each reagent until the last aqueous extracts contained no appreciable quantities of phenols or bases.

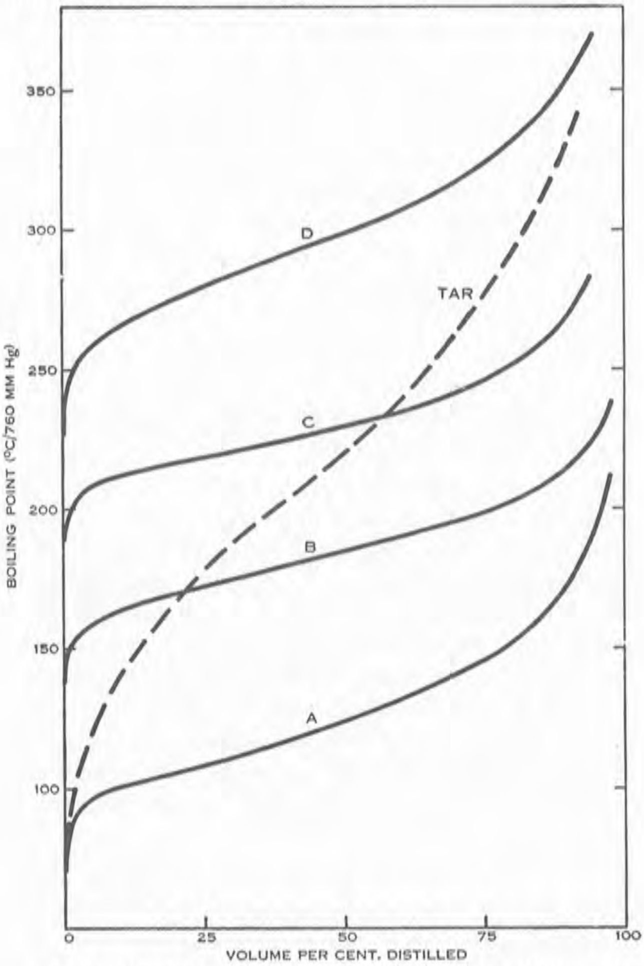

Fig. 3.—Engler distillation curves of tar and distillates.

The bicarbonate extracts were acidified and the traces of acids present extracted with ether. The phenols were recovered by acidification and extraction of the aqueous layer with ether, being finally dried by distilling off the water.

The acid extracts were freed from neutral oil by extraction with ether, made alkaline, and the bases separated as before except that they were dried over anhydrous calcium chloride. The neutral oils were also dried over this reagent.

TABLE 4

COMPARISON OF EXTRACTION METHODS

Yields in weight per cent. of fraction

Components	From Fraction C_1	From Fraction C_2	Components	From Fraction C_1	From Fraction C_2
Phenols (first)	27·4	27·9	Bases (total)	1·8	2·0
Phenols (second)	0·3	0·7	Neutrals	66·9	67·1
Phenols (total)	27·7	28·6	Acids	0·04	0·05
Bases (first)	0·8	1·9	Losses	3·6	2·1
Bases (second)	1·0	0·1			

In the treatment of fractions A and B, acid extraction was used first, followed by bicarbonate and then sodium hydroxide; but for fraction B it was found necessary to make a second series of extractions for both phenols and bases with reduced quantities of reagents. To determine the best sequence, fraction C was divided into two parts C_1 and C_2. Part C_1 was extracted in the order H_2SO_4, $NaHCO_3$, NaOH, H_2SO_4, NaOH. Part C_2 was extracted in the order $NaHCO_3$, NaOH, H_2SO_4, NaOH, H_2SO_4. The results given in Table 4 show the latter procedure facilitates

TABLE 5

RESULTS OF ACID AND ALKALI EXTRACTIONS

Yield of component types in weight per cent. of distillate fraction

Components	Distillate Code			
	A	B	C	D
	70–200°C*	138–230°C*	188–275°C*	228–360°C*
Phenols	2·0	19·0	28·2	16·4
Bases	0·5	1·9	1·9	3·0
Neutrals	94·8	74·3	66·9	78·5
Acids	0	0·04	0·05	0·04
Losses	2·7	4·8	3·0	2·1

* Engler boiling range.

extraction of the bases and gives slightly higher yields of both phenols and bases. In agreement with the findings of Fisher and Eisner (1937) it appears that complete extraction of the bases is difficult when large quantities of phenols are present. The results of these extractions are shown in Table 5 and in Figure 1. The second sodium hydroxide extraction gave phenols of slightly higher boiling point than those of the first; the second acid extraction gave bases with a quinoline-like odour while the first gave bases having the smell of pyridine. The total amount of fatty acids present in the tar was less than 0·04 per cent.

TABLE 6

DETAILS OF FRACTIONAL DISTILLATION OF NEUTRAL OILS A, B, C, D

Fraction Code	Boiling Point (°C/mm Hg)	Equivalent Boiling Point (760 mm Hg)	Yield		Type of Product
			(g)	(wt. %)	
N/I	30–130/762	30–130	911	19·5	Colourless liquid
N/II	66–115/105	130–170	884	19·0	Yellow oil
N/III	94–122/52	180–215	629	13·5	Yellow oil
N/IV	122–125/52	215–220	418	9·0	Orange, semi-solid
N/V	106–126/20	220–260	831	17·8	Orange fluorescent oil
N/VI	126–140/20	260–270	400	8·6	Orange fluorescent oil
N/VII	90–154/2	270–370	395	8·4	Red fluorescent oil
N/VIII	155–220/1·5	370–420	117	2·5	Viscous dark oil Fluorsecent oil
Residue	>220/1·5	>420	52	1·1	Black brittle solid
Loss	—	—	27	0·6	

(c) *Fractionation of Neutral Oils*

(i) *Fractional Distillation.*—The neutral oil fractions from A, B, C, and D have wide and overlapping boiling ranges so that these were distilled into a larger number of fractions of smaller boiling range. It was felt that far less change of the constituents would occur if this fractionation was made after the removal of the phenols and bases rather than if it was made on the whole tar. Aliquots of 45 weight per cent. of each of the neutral fractions A, B, C, D were mixed (4664 g) and distilled.

This fractionation was made as rapidly as possible using a 1 in. dia. by 12 in. column packed with 3 mm glass helices and operated under a reflux ratio of about 5 : 1. It was done in stages to reduce the time of heating of the higher boiling material. First the volatile portion of neutral oil A was distilled at atmospheric pressure until a boiling point of 130°C was reached, and then neutral oil B was added and a second fraction removed under a pressure of 105 mm Hg until a temperature of 115°C was reached. Then neutral oil C was added and so on. When the seventh fraction boiling from 90 to 154°C at 2 mm Hg had been distilled, the remainder was transferred to a smaller flask fitted with a short empty column and the distillation continued. Details of these distillations are given in Table 6.

A number of solid compounds was isolated from some of the higher boiling fractions by cooling and filtering the oils. For example, fraction N/IV gave 140 g of naphthalene which shows that this compound is present to the extent of at least 2 per cent. in the tar.

(ii) *Preliminary Estimation of Hydrocarbon Types.*—The approximate amounts of paraffins, olefines, and aromatics present in the lower boiling fractions of the neutral oil were determined on 0·75 ml samples by absorption on silica gel, using the fluorescent indicator method of analysis described by Criddle and Le Torneau (1951). No accurate analysis could be made by this method on the higher boiling fractions as the fluorescence of the oils themselves obscured the blue fluorescence of the aromatic indicator. The results indicate that the neutral oils are approximately 80 per cent. aromatic, 15 per cent. olefinic, and 5 per cent. paraffinic. The aromatic portion includes sulphur compounds, non-basic nitrogen compounds, and non-phenolic oxygen compounds which are present in small amounts.

Table 7

ELEMENTAL COMPOSITION OF FRACTIONS

Weight per cent.

Fraction	Oxygen	Nitrogen	Sulphur	Fraction	Oxygen	Nitrogen	Sulphur
Light tar	5·4	0·4	0·5	N/III	3·7	0·2	0·3
N/A	2·5	<0·1	0·4	N/IV	2·8	0·4	0·2
N/B	2·6	0·1	0·5	N/V	2·2	0·2	0·2
N/C	2·6	0·2	0·4	N/VI	2·9	0·3	0·3
N/D	2·9	0·2	0·3	N/VII	2·8	0·5	0·2
N/I	2·7	0·3	0·5	N/VIII	2·6	0·3	0·5
N/II	2·5	0·7	0·4	E*	5·7	0·8	0·6

* The residue E contains 84·9 per cent. carbon and 8·5 per cent. hydrogen.

(*d*) *The Distribution of Oxygen, Nitrogen, and Sulphur*

Elemental analyses were made on the whole tar and a number of the fractions with the results shown in Table 7. From these data and those given in Figure 1, it was concluded that about 65 per cent. of the oxygen is present as phenols and 35 per cent. is present as oxygen compounds in the neutral oil.

The distribution of nitrogen is approximately 65 per cent. in the bases and 35 per cent. in non-basic nitrogen compounds present in the neutral oil. Most of the sulphur compounds are present in the neutral oil. The percentages of these elements do not vary appreciably with the boiling point of the fractions.

III. Conclusions

The overall composition of the tar is shown in Figure 4, where the amounts of the main types of compounds present in the broad fractions A, B, C, D, and E are shown as percentages by weight of the whole light tar.

The tar contains compounds boiling from 30°C to over 400°C. Eighty-three per cent. of the tar boils below 380°C. This 83 per cent. of the tar is made up of approximately 15 per cent. of phenols, 1·5 per cent. of pyridine and quinoline bases, 53 per cent. aromatic hydrocarbons, 10 per cent. olefinic hydrocarbons, and 3·5 per cent. paraffinic hydrocarbons. Small amounts of non-phenolic oxygen compounds, non-basic nitrogen compounds and sulphur compounds are also present.

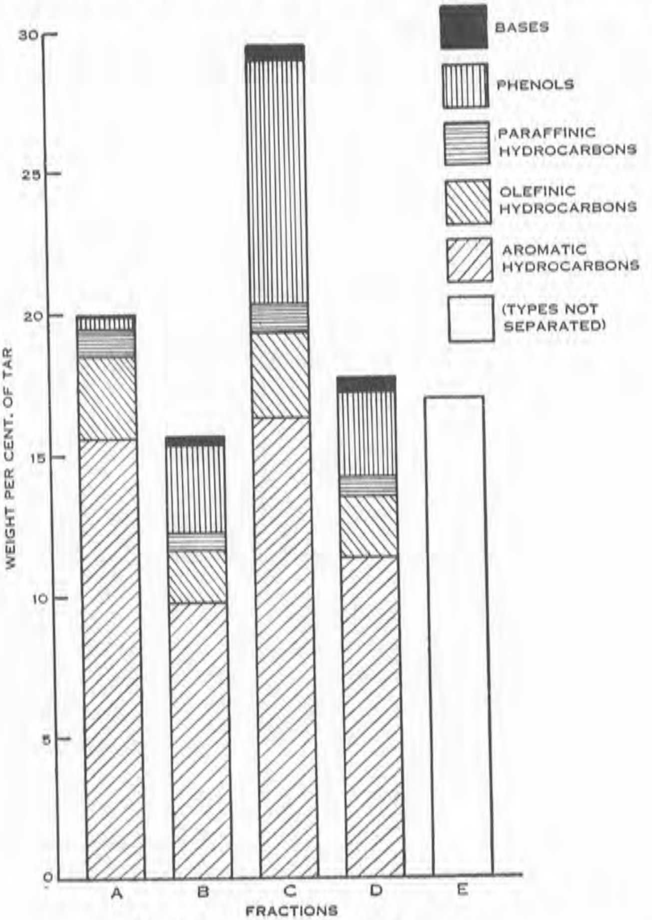

Fig. 4.—Composition of tar.

Subsequent analysis of the various tar fractions will enable more accurate and more detailed estimates to be made of the amounts of individual compounds present and will enable a comparison to be made with the composition of tars from other sources.

IV. Acknowledgments

The author is grateful to the Chairman of The Gas and Fuel Corporation of Victoria for the facilities afforded for obtaining material and information and to officers of the Corporation, particularly Mr. H. F. Hartmann, for their advice. The help of Dr. J. S. Fitzgerald and Mr. O. Rigby of the C.S.I.R.O. Chemical Research Laboratories, is also gratefully acknowledged. The author is indebted to Dr. K. W. Zimmerman of the C.S.I.R.O. and University of Melbourne Microanalytical Laboratories for the elemental analyses reported.

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Reprinted from the
AUSTRALIAN JOURNAL OF APPLIED SCIENCE
VOLUME 11, NUMBER 4, PAGES 403–433, 1960

THE COMPOSITION OF A LURGI BROWN COAL TAR

III. THE NEUTRAL OIL FRACTIONS BOILING FROM 30 TO 130°C AND 130 TO 172°C

By I. Brown

Reprinted for the
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Australia

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III. THE NEUTRAL OIL FRACTIONS BOILING FROM 30 TO 130°C AND 130 TO 172°C

By I. Brown*

[*Manuscript received July 27, 1960*]

Summary

The composition has been determined of two neutral oil fractions of a Lurgi brown coal tar from the plant of The Gas and Fuel Corporation of Victoria at Morwell.

The two neutral oil fractions were separated from the tar as described in Part I of this series (Brown 1959). Fraction N/I which had a boiling range from 30 to 130°C amounted to 13·03 wt % of the tar and fraction N/II with a boiling range from 130 to 172°C was 12·69 wt % of the tar.

These fractions were first separated as liquids by displacement chromatography on silica gel into paraffins, olefins, aromatics, and non-hydrocarbons. Some of these type fractions were further separated into subfractions by distillation. Gas chromatography was used to identify and determine the relative amounts of the components present in the type fractions and distillate fractions. Relative retention data were determined for a large number of compounds and specific retention volumes are given for the reference compounds.

Neutral oil fraction N/I was found to contain aromatics (78 wt %), olefins (10%), paraffins (5%), and non-hydrocarbons (7%); neutral oil fraction N/II contained aromatics (67%), olefins (15%), paraffins (7%), and non-hydrocarbons (11%). The aromatics were mostly benzenes with short side chains, the olefins chiefly straight-chain α-olefins, and the paraffins were mainly n-alkanes. The non-hydrocarbons were mainly methyl-n-alkyl ketones and furans with some thiophenes.

In the two neutral oils 144 compounds were shown to be present and more than half of these have been identified. Thirty-three major compounds account for 91% of N/I and 83% of N/II.

I. Introduction

The properties of the tar and the preliminary separation into phenols, bases, and neutral oils were described in Part I of this series by Brown (1959). The composition of the lower-boiling phenols has been described in Part II by Fitzgerald (1959).

The investigation of the composition of the neutral oil fractions is being made to determine if the amounts and identities of the compounds present differ from those found in black coal tars, and to determine the potential economic value of the tar.

The separation of multicomponent mixtures containing a number of homologous series of different types can only be achieved by the combination of separation methods used in the optimum sequence to divide the mixture into fractions containing a limited number of components which can then be identified and determined by additional physical or chemical methods. As examples of separation methods,

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Rossini, Mair, and Streiff (1953) have used in various combinations, fractional distillation, azeotropic distillation, and adsorption (displacement chromatography) on silica gel to separate various types of hydrocarbons. The separation of sulphur compounds from petroleum has been achieved by Thompson *et al.* (1955) using a combination of distillation, alumina percolation, and liquid thermal diffusion.

Gas chromatography has become one of the most potent tools for both the separation and identification of individual components in complex mixtures of volatile substances. For the identification of components in separated fractions it has been used, for example, in combination with infra-red analysis by Chang and Karr (1959), and with mass spectrometry by Witham (1957).

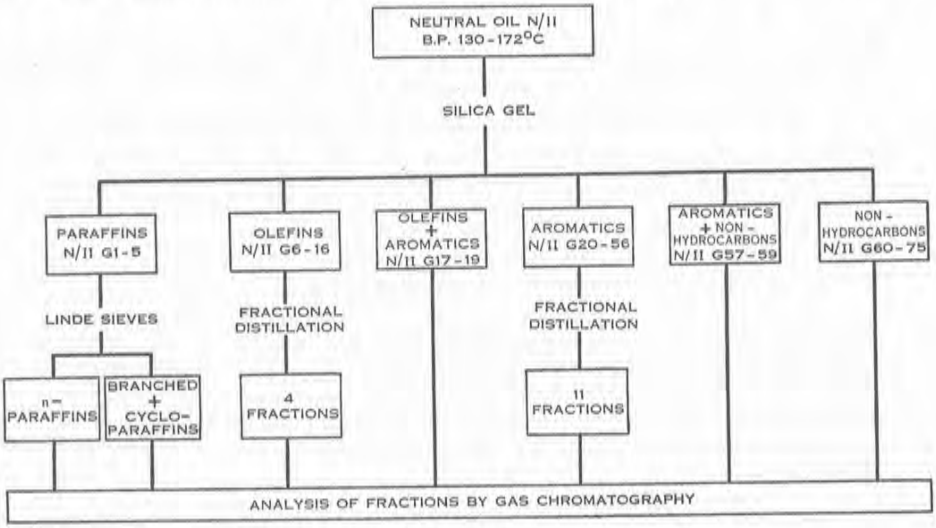

Fig. 1.—Outline of separation methods used.

Modern examples of the application of various separation methods to the analysis of coal tars are: The investigation of a South African coal tar by Terres and Hahn (1959), the analysis of the aromatic hydrocarbons in a low temperature tar by Chang and Karr (1959), and studies of a Texas lignite tar by Kahler *et al.* (1960).

In this investigation the constituents present in two neutral oil fractions have been determined. The neutral oil boiling from 30 to 130°C, which amounted to 13·03 wt % of the tar, is designated N/I and the fraction boiling from 130 to 172°C which was 12·69 wt % of the tar is designated N/II. Each of these fractions was treated separately by substantially the same methods. An outline of the methods used is given in Figure 1 using fraction N/II as an example.

The use of fractional distillation for the separation of the whole neutral oil fraction would not have been very successful owing to the formation of a large number of azeotropes between the many compounds of different type present. An aliquot of the neutral oil was therefore first separated by displacement chromatography on a silica gel column into a large number of small fractions. The individual fractions were then combined into paraffin, olefin, and aromatic groups which were then separately fractionally distilled into from 3 to 10 fractions to reduce the number of components in the subfractions and thus facilitate subsequent analysis by gas chromatography. The individual non-hydrocarbon fractions from the silica gel separation were not combined.

The distillate subfractions and a number of the individual silica gel fractions were then analysed by gas chromatography on three different stationary phases at 100°C. Some of the lower boiling fractions of N/I were also gas chromatographed on two of the phases at 75°C. A large number of known compounds were chromatographed on the three stationary phases to permit the identification of the components present in the subfractions. The identity of a component of the tar was determined from its relative retention times on the three stationary phases and the amounts present were determined from the areas under the peaks in the gas chromatograms.

Details of the apparatus and methods used are described in the following sections, together with the amounts and probable identity of the components found in the neutral oils.

II. SEPARATION APPARATUS AND METHODS

(a) *Silica Gel Type Separations*

The large-scale (350 to 400 g) separation of the neutral oils into the main types was carried out by displacement chromatography on silica gel using 95 per cent. ethanol as displacing liquid. This is a large-scale application of the method of Criddle and Le Torneau (1951). The apparatus used consisted of four, 6 ft lengths of industrial glass pipe mounted vertically and connected in tandem with $\frac{1}{16}$ in. I.D. Monel capillaries. The nominal diameters of the pipes were 2, $1\frac{1}{2}$, 1, and $\frac{5}{8}$ in. giving cross-sectional areas in the approximate ratios of 8 : 4 : 2 : 1. These columns were packed with Davison grade 923 silica gel which had been activated by heating for 5 hr at 300°C. This gel was chosen to minimize the polymerization of olefins. The percentage values of the size distribution of the gel were: +100 mesh 9·5, 100–200 mesh 3·5, 200–300 mesh 67, −300 mesh 20. The dry gel (4400 g) was poured as rapidly as possible into the columns through an earthed metal funnel while the columns were vibrated by an electric motor with an eccentric weight fitted to the column support. The gel was enclosed at each end of the columns on two layers of cotton filter cloth supported on Monel gauze.

The assembled column unit was flushed with oxygen-free nitrogen and the sample of the neutral oil containing 0·01 vol. % of fluorescent indicator (Patent Chemicals Inc. F.I.A. Dye) was pumped slowly into the bottom of the 2 in. column using a Bosch diesel pump driven by an electric motor through a variable speed drive. The sample was followed by 95 per cent. ethanol pumped in with the same pump. The rate of flow of sample and ethanol was regulated to give a linear rate of the hydrocarbon front of 6 in/hr and the flowrate was adjusted to maintain this rate as the front passed into each successive column. The flow was run upwards in all columns to permit uniform displacement of the nitrogen from the gel and to prevent backmixing due to differences in density of the separated types of hydrocarbon.

The product emerging from the top of the $\frac{5}{8}$ in. diameter column passed to an automatic fraction collector where fractions of 5 g each were collected in test tubes which were then automatically covered by glass balls to prevent evaporation.

The progress of the separation, which took about 75 hr to complete, was followed by observing the fluorescent indicator bands in ultraviolet light. The yellow fluorescent band between the paraffins and olefins and the brown band between the aromatics and the ethanol were well defined, but the blue fluorescent olefin-aromatic zone gradually disappeared during the run. The use of the glass columns and the fluorescent indicator enabled the shape of the front between the paraffins and olefins to be watched and it was found that this became less sharp as this zone reached the top of each column, but became sharp again as the zone entered the bottom of the next smaller column. This front sharpening is due to the reduction in diameter and to the small hold-up at the ends of the columns.

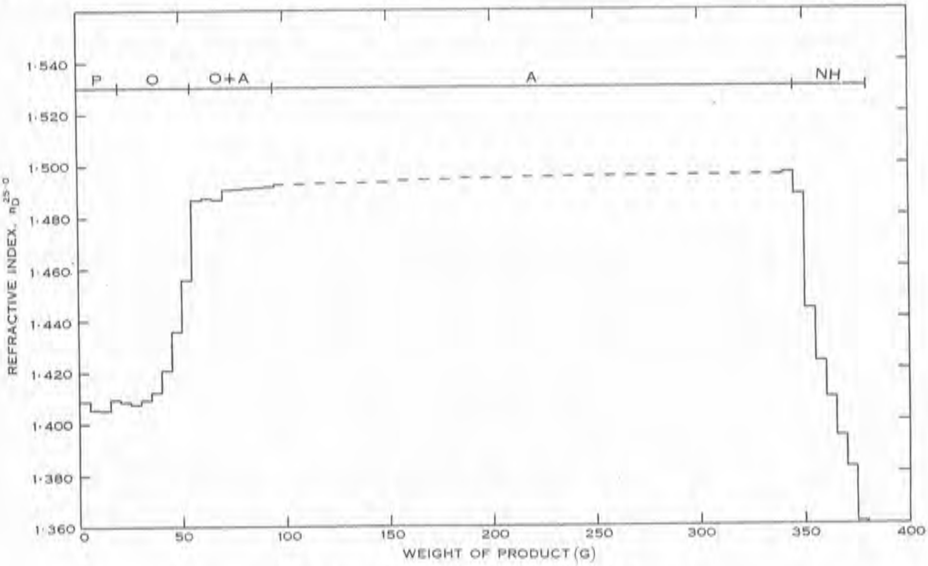

Fig. 2.—Silica gel separation of N/I.
P, Paraffins; O, olefins; A, aromatics; NH, non-hydrocarbons.

The refractive index of the 75 fractions was measured to estimate the separation of the various hydrocarbon types. The results of the silica gel separations for oils N/I and N/II are shown in Figures 2 and 3 respectively. A more accurate determination of the distribution of hydrocarbon types was made by doing small-scale (0·5 ml) silica gel separations on selected fractions by the fluorescent indicator method described by Criddle and Le Torneau (1951), and by analysis of selected fractions by gas chromatography. The fractions were combined into six groups, the four largest of which contained predominantly one type. Details of these for oil N/II are shown in Table 1. The last 10 of the non-hydrocarbon silica gel fractions were washed with water to remove ethanol.

The separation between some types was quite sharp. For example, in the separation of N/II the fraction collector was manually operated between the paraffin and olefin fractions at the first sign of yellow fluorescent indicator; the olefin content of silica gel fraction No. 5 was only 7·3 per cent. and the paraffin content of fraction 6 was only 2·2 per cent. Fraction No. 60, which had the highest refractive index, contained 74 per cent. of coumarone.

The order of displacement from the silica gel column can be seen from Table 1 to be paraffins, olefins, benzenes, thiophenes, indenes, styrenes, furans, and ketones. The indenes and styrenes were less sharply separated from the mixture than the other types.

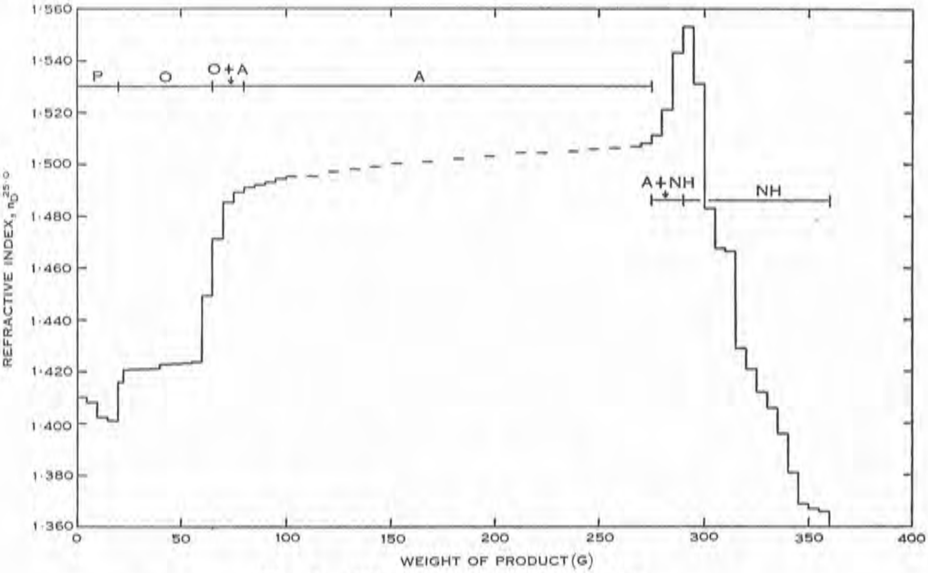

Fig. 3.—Silica gel separation of N/II.

P, Paraffins; O, olefins; A, aromatics; NH, non-hydrocarbons.

(*b*) *Fractional Distillation of Grouped Silica Gel Fractions*

The main olefin and aromatic groups of the silica gel fractions from N/I and N/II were fractionally distilled to give from 3 to 10 fractions and a residue.

These distillations were made in a small, vacuum-jacketed spinning-band column 100 cm long and 8 mm in diameter. Charges of from 10 to 50 ml were used at a reflux ratio of approximately 30 : 1, with the pressure regulated at 760·0 mmHg: The aromatic fraction group of N/I was distilled in a 100 cm long, 13 mm diameter column packed with $\frac{1}{16}$ in. Dixon rings at 760·0 mmHg and a reflux ratio of about 40 : 1 with a charge of 200 g.

No attempt was made to isolate fractions containing single components although some distillate fractions contained a high percentage of major components such as toluene, n-octane, and 1-octene. The chief value of the distillations was to give fractions containing a limited number of components to help in their subsequent identification by gas chromatography.

TABLE 1

COMPOSITION OF GROUPED SILICA GEL FRACTIONS OF N/II

N/II Silica Gel Fractions in Group	Weight (g)	Composition of Fraction Group (wt %)	
G1–5	23·1	n-Paraffins	77·2
		Branched paraffins	20·8
		Cycloparaffins	1·7
		Olefins	0·3
G6–16	43·8	1-n-Olefins	73·2
		Branched olefins	26·8
G17–19	14·9	Aromatics	87·5
		Olefins	12·5
G20–56	191·2	Aromatics	87·1
		Indenes	6·7
		Styrenes	3·3
		Olefins	2·0
		Thiophenes	0·9
G57–59	15·8	Aromatics	72·9
		Indenes	14·3
		Styrenes	9·2
		Coumarone	2·9
		Thiophenes	0·7
G60–75	36·1	Coumarone	48·9
		Ketones	42·6
		Aromatics	4·2
		Styrenes	2·8
		Indenes	1·5
Total G1–75	324·9	Aromatics	59·2
		Olefins	15·3
		Paraffins	7·1
		Furans	5·6
		Indenes	4·8
		Ketones	4·7
		Styrenes	2·7
		Thiophenes	0·6

III. GAS CHROMATOGRAPHIC ANALYSIS OF FRACTIONS

Gas chromatography on three different stationary phases was used for the identification of the components present in the various silica gel and distillate fractions and for the determination of the amounts present.

(a) *Apparatus*

The gas chromatograph was designed and built in the Chemical Research Laboratories and had the following major features; A pressure-regulated nitrogen supply, an air-thermostatted column unit, and a gas density meter detector.

(b) *Mobile Phase*

Dry, oxygen-free nitrogen was supplied to the columns through a reducing valve and a Negretti and Zambra precision pressure regulator. A pressure gauge (0–1550 mmHg) was used to measure the column inlet pressure. Column outlet pressure was atmospheric. Flowrates were measured by a soap-film meter.

(c) *Column Unit*

The column unit consisted of three working columns (with different stationary phases) and one dummy column, each of 4 m of 4·44 mm I.D. copper tubing coiled after packing on a mean diameter of 20 cm. For some of the earlier work on neutral oil N/I, columns of 2·5 m were used. The columns were mounted in a well-stirred, electrically heated, air thermostat with the air temperature controlled to ±0·2°C by a Transitrol controller switching 20 per cent. of the heater and operating from a nichrome-constantan thermocouple with an ice-cold junction. The temperature was measured with a mercury-in-glass thermometer. The inlet ends of the three columns were connected by unions to a rotary three-way valve similar to that described by Atkinson and Tuey (1958). This enabled any one of the three columns to be selected for use. The outlets of the columns were connected to a low hold-up manifold. Separate inlet and outlet were provided for the dummy column.

(d) *Sample Introduction*

The method of sample introduction was similar to that of Tenney and Harris (1957). Samples of from 0·5 to 8 μl were delivered by stainless steel capillary probes, introduced through an O ring seal and a Teflon stainless steel rotary valve to a seat at the inlet of a heated vaporizer where the sample was blown out of the probe by preheated nitrogen. The vaporizer temperature was kept about 20–30°C higher than the column temperature.

(e) *The Detector*

This was a gas density meter similar to that described by Murray (1959). It was separate from the column unit and was mounted in a Dewar vessel and kept at a higher tempetature (170°C) than the column unit by means of an electric heater operated from a stabilized voltage supply. The working column and dummy column were connected to the detector by fine stainless steel capillaries heated to the detector temperature by applying a low voltage to them.

The chromatograms were recorded on a Brown recorder (100 μV full-scale, pen speed 4 sec, chart speed 20 in/hr) fitted with an attenuator giving spans of 1, 2, 4, 8, 16, and 32 times the nominal value.

(*f*) *Stationary Phases*

Three stationary phases were used: Apiezon L (APL), benzyldiphenyl (BD), and the di-n-octyl ester of 4,4′-dinitrodiphenic acid (DIN), which was made by esterification of the acid prepared from 2,7-dinitrophenanthraquinone by the method of Underwood and Kochmann (1924).

The stationary phase compounds were supported on sieved and water-washed "Celite 545" of particle size 0·0043 to 0·0063 in. (bulk density 0·188 g/ml) in the proportion of 15 g of phase to 100 g Celite. The columns were packed before bending. The loaded Celite was introduced a little at a time with the column vibrated transversely and then bumped up and down on the floor after each addition to consolidate the packing. Each 4 m column contained approx. 2 g of stationary phase. A 4 m column of APL was used for the dummy column.

(*g*) *Column Efficiency*

A 4 m column of 15 per cent. APL was tested with a mixture containing n-decane and the number of theoretical plates was determined at 100 and 150°C at various flowrates. The amount of n-decane in the sample was 0·15 μl. When the number of theoretical plates was plotted against the flowrate it could be seen that the maximum efficiency was approximately 7400 theoretical plates (H.E.T.P. = 0·54 mm). For a column temperature of 100°C this occurred at a flowrate from 55–60 ml/min (at column temp.) and at 150°C at a flowrate slightly above 90 ml/min. Most of the chromatograms carried out in this work were run at 100°C on 4 m columns with the inlet pressure 1550 mmHg above the outlet pressure which was atmospheric. Under these conditions the number of theoretical plates for a 0·5 μl sample of n-decane was approximately 5500 on APL. On the phases BD and DIN where the retention time for n-decane was less, the efficiency was approx. 3900 and 3500 respectively.

(*h*) *Calibration of Stationary Phases*

A number of hydrocarbons of different types and various non-hydrocarbons were run singly or in mixtures on each of the stationary phases using 0·5 μl samples at a recorder sensitivity of 100 to 400 μV full scale. The results are shown in Appendix I, Tables 7 to 15, as relative retention times (RRT) measured from the air (oxygen) peak on the chromatograms. The values shown are averages of at least three measurements. The RRT values at 75°C are calculated relative to benzene as a reference substance, the values at 100°C relative to toluene and the values at 150°C relative to *p*-xylene.

The RRT data on each stationary phase were correlated by plotting log RRT against the normal boiling point. This gave a slightly curved line or a series of parallel straight lines for each homologous series of compounds. Graphs were also drawn of log RRT on BD (and on DIN) against log RRT on APL. These graphs gave straight lines for each series of compounds. Some of the types of compounds calibrated were not found in the neutral oils but their calibration was necessary to confirm their absence.

A number of hydrocarbons suspected of being present in the tar were not available for calibration, RRT values for some of these could be estimated from the correlation graphs. Additional RRT values at 100°C for unavailable aromatic hydrocarbons were estimated in the following way: Chang and Karr (1959) give RRT values for a number of aromatic hydrocarbons on APL at 150 and 200°C, those at the former temperature were in agreement with the present measured values to within 1 to 2 per cent. for compounds which were available.

A plot of log RRT against $10^4/T$ showed that the data of Chang and Karr at 200 and 150°C and the values at 100°C shown in Table 10 (all expressed relative to the same reference compound) gave a linear plot for all compounds boiling above n-propylbenzene. This plot was then used to estimate RRT values at 100°C for compounds listed by Chang and Karr but not available to us. These data are shown in ( ) in Table 10.

A second method was used for estimating values for other compounds which were not available. Following the practice of Chang and Karr, plots were prepared for each stationary phase of log RRT at 100°C against the normal boiling point of the compounds. This gave a series of parallel straight lines, one for each C_8, C_9, etc. group of aromatics. From these graphs RRT values were estimated for the unavailable compounds and these are shown in [ ] in Table 10.

Some useful relations were found between log RRT values at 100°C and the boiling points of the compounds. The data on paraffins were found to fall into three groups. (i) The normal paraffins and unsymmetrical methyl branched paraffins, (ii) the symmetrical methyl branched paraffins and the di- and trimethyl branched paraffins with branching on adjacent carbon atoms, and (iii) those branched paraffins having one or two CH_2 groups between the methyl branches. On stationary phase DIN the three types show separate calibration curves but on phase BD and APL less difference was shown between the curves for groups (i) and (ii).

A reasonable correlation of the type found by Chang and Karr on grouping aromatics with the same number of carbons was found on all three phases for olefins, but this could not be followed above a boiling point of 130°C owing to lack of calibrating compounds. Some correlation of this type was also found with the paraffins on phases BD and APL up to a boiling point of 150°C. With the aromatic compounds it was also found that the *ortho*-compounds had the highest RRT value on BD, while the *para*-compounds had the highest RRT value on APL.

(*i*) *Specific Retention Volumes*

To enable full use to be made of the data the specific retention volumes, Vg, of the reference compounds and the densities of the stationary phase liquids were determined. The specific retention volumes were calculated using the expression

$$Vg = (273F_m jt)/(wT_m),$$

where F_m = dry nitrogen (ml/min) at atmospheric pressure and at T_m,
$j = 3(a^2-1)/2(a^3-1)$,
a = the ratio of inlet to outlet pressure, P_i/P_o,
t = time (min) from air (oxygen) peak to the maximum of the reference compound peak,
w = stationary phase liquid (g) on the column,
T_m = temperature of N_2 in soap-film meter, 294–296 °K.

The values of Vg for the reference substances are shown in Table 2 and the densities of the stationary phase liquids are given in Table 3.

TABLE 2

SPECIFIC RETENTION DATA FOR REFERENCE SUBSTANCES

Column Temperature (°C)	Reference Substance	Stationary Phase	Vg (ml/g)
75	Benzene	BD	110
75	Benzene	APL	86
100	Toluene	BD	101
100	Toluene	APL	77
100	Toluene	DIN	104
150	*p*-Xylene	APL	42

TABLE 3

DENSITIES OF STATIONARY PHASE LIQUIDS

Grams/millilitre

Stationary Phase	Temperature (°C)		
	75	100	150
BD	1·03	1·02	0·99
APL	0·84	0·83	0·81
DIN	1·06	1·05	1·01

(*j*) *Identification of Components in Neutral Oils*

Samples of from 0·5 to 4 μl of the individual and grouped fractions obtained from the neutral oils by silica gel separation and individual distillation fractions were gas chromatographed on the three stationary phases BD, APL, and DIN at 100°C at a recorder sensitivity of 100 to 400 μV full scale. The RRT values of the maxima of component peaks were then calculated relative to toluene. (For some volatile fractions runs were made at 75°C on BD and APL and the RRT values calculated relative to benzene.)

The identities of the peaks were determined from the RRT values on the three phases with the help of the calibration graphs described above and boiling point data from various sources. There was a small variation in the RRT values for the maxima of a given component peak determined from samples of different composition due to the wide variation in the percentage of the given component in the mixtures and also, in a few chromatograms, due to interference from another compound having an almost equal RRT value.

With most fractions it was possible to determine which peak of the chromatogram on one phase corresponded to a given peak on that run on another phase by the size and position of the peaks. However, when a fraction contained a number of compounds of two or more types, the order of the peaks sometimes changed on going from one stationary phase to another. When this occurred the matching of peaks was done by comparing the chromatograms of a number of adjacent silica gel or distillate fractions of gradually varying composition each run on the two or three stationary phases. The growth and disappearance of chosen peaks was found to occur between different fractions depending on the type or boiling point of the compound being followed. The calibration graphs were also used to predict the position of the peak of a given compound on one chromatogram from its position on the corresponding chromatogram run on another phase. The addition of authentic compounds to the mixture being analysed was also used to confirm the identity of components.

TABLE 4

RRT VALUES OF PEAK MAXIMA FOR INTERFERING COMPOUNDS

Compound	RRT 100°C (toluene = 1·00)		
	BD	APL	DIN
2-Heptanone	2·60	1·60	2·65
1,2-Dimethylbenzene	2·65	2·61	2·60
Styrene	2·95	2·61	2·91
Isopropylbenzene	2·95	2·86	2·91
1,3,5-Trimethylbenzene	4·46	4·66	4·29
1-Methyl-2-ethylbenzene	4·74	4·66	4·29
1-Methyl-3-isopropylbenzene	5·37	5·55	4·75
1,2,4-Trimethylbenzene	5·37	5·55	5·17

The use of three stationary phases was very helpful in identifying the compounds present in the fractions. This is well illustrated in Table 4, which gives the RRT values found for peak maxima of interfering compounds in the chromatograms of N/II silica gel fractions Nos. 57 to 60.

The presence of n-paraffins in the early silica gel fractions was confirmed by the use of a composite gas chromatographic column being a 20 cm column of 5A Linde sieves and a 2·5 m BD column. This removed the n-paraffins but left only small peaks for the branched and cycloparaffins as these were present in small amounts. The combined column also gave slightly different RRT values from those found using BD alone. To obtain more reliable RRT values for the branched and cycloparaffins, samples of the liquid fractions were eluted at room temperature from a 20 cm column of 40–60 mesh 5A Linde sieves with isopentane, the bulk of the latter evaporated and 2 μl samples of the product gas chromatographed on the three stationary phases.

The presence of methyl ethyl ketone in N/I was confirmed by the preparation of a 2,4-dinitrophenylhydrazone. The identity of coumarone in fraction N/II G60 was confirmed by infra-red spectrophotometry.

Infra-red spectrophotometry was also used to determine the relative amounts of 1,3- and 1,4-dimethylbenzene and 1,3- and 1,4-methylethylbenzene as these pairs were not adequately resolved by gas chromatography. This was done on a sample of N/II G20–56 which was brominated at room temperature to remove traces of olefins and styrene, and the distilled product after removal of bromine compounds by silica gel was separated on a large-scale gas chromatograph to isolate the peaks containing the above pairs of compounds. The infra-red absorbance data of Frankel and Johnson (1958) and of Ehlers (1958) were used.

A comparison of the chromatograms of the aromatic fraction N/II G20–56 before and after bromination confirmed the identity of indene, styrenes, and thiophenes in this fraction, as the peaks corresponding to these compounds, which are readily brominated, were absent from the chromatograms of the brominated sample.

(*k*) *Quantitative Analysis*

The quantities of the components present in individual fractions and groups of fractions were determined by internal normalization from the areas under the peaks of gas chromatograms run on one or more stationary phases. The areas of peaks were determined by drawing tangents to the inflection points and measuring the product of apex height and the width of their intersection on the base line. For large peaks which showed tailing, additional small triangles were drawn to measure the areas of that part of the peaks.

With a density meter as detector it was necessary to correct the measured areas by multiplying by the factor $M/(M-28)$, where M is the molecular weight of the compound and 28 that for nitrogen. This gave the composition in wt % of the components.

IV. RESULTS

The distribution of the various types of compound in the neutral oils N/I and N/II is shown in Table 5. Over 80 per cent. of both these oils is made up of only 33 main components which are shown in Table 6.

The identity and quantities of the individual components present in neutral oil N/I are shown in Appendix II, Tables 16 to 18, and those present in neutral oil N/II in Appendix II, Tables 19 to 22. The composition of the neutral oil is expressed in wt % on a no-loss basis.

The identity of the components for which authentic samples were available for calibration is reasonably certain. For the compounds of higher molecular weight where a limited number of homologues were available for calibration and where

Table 5

THE DISTRIBUTION OF COMPOUNDS BY TYPES IN N/I AND N/II

Type of Compound	Wt % in N/I	Wt % in N/II	Type of Compound	Wt % in N/I	Wt % in N/II
n-Paraffins	3·5	5·5	Benzenes	78·0	59·0
Branched paraffins	1·2	1·5	Indenes	—	5·0
Cycloparaffins	0·4	0·12	Styrenes	—	3·0
Total paraffins	5·1	7·1	Total aromatics	78·0	67·0
1-n-Olefins	6·0	10·7	Ketones	5·8	4·7
Branched olefins	4·2	4·6	Furans	0·92	5·6
Cyclo-olefins	0·03	—	Thiophenes	0·47	0·6
Total olefins	10·2	15·3	Total non-hydrocarbons	7·2	10·9

Table 6

MAJOR COMPONENTS OF N/I AND N/II

Compound	Wt % in N/I	Wt % in N/II	Compound	Wt % in N/I	Wt % in N/II
n-Hexane	0·2	—	*m*-Methylethylbenzene	—	5·0
n-Heptane	0·9	—	*p*-Methylethylbenzene	—	2·9
n-Octane	2·0	0·1	*o*-Methylethylbenzene	—	2·8
n-Nonane	0·5	2·1	1,3,5-Trimethylbenzene	—	1·8
n-Decane	—	2·8	1,2,4-Trimethylbenzene	—	5·9
n-Undecane	—	0·5	1,2,3-Trimethylbenzene	—	3·2
1-Hexene	0·9	—	Indan	—	2·3
1-Heptene	1·8	—	Indene	—	2·7
1-Octene	2·6	0·1	Styrene	—	1·7
1-Nonene	0·7	3·8	Methyl ethyl ketone	1·1	—
1-Decene	—	5·9	Methyl n-propyl ketone	1·7	—
1-Undecene	—	0·9	Methyl n-butyl ketone	0·7	0·1
Benzene	24·0	—	Methyl n-amyl ketone	—	0·8
Toluene	44·0	0·2	Methyl n-hexyl ketone	—	0·6
Ethylbenzene	2·9	5·2	Coumarone	—	5·6
m-Xylene	4·3	13·0			
p-Xylene	1·5	4·7	Total	91·0	83·0
o-Xylene	1·2	8·1			

the number of possible isomers is large, it was only possible to determine the type of compound and its approximate boiling point from the calibration graphs. However, all the main components, which are those likely to be of commercial value, have been identified with certainty.

The quantitative data given for each compound in the tables is estimated to be accurate to approximately ±5 per cent. of the amount shown for major components and approximately ±10 to ±20 per cent. for minor components.

The sum of the amounts of a compound (expressed as p.p.m. by wt in the tar) found in N/I and N/II will represent the total amount present in the tar for compounds boiling below about 180°C; appreciable amounts of the higher boiling compounds will be found in the neutral oil fraction N/III.

V. DISCUSSION

The two neutral oils N/I and N/II contain between them 144 compounds; about two-thirds of these are present in amounts greater than 0·1 per cent. of the weight of the neutral oil fraction N/I or N/II.

The major hydrocarbon constituents are benzenes with short alkyl side chains, with smaller amounts of olefins and paraffins and some indan, indene, and styrene. The oxygen compounds present are ketones and furans of which methyl n-alkyl ketones and coumarone predominate. Small amounts of thiophenes were also present but no non-basic nitrogen compounds were found. The sulphur and non-basic nitrogen compounds in the tar will be determined more accurately using different separation methods.

The ratio of *m*- to *p*-xylene was found to be 2·80 : 1. The ratios of ethylbenzene to *o*-, *m*-, and *p*-xylenes found were compared with values calculated for a variety of tars from data given by the Coal Tar Research Association (1955). The ratios were very similar to those for a Lurgi tar and a low temperature tar, but were higher for ethylbenzene and lower for *m*- and *p*-xylene than those for coke-oven, vertical retort, and horizontal retort tars.

When the investigation of the composition of the higher boiling neutral oils is complete it will be possible to make a more detailed comparison with other tars.

VI. ACKNOWLEDGMENTS

The author is grateful to Officers of The Gas and Fuel Corporation of Victoria; to Mr. H. F. Hartmann and Mr. G. Brown for valuable discussions and to Messrs. N. Kotzmann, B. Smith, J. Satsmadjis, and L. M. Wisse for their help with some of the silica gel separations and gas chromatography.

The author is also grateful to Officers of these Laboratories; to Dr. J. S. Fitzgerald for useful discussions, to Mr. K. E. Murray for help in the design of the gas chromatographic apparatus, to Mr. A. C. K. Triffet and Dr. N. S. Ham for infra-red measurements and data, and to Messrs. W. Fock, F. Smith, and O. H. Rigby for help with some of the silica gel runs and gas chromatography.

The author is also indebted to Dr. G. A. Vaughan of the Coal Tar Research Association, to Dr. J. S. Ball and Dr. H. T. Rall of the U.S. Bureau of Mines, Professor J. S. Smith, University of Oxford, the late Dr. S. F. Birch, British Petroleum Co. Ltd., Professor W. Davies of the University of Melbourne, and to Dr. D. L. Ford, Timbrol Ltd., Sydney, for gifts of samples of pure compounds and details of their physical properties.

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APPENDIX I

RELATIVE RETENTION DATA: TABLES 7 TO 15

TABLE 7

RELATIVE RETENTION TIMES AT 75°C

Compound	Boiling Point (°C/760)	RRT 75°C (benzene = 1·00)	
		BD	APL
2-Methylbutane	27·9	0·076	0·167
n-Pentane	36·1	0·095	0·216
2,2-Dimethylbutane	49·7	0·120	0·303
2,3-Dimethylbutane	58·0	0·164	0·398
2-Methylpentane	60·3	0·171	0·381
3-Methylpentane	63·3	0·189	0·450
n-Hexane	68·7	0·223	0·505
2,4-Dimethylpentane	80·5	0·266	0·659
2,2,3-Trimethylbutane	80·9	0·295	0·734
2,3-Dimethylpentane	89·8	0·408	0·982
n-Heptane	98·4	0·522	1·19
3-Methylheptane	118·9	0·937	2·29
Cyclopentane	49·3	0·232	0·482
Methylcyclopentane	71·8	0·362	0·718
Cyclohexane	80·7	0·520	1·04
Methylcyclohexane	100·9	—	1·76
2-Methyl-1-butene	31·2	0·114	0·223
cis-2-Pentene	36·9	0·133	0·230
2-Methyl-2-butene	38·6	0·148	0·284
4-Methyl-1-pentene	53·9	0·178	0·374
cis-4-Methyl-2-pentene	56·3	0·193	0·349
trans-4-Methyl-2-pentene	58·6	0·202	0·372
1-Hexene	63·5	0·248	0·488
2,3-Dimethyl-2-butene	73·2	0·376	0·687
1-Heptene	93·6	0·578	1·06
2,4,4-Trimethyl-2-pentene	104·9	0·732	1·41
Furan	32·0	0·208	0·190
2-Methylfuran	62·5	0·519	0·476
Tetrahydrofuran	66·0	0·782	0·619
2,5-Dimethylfuran	94·0	1·21	1·16
Diethyl ether	34·5	0·151	0·183
2-Propanone	56·1	0·300	0·145
2-Butanone	79·6	0·705	0·368
Ethanol	78·3	0·189	0·110
Methyl acetate	57·2	0·330	0·194
Acetonitrile	81·6	0·475	0·124
Propionitrile	97·2	0·952	0·274
Pyrrole	130·1	4·35	1·36
Thiophene	84·2	1·33	1·10

Table 8

RELATIVE RETENTION TIMES 100°C

Compound	Boiling Point (°C/760)	RRT 100°C (toluene = 1·00)		
		BD	APL	DIN
n-Pentane	36·1	0·054	0·118	—
2,2-Dimethylbutane	49·7	0·067	0·150	—
2,3-Dimethylbutane	58·0	0·092	0·196	0·100
2-Methylpentane	60·3	0·098	0·196	0·096
3-Methylpentane	63·3	0·106	0·220	0·111
n-Hexane	68·7	0·124	0·252	0·115
2,4-Dimethylpentane	80·5	0·136	0·297	0·145
2,2,3-Trimethylbutane	80·9	0·160	0·354	0·171
2,3-Dimethylpentane	89·8	0·201	0·432	0·215
3-Methylhexane	91·9	0·204	0·437	0·212
3-Ethylpentane	93·5	0·228	0·487	0·233
n-Heptane	98·4	0·255	0·531	0·240
2,2,4-Trimethylpentane	99·2	0·219	0·488	0·243
2,5-Dimethylhexane	109·1	0·285	0·620	0·292
2,3,4-Trimethylpentane	113·5	0·378	0·820	0·393
3-Ethylhexane	118·5	0·427	0·906	0·421
3-Methylheptane	118·9	0·421	0·888	0·411
n-Octane	125·7	0·529	1·08	0·493
2,2,5-Trimethylhexane	124·1	0·397	0·870	0·413
2,3,5-Trimethylhexane	131·3	0·372	0·882	0·423
n-Nonane	150·8	1·08	2·27	0·990
3,3-Diethylhexane	166·3	1·79	3·77	—
n-Decane	174·1	2·23	4·60	1·92
n-Undecane	195·9	4·47	9·38	3·72
n-Dodecane	216·3	9·27	19·2	7·40
Cyclopentane	49·3	0·131	0·228	0·121
Methylcyclopentane	71·8	0·191	0·352	0·174
Cyclohexane	80·7	0·270	0·482	0·240
Methylcyclohexane	100·9	0·403	0·774	0·378
trans-1,2-Dimethylcyclohexane	123·4	0·688	1·38	0·661
cis-1,2-Dimethylcyclohexane	129·7	0·903	1·72	0·834
Ethylcyclohexane	131·8	0·917	1·74	0·827

Table 9

RELATIVE RETENTION TIMES 100°C

Compound	Boiling Point (°C/760)	RRT 100°C (toluene = 1·00)		
		BD	APL	DIN
2-Methyl-1-butene	31·2	0·070	0·131	0·073
cis-2-Pentene	36·9	0·083	0·140	0·085
2-Methyl-2-butene	38·6	0·084	0·147	0·087
4-Methyl-1-pentene	53·9	0·100	0·172	0·098
cis-4-Methyl-2-pentene	56·3	0·102	0·167	0·100
trans-4-Methyl-2-pentene	58·6	0·105	0·176	0·105
2-Methyl-1-pentene	60·7	0·127	0·221	0·128
1-Hexene	63·5	0·135	0·229	0·137
2-Ethyl-1-butene	64·7	0·145	0·247	0·146
2,3-Dimethyl-2-butene	73·2	0·193	0·311	0·189
1-Heptene	93·6	0·278	0·475	0·260
2,4,4-Trimethyl-1-pentene	101·4	0·298	0·571	0·323
2,4,4-Trimethyl-2-pentene	104·9	0·302	0·572	0·322
2-Ethyl-1-hexene	120·0	0·562	0·960	0·527
1-Octene	121·3	0·582	0·980	0·528
trans-2-Octene	125·0	0·661	0·995	0·577
cis-2-Octene	125·6	0·695	1·16	0·625
2,6-Dimethyl-3-heptene	127·0	0·548	1·08	0·540
1-Nonene	146·9	1·15	2·00	1·08
1-Decene	170·6	2·48	4·20	2·05
1-Undecene	192·7	4·70	8·40	4·14
1-Dodecene	213·4	9·34	17·2	7·88
Cyclohexene	82·9	0·369	0·539	0·333
4-Methyl-1-cyclohexene	102·7	0·526	0·833	0·500

TABLE 10

RELATIVE RETENTION TIMES 100°C

Compound	Boiling Point (°C/760)	RRT 100°C (toluene = 1·00)		
		BD	APL	DIN
Benzene	80·1	0·467	0·456	0·461
Methylbenzene	110·6	1·00	1·00	1·00
Ethylbenzene	136·2	1·95	1·92	1·79
1,4-Dimethylbenzene	138·4	2·07	2·15	2·07
1,3-Dimethylbenzene	139·1	2·14	2·18	2·12
1,2-Dimethylbenzene	144·4	2·63	2·60	2·60
Isopropylbenzene	152·4	2·93	2·89	2·90
n-Propylbenzene	159·2	3·51	3·61	3·19
1-Methyl-3-ethylbenzene	161·3	[3·93]*	(3·90)*	[3·54]
1-Methyl-4-ethylbenzene	162·0	3·92	4·07	3·65
1,3,5-Trimethylbenzene	164·7	4·47	4·66	4·22
1-Methyl-2-ethylbenzene	165·2	4·76	4·58	4·37
1,2,4-Trimethylbenzene	169·4	5·34	5·58	5·14
1,2,3-Trimethylbenzene	176·1	6·97	6·95	6·57
t-Butylbenzene	169·1	4·50	4·55	4·05
Isobutylbenzene	172·8	[4·97]	(5·18)	[4·30]
s-Butylbenzene	173·3	5·03	5·25	4·35
1-Methyl-3-isopropylbenzene	175·1	[5·46]	(5·72)	[4·80]
1-Methyl-4-isopropylbenzene	177·1	5·65	6·08	5·17
1-Methyl-2-isopropylbenzene	178·2	[6·67]	(6·61)	[5·45]
1,3-Diethylbenzene	181·1	6·83	6·76	5·78
1-Methyl-3-n-propylbenzene	181·8	[7·00]	(7·26)	[6·35]
n-Butylbenzene	183·3	7·29	7·45	6·36
1-Methyl-4-n-propylbenzene	183·3	[7·40]	(7·22)	[6·80]
1,2-Diethylbenzene	183·4	[7·45]	(7·66)	[6·85]
1,4-Diethylbenzene	183·7	7·32	7·45	6·22
1,3-Dimethyl-5-ethylbenzene	183·8	[7·50]	(7·73)	[6·95]
1-Methyl-2-n-propylbenzene	184·8	7·96	7·93	7·33
1,4-Dimethyl-2-ethylbenzene	186·9	[8·50]	(9·06)	[7·90]
1,3-Dimethyl-4-ethylbenzene	188·4	[8·95]	[9·10]	[8·45]
1,2-Dimethyl-4-ethylbenzene	189·8	[9·10]	(9·38)	[9·00]
1,3-Dimethyl-2-ethylbenzene	190·0	[9·50]	[9·70]	[9·10]
1,2-Dimethyl-3-ethylbenzene	193·9	[10·8]	(11·7)	[10·7]
1,2,4,5-Tetramethylbenzene	196·8	11·9	12·4	12·2
1,2,3,5-Tetramethylbenzene	198·0	13·3	13·6	13·1
1,2,3,4-Tetramethylbenzene	205·0	[18·0]	(16·6)	[17·5]

* Values shown in brackets are estimated values, for methods see text, p. 411.

Table 11

relative retention times 100°C

Compound	Boiling Point (°C/760)	RRT 100°C (toluene = 1·00)		
		BD	APL	DIN
Styrene	145·1	2·97	2·51	2·94
α-Methylstyrene	165·5	5·23	4·55	4·89
Indan	177·8	8·32	7·32	6·85
Indene	182·4	10·4	7·60	9·77
Naphthalene	218·0	—	24·4	—
Furan	32·0	0·108	0·100	0·125
2-Methylfuran	62·5	0·201	0·397	0·244
Tetrahydrofuran	66·0	0·361	0·283	0·356
2-Methyltetrahydrofuran	80·2	0·423	0·381	0·423
2,5-Dimethylfuran	94·0	0·539	0·488	0·501
Benzofuran	171·4	7·44	5·12	8·13
Diethyl ether	34·5	0·082	0·092	0·083
Di-isopropyl ether	68·5	0·142	0·190	0·146
Di-n-propyl ether	89·8	0·297	0·378	0·275
Di-n-amyl ether	187·5	2·60	3·86	2·38
Methyl phenyl ether	154·0	4·21	2·64	4·08
Methyl-*o*-cresyl ether	171·0	7·53	5·01	6·50
Methyl-*m*-cresyl ether	177·0	8·61	5·53	8·42
Methyl-2,6-xylenyl ether	182·0	9·58	7·25	—
Methyl-2,4-xylenyl ether	192·0	14·6	10·2	13·3
n-Propionaldehyde	47·9	0·153	0·096	0·163
n-Butyraldehyde	74·8	0·296	0·201	0·322
Furfural	161·7	3·22	1·11	3·97
Benzaldehyde	179·0	7·77	3·56	8·61
Mesityl oxide	130·0	1·57	0·870	1·62
Acetyl acetone	139·0	1·63	0·818	2·02
Diacetone alcohol	164·0	2·70	1·07	3·52
Acetophenone	202·3	—	7·33	—

Table 12

RELATIVE RETENTION TIMES 100°C

Compound	Boiling Point (°C/760)	RRT 100°C (toluene = 1·00)		
		BD	APL	DIN
2-Propanone	56·1	0·152	0·076	0·178
2-Butanone	79·6	0·320	0·174	0·354
3-Methyl-2-butanone	93·4	0·470	0·285	0·515
2-Pentanone	102·3	0·602	0·350	0·650
3-Pentanone	102·7	0·636	0·382	0·651
3,3-Dimethyl-2-butanone	106·4	0·613	0·437	0·702
4-Methyl-2-pentanone	116·2	0·818	0·522	0·922
3-Hexanone	123·2	1·17	0·742	1·15
2,4-Dimethyl-3-pentanone	123·7	1·01	0·777	1·08
2-Hexanone	127·2	1·25	0·767	1·30
5-Methyl-3-hexanone	136·0	1·52	1·04	1·56
4-Heptanone	143·5	2·07	1·41	2·04
5-Methyl-2-hexanone	144·0	1·95	1·21	2·09
3-Heptanone	148·5	2·35	1·54	2·29
2-Heptanone	151·5	2·60	1·55	2·66
6-Methyl-3-heptanone	163·5	3·25	2·32	3·34
6-Methyl-2-heptanone	165·0	3·88	2·46	3·90
2,6-Dimethyl-4-heptanone	168·2	3·45	2·86	3·74
3-Octanone	169·0	4·79	3·20	4·68
2-Octanone	172·9	5·26	3·22	5·25
5-Nonanone	187·7	8·22	5·82	8·11
3-Nonanone	190·0	9·35	6·30	8·75
Cyclopentanone	130·7	1·99	0·840	1·88
Cyclohexanone	155·7	4·25	1·90	4·02
p-Methylcyclohexanone	169·0	6·00	2·86	5·81
Ethanol	78·3	0·099	0·053	0·119
2-Propanol	82·4	0·125	0·086	0·156
2-Methyl-2-propanol	82·4	0·153	0·111	0·192
1-Propanol	97·2	0·216	0·134	0·267
2-Butanol	99·5	0·292	0·204	0·344
2-Methyl-1-propanol	107·9	0·352	0·244	0·427
1-Butanol	117·7	0·468	0·296	0·575
1-Hexanol	157·1	2·12	1·37	2·44
1-Octanol	195·3	8·79	5·78	9·18

TABLE 13

RELATIVE RETENTION TIMES 100°C

Compound	Boiling Point (°C/760)	RRT 100°C (toluene = 1·00)		
		BD	APL	DIN
Methyl acetate	57·2	0·168	0·097	0·165
Isopropyl formate	68·8	0·219	0·152	0·234
Ethyl acetate	77·2	0·291	0·177	0·288
n-Propyl formate	80·9	0·314	0·204	0·333
Isopropyl acetate	89·0	0·362	0·234	0·355
Isobutyl formate	98·3	0·485	0·348	0·518
Methyl butyrate	102·3	0·640	0·416	0·592
n-Butyl formate	106·6	0·668	0·448	0·705
Isobutyl acetate	116·5	0·846	0·566	0·820
n-Amyl acetate	148·0	1·85	1·24	1·75
Methyl caproate	151·3	2·80	1·84	2·37
Thiophene	84·2	0·586	0·489	0·570
2-Methylthiophene	112·6	1·18	1·03	1·13
3-Methylthiophene	115·4	1·29	1·10	1·22
2-Ethylthiophene	134·0	2·23	1·98	2·02
2,5-Dimethylthiophene	136·7	2·20	2·04	2·07
Tetrahydrothiophene	121·1	1·71	1·34	1·42
3-Methyl-2-thiabutane	84·7	0·418	0·422	0·400
4-Methyl-3-thiahexane	133·7	1·42	1·52	1·30
Thiacyclohexane	141·8	2·78	2·39	2·31
Acetonitrile	81·6	0·227	0·067	0·268
n-Propionitrile	97·2	0·412	0·133	0·460
n-Butyronitrile	117·9	0·813	0·278	0·878
Benzonitrile	191·1	10·9	3·64	11·5
Nitromethane	101·2	0·392	0·129	0·490
1-Methylpyrrole	115·0	1·18	0·645	1·10
Pyrrole	129·8	1·73	0·562	2·02
1-Isopropylpyrrole	—	2·55	1·56	2·34
2-Methylpyrrole	147·5	3·31	1·16	3·68
2,5-Dimethylpyrrole	164·5	6·08	2·29	6·50

TABLE 14

RELATIVE RETENTION TIMES 150°C

Compound	Boiling Point (°C/760)	RRT 150°C APL (p-xylene = 1·00)
3-Methylpentane	63·3	0·162
n-Hexane	68·7	0·173
2,2,3-Trimethylbutane	80·9	0·236
3-Ethylpentane	93·5	0·288
n-Heptane	98·4	0·301
2,2,4-Trimethylpentane	99·2	0·293
n-Octane	125·7	0·537
n-Decane	174·1	1·63
n-Undecane	195·9	2·84
n-Dodecane	216·3	4·90
n-Tridecane	235·4	8·52
n-Tetradecane	253·5	14·7
Methylcyclopentane	71·8	0·236
Cyclohexane	80·7	0·306
Methylcyclohexane	100·9	0·448
cis-1,2-Dimethylcyclohexane	129·7	0·848
Dicylohexyl	239·0	12·6
Cyclohexene	82·9	0·339
1-Heptene	93·6	0·275
2,2,4-Trimethyl-2-pentene	104·9	0·337
1-Octene	121·3	0·492
trans-2-Octene	125·0	0·539
1-Decene	170·6	1·52
1-Dodecene	213·4	4·57
1-Tetradecene	251·1	14·0
Benzene	80·1	0·302
Methylbenzene	110·6	0·553
Ethylbenzene	136·2	0·923
1,4-Dimethylbenzene	138·4	1·00
1,3-Dimethylbenzene	139·1	1·00
1,2-Dimethylbenzene	144·4	1·18
Isopropylbenzene	152·4	1·27
n-Propylbenzene	159·2	1·51
1-Methyl-4-ethylbenzene	162·0	1·65
1,3,5-Trimethylbenzene	164·7	1·79
t-Butylbenzene	169·1	1·84
s-Butylbenzene	173·3	2·01

TABLE 15

RELATIVE RETENTION TIMES AT 150°C

Compound	Boiling Point (°C/760)	RRT 150°C APL (p-xylene = 1·00)
1-Methyl-4-isopropylbenzene	177·1	2·23
1,3-Diethylbenzene	181·1	2·44
n-Butylbenzene	183·3	2·68
1,2-Diethylbenzene	183·4	2·74
1,4-Diethylbenzene	183·8	2·71
1,2,4,5-Tetramethylbenzene	196·8	4·16
Pentamethylbenzene	231·8	9·35
Indene	182·4	2·94
trans-Decahydronaphthalene	187·3	3·56
cis-Decahydronaphthalene	195·7	4·57
Naphthalene	218·0	6·97
2-Methylnaphthalene	241·1	12·7
1-Methylnaphthalene	244·6	15·0
Thiophene	84·2	0·320
3-Pentanone	102·7	0·235
n-Butanol	117·7	0·180
Pyridine	115·3	0·470
2,6-Dimethylpyridine	144·0	0·962
2,5-Dimethylpyridine	157·0	1·34

APPENDIX II

IDENTITY AND AMOUNTS OF COMPOUNDS IN NEUTRAL OILS N/I AND N/II: TABLES 16 TO 22

TABLE 16

PARAFFIN HYDROCARBONS IN N/I

RRT 100°C (toluene = 1·00)			Probable Compound	Wt % in N/I	P.P.M. in Tar
BD	APL	DIN			
(0·07)*	(0·18)	—	2-Methylbutane	0·001	1
(0·095)	(0·220)	—	n-Pentane	0·01	10
(0·165)	(0·400)	—	2,3-Dimethylbutane	0·01	15
0·100	0·204	0·105	3-Methylpentane	0·01	10
0·124	0·253	0·117	n-Hexane	0·19	250
0·188	0·348	0·192	Methylcyclopentane	0·09	115
0·204	0·433	0·220	2,3-Dimethylpentane	0·02	30
0·274	0·480	0·260	Cyclohexane	0·10	130
0·247	0·530	0·251	n-Heptane	0·90	1150
0·390	0·754	0·383	Methylcyclohexane	0·16	210
0·362	0·829	0·383	2,3,3-Trimethylpentane	0·43	570
0·512	1·08	0·485	n-Octane†	2·0	2600
0·552	1·18	0·563	C_9 branched b.p. 132–133°C	0·04	50
0·560	1·27	0·580	C_9 branched b.p. 133–135°C†	0·11	140
0·640	1·36	0·662	C_9 branched b.p. 137–138°C	0·12	160
0·710	1·62	0·752	C_9 branched b.p. 138–139°C†	0·11	140
0·777	1·74	0·813	C_9 branched b.p. 141–143°C†	0·31	400
1·01	2·18	0·951	n-Nonane†	0·50	600
			Total N/I paraffins	5·10	

* ( ): These RRT values are at 75°C relative to benzene.

† Also occurs in N/II.

TABLE 17

OLEFIN HYDROCARBONS IN N/I

RRT 100°C (toluene = 1·00)			Probable Compound	Wt % in N/I	P.P.M. in Tar
BD	APL	DIN			
(0·103)*	(0·191)	—	1-Pentene	0·003	5
(0·118)	(0·227)	—	2-Methyl-1-butene	0·01	10
(0·142)	(0·247)	—	2-Pentene	0·06	80
(0·141)	(0·300)	—	2-Methyl-2-butene	0·03	35
(0·205)	(0·387)	—	*trans*-4-Methyl-2-pentene	0·06	80
0·139	0·230	0·134	1-Hexene	0·90	1200
0·150	0·313	—	C_6 branched b.p. 65–70°C	0·08	110
0·225	0·390	0·226	C_7 branched b.p. 85–86°C	0·29	375
0·275	0·398	—	C_7 branched b.p. 86–90°C	0·13	170
0·280	0·463	0·263	1-Heptene	1·80	2300
0·354	0·531	0·318	C_8 branched b.p. 102–106°C	0·42	540
0·396	0·620	0·382	C_8 branched b.p. 107–110°C	0·10	130
0·418	0·670	—	C_8 branched b.p. 109–111°C	0·07	90
0·432	0·740	0·417	C_8 branched b.p. 112–113°C	0·20	260
0·483	0·824	0·490	C_8 branched b.p. 115–116°C	0·43	560
0·488	0·843	0·490	C_8 branched b.p. 116–117°C	0·25	320
0·544	0·870	0·532	C_8 branched b.p. 117–119°C	0·19	250
0·567	0·960	0·532	1-Octene†	2·60	3400
0·640	1·00	0·532	*trans*-2-Octene	0·14	180
0·694	1·06	0·613	*cis*-2-Octene	0·80	1000
0·742	1·17	0·718	C_9 branched b.p. 127–129°C	0·17	230
0·820	1·30	0·753	C_9 branched b.p. 132–134°C	0·06	85
—	1·44	—	C_9 branched b.p. 135–137°C	0·04	55
0·920	1·44	0·800	C_9 branched b.p. 137–138°C†	0·14	190
0·985	1·54	0·800	C_9 branched b.p. 138–140°C	0·11	140
0·910	1·55	0·850	C_9 branched b.p. 140–141°C†	0·23	300
1·06	1·68	0·927	C_9 branched b.p. 140–142°C	0·06	85
1·06	1·81	0·940	C_9 branched b.p. 143–144°C†	0·04	50
1·18	1·97	1·06	1-Nonene†	0·65	850
1·25	2·04	1·13	C_9 branched b.p. 149–150°C†	0·03	35
1·33	2·12	1·30	C_9 branched b.p. 152–153°C†	0·04	60
0·377	0·531	—	Cyclohexene	0·03	40
			Total N/I olefins	10·2	

* ( ): These RRT values are at 75°C relative to benzene.

† Also occurs in N/II.

TABLE 18

AROMATIC HYDROCARBONS AND NON-HYDROCARBONS IN N/I

RRT 100°C (toluene = 1·00)			Probable Compound	Wt % in N/I	P.P.M. in Tar
BD	APL	DIN			
			Aromatics		
0·466	0·460	0·468	Benzene*	24·0	31000
1·00	1·00	1·00	Methylbenzene*	44·0	57000
1·90	1·91	1·80	Ethylbenzene*	2·9	3800
2·09	2·15	2·08	1,3-Dimethylbenzene*	4·3	5600
2·09	2·15	2·08	1,4-Dimethylbenzene*	1·5	2000
2·59	2·58	2·55	1,2-Dimethylbenzene*	1·2	1500
			Total aromatics	78·0	—
			Thiophenes		
0·584	0·490	0·590	Thiophene	0·26	340
1·15	1·00	1·12	2-Methylthiophene*	0·08	100
1·26	1·10	1·26	3-Methylthiophene	0·13	170
			Total thiophenes	0·47	—
			Furans		
0·251	0·238	0·263	2-Methylfuran	0·15	190
0·340	0·231	0·332	2,4-Dimethylfuran	0·09	110
0·532	0·495	0·497	2,5-Dimethylfuran	0·19	250
1·00	0·932	0·885	2-Methyl-5-ethylfuran	0·22	280
1·34	1·08	1·25	2-Methyl-5-isopropylfuran	0·22	290
1·98	1·58	1·94	(furan) b.p. 145–146°C	0·05	80
			Total furans	0·92	—
			Ketones		
0·321	0·190	0·356	2-Butanone	1·20	1500
0·461	0·306	0·525	3-Methyl-2-butanone	0·53	690
0·598	0·360	0·652	2-Pentanone	1·70	2300
0·640	0·380	0·654	3-Pentanone	0·22	280
0·810	0·596	0·906	4-Methyl-2-pentanone	0·23	300
0·895	0·550	1·00	3-Methyl-2-pentanone	0·28	370
1·12	0·650	1·18	3-Hexanone*	0·27	350
1·12	0·755	1·18	2,4-Dimethyl-3-pentanone	0·15	190
1·24	0·775	1·34	2-Hexanone*	0·66	860
1·45	0·930	1·56	C_7 ketone b.p. 132–136°C	0·05	70
1·52	0·914	1·62	5-Methyl-3-hexanone*	0·13	170
1·65	1·01	1·77	C_7 ketone b.p. 136–140°C	0·20	260
2·20	1·73	2·46	2-Heptanone*	0·05	75
2·40	1·26	2·32	(Methyl cyclopentanone b.p. 142°C)	0·12	160
2·79	1·41	2·63	(Methyl cyclopentanone b.p. 146°C)	0·05	70
			Total ketones	5·80	—

* Also occurs in N/II.

TABLE 19

PARAFFIN HYDROCARBONS IN N/II

RRT 100°C (toluene = 1·00)			Probable Compound	Wt % in N/II	P.P.M. in Tar
BD	APL	DIN			
0·521	1·08	0·489	n-Octane*	0·09	120
0·576	1·27	0·580	C_9 branched b.p. 133–135°C*	0·03	40
0·708	1·62	0·749	C_9 branched b.p. 138–139°C*	0·14	180
0·773	1·74	0·814	C_9 branched b.p. 141–143°C*	0·12	160
0·880	1·82	0·82	C_8 cyclo b.p. 130–134°C	0·03	40
1·05	2·27	0·970	n-Nonane*	2·10	2700
1·22	2·46	1·14	C_9 cyclo b.p. 144–147°C	0·09	120
1·22	2·77	1·20	C_{10} branched b.p. 157–159°C	0·17	220
1·35	2·98	1·31	C_{10} branched b.p. 160–161°C	0·30	380
1·45	3·25	1·46	C_{10} branched b.p. 163–166°C	0·07	90
1·55	3·43	1·6	C_{10} branched b.p. 164–166°C	1·14	180
1·68	3·71	1·53	C_{10} branched b.p. 166–168°C	0·05	60
1·88	4·5	1·61	C_{10} branched b.p. 169–170°C	0·004	5
2·15	4·58	1·90	n-Decane	2·80	3500
2·26	4·94	2·13	C_{11} branched b.p. 176–178°C	0·05	60
2·26	5·16	2·15	C_{11} branched b.p. 176–179°C	0·21	270
2·87	5·65	2·50	C_{11} branched b.p. 183–185°C	0·04	45
3·37	6·66	2·85	C_{11} branched b.p. 189–190°C	0·12	150
3·16	7·08	3·06	C_{11} branched b.p. 187–191°C	0·04	45
4·35	9·34	3·71	n-Undecane	0·54	690
			Total N/II paraffins	7·10	—

* Also occurs in N/I.

Table 20

OLEFIN HYDROCARBONS IN N/II

RRT 100°C (toluene = 1·00)			Probable Compound	Wt % in N/II	P.P.M. in Tar
BD	APL	DIN			
0·570	1·01	0·535	1-Octene*	0·10	130
0·822	1·48	0·78	C_9 b.p. 137–138°C*	0·13	170
0·898	1·65	0·86	C_9 b.p. 140–141°C*	0·26	330
1·03	1·81	0·94	C_9 b.p. 143–144°C*	0·21	270
1·15	2·00	1·08	1-Nonene*	3·80	4800
1·30	2·20	1·14	C_9 b.p. 149–150°C*	0·84	1060
1·40	2·37	1·22	C_9 b.p. 152–153°C*	0·21	280
1·62	2·77	1·40	C_{10} b.p. 158–159°C	0·22	290
1·70	3·10	1·60	C_{10} b.p. 161–163°C	0·51	650
1·90	3·49	1·75	C_{10} b.p. 164–165°C	0·48	600
2·15	3·85	1·92	C_{10} b.p. 166–169°C	0·10	130
2·42	4·17	2·08	1-Decene	5·90	7400
2·42	3·85	2·30	C_{10} b.p. 170–174°C	0·22	280
2·60	4·63	2·38	C_{10} b.p. 173–175°C	1·10	1400
2·96	5·35	2·70	C_{11} b.p. 179–181°C	0·15	190
3·26	5·95	3·00	C_{11} b.p. 182–184°C	0·12	150
3·70	7·82	3·82	C_{11} b.p. 188–191°C	0·03	40
4·70	8·40	4·14	1-Undecene	0·91	1150
			Total N/II olefins	15·3	—

* Also occurs in N/I.

TABLE 21

AROMATIC HYDROCARBONS IN N/II

RRT 100°C (toluene = 1·00)			Probable Compound	Wt % in N/II	P.P.M. in Tar
BD	APL	DIN			
1·00	1·00	1·00	Methylbenzene*	0·16	210
1·97	1·92	1·77	Ethylbenzene*	5·20	6500
2·12	2·20	2·10	1,3-Dimethylbenzene*	13·0	16500
2·12	2·20	2·10	1,4-Dimethylbenzene*	4·60	5900
2·68	2·61	2·57	1,2-Dimethylbenzene*	8·10	10300
2·95	2·86	2·91	Isopropylbenzene	0·72	910
3·56	3·62	3·16	n-Propylbenzene	1·20	1500
3·97	3·94	3·54	1-Methyl-3-ethylbenzene	5·00	6300
3·97	3·99	3·54	1-Methyl-4-ethylbenzene	2·90	3700
4·46	4·66	4·29	1,3,5-Trimethylbenzene	1·80	2200
4·74	4·66	4·29	1-Methyl-2-ethylbenzene	2·80	3500
5·37	5·55	4·75	1-Methyl-3-isopropylbenzene	0·27	340
5·37	5·55	5·17	1,2,4-Trimethylbenzene	5·90	7400
5·60	6·06	5·17	1-Methyl-4-isopropylbenzene	1·40	1800
6·89	6·86	5·78	1,3-Diethylbenzene	0·51	650
6·89	6·86	6·61	1,2,3-Trimethylbenzene	3·20	4100
8·06	8·08	7·30	1-Methyl-2-n-propylbenzene	0·50	630
8·84	8·97	7·77	(1,4-Dimethyl-2-ethylbenzene)	0·13	160
9·21	9·52	8·18	(1,2-Dimethyl-4-ethylbenzene)	0·20	260
9·58	9·82	8·78	(1,3-Dimethyl-2-ethylbenzene)	0·68	870
10·2	10·8	10·0	(1,2-Dimethyl-3-ethylbenzene)	0·66	840
8·10	7·30	6·84	Indan	2·30	2900
10·2	7·67	9·70	Indene	2·70	3400
2·95	2·61	2·91	Styrene	1·70	2200
5·37	5·55	5·07	α-Methylstyrene	0·04	60
6·25	5·65	5·90	(*m*-Methylstyrene)	1·20	1500
			Total N/II aromatics	67·0	—

* Also occurs in N/I.

TABLE 22

NON-HYDROCARBONS IN N/II

RRT 100°C (toluene = 1·00)			Probable Compound	Wt % in N/II	P.P.M. in Tar
BD	APL	DIN			
			Thiophenes		
1·20	1·00	1·10	2-Methylthiophene*	0·004	5
2·44	2·36	2·24	Dimethylthiophene b.p. 137–139°C	0·34	430
2·82	2·71	2·60	Dimethylthiophene b.p. 142–145°C	0·25	310
			Furans		
7·35	5·00	8·08	Coumarone	5·60	7100
			Ketones		
1·16	0·810	1·20	3-Hexanone*	0·06	75
1·30	0·795	1·34	2-Hexanone*	0·10	130
1·51	1·00	1·62	5-Methyl-3-hexanone*	0·11	140
1·80	1·15	1·82	C_7 ketone b.p. 140–142°C	0·14	180
2·04	1·37	2·10	4-Heptanone	0·22	280
2·33	1·48	2·34	3-Heptanone	0·26	340
2·50	1·60	2·46	C_7 ketone b.p. 151–153°C	0·29	370
2·58	1·65	2·65	2-Heptanone*	0·77	980
2·80	1·90	2·80	C_8 ketone b.p. 156–157°C	0·09	110
3·30	2·22	3·52	C_8 ketone b.p. 162–164°C	0·21	270
4·20	1·95	4·02	Cyclohexanone	0·41	520
4·03	2·60	4·02	C_8 ketone b.p. 167–169°C	0·11	140
4·35	2·99	4·44	C_8 ketone b.p. 171–173°C	0·11	140
4·70	3·25	4·60	3-Octanone	0·07	95
4·70	3·40	4·86	C_9 ketone b.p. 173–176°C	0·37	470
5·23	3·49	5·25	2-Octanone	0·56	710
5·67	3·98	5·80	C_9 ketone b.p. 180–183°C	0·32	400
8·20	5·50	8·20	5-Nonanone	0·53	670
			Total N/II non-hydrocarbons	10·90	—

* Also occurs in N/I.

Identification of Organic Compounds by Gas Chromatography

The identification of unknown compounds separated by gas chromatography is often effected by comparison of their retention values with those of known compounds together with infra-red spectrophotometry or mass spectrometry. For this purpose graphs are prepared of log r against boiling point or log r on one stationary phase against log r on another stationary phase, where r is the retention time, relative retention time or the retention volume. Both non-polar and polar stationary phases are used to indicate the nature of the unknown substance. Wehrli and Kovats[1] have shown a relation between the structure of the substance and its retention values on two such phases. Stationary phase liquids which can take part in electron donor–electron acceptor interactions have also been used by Langer *et al.*[2] and Janak and Hrivnac[3] to separate closely similar pairs of compounds. I have also found[4] three different stationary phases to be useful in identifying components of a brown coal tar.

A method has been developed for the identification of compounds by gas chromatography alone using three stationary phases; one non-polar, one an electron donor and one an electron acceptor.

If r_1, r_2 and r_3 are the retention times (or volumes) of a substance on the three stationary phases 1, 2 and 3 under fixed conditions, we can define an 'affinity fraction' A of the substance for each phase. For phase 1 we have $A_1 = r_1/(r_1 + r_2 + r_3)$. This enables the data for a particular substance to be plotted as a point on a triangular graph.

The retention value r_b of a compound a on stationary phase b under a fixed set of conditions is proportional to $RT/(\gamma^0_a p^0_a)$, where γ^0_a is the activity coefficient of a at infinite dilution in b and p^0_a is the vapour pressure of a at column temperature. For ideal solution behaviour r_b is governed by p^0_a. In non-ideal solution the value of γ^0_a is governed by the balance of interaction energies E between like

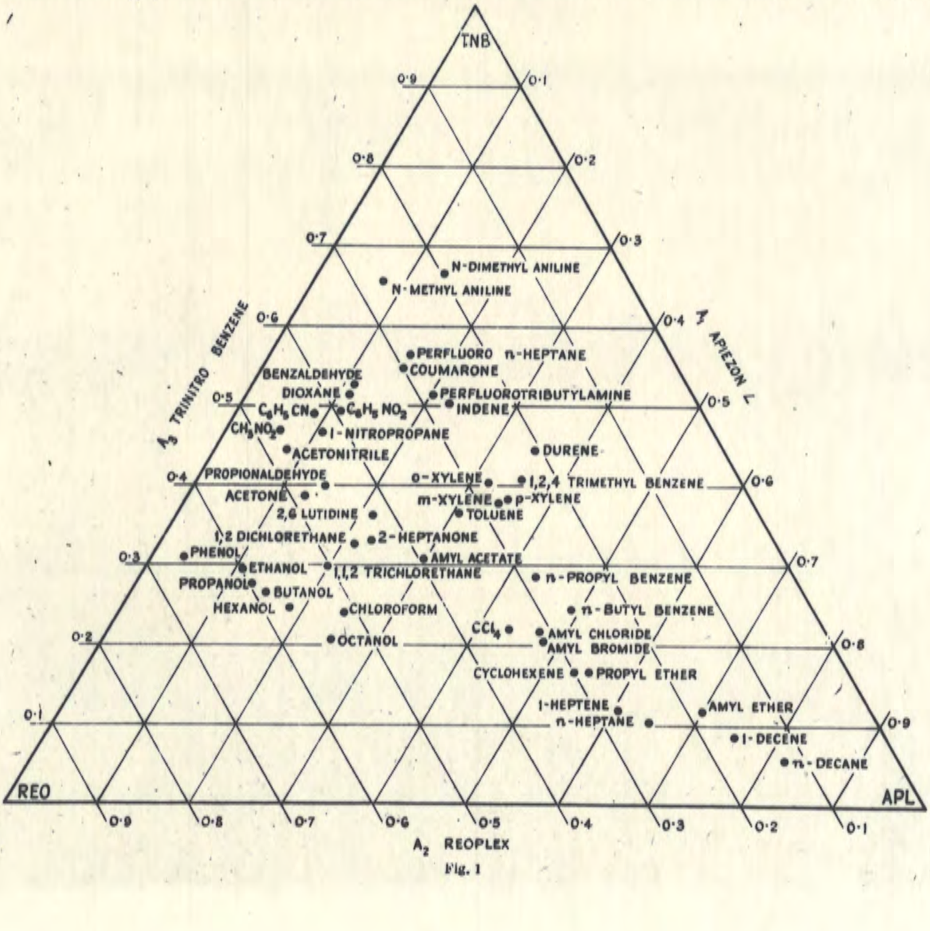

Fig. 1

and unlike molecules. For the simple case of a regular solution $\gamma^0_a = \exp(w/RT)$, where w is proportional to $(E_{aa} + E_{bb} - 2E_{ab})$. Thus a strong specific interaction of donor-acceptor type between the substance and the stationary phase liquid leads to a large retention value.

Retention times were measured for a number of substances at 125° C. on three 2·5-m. columns each containing 1·5 gm. of stationary phase on 9 gm. of 'Celite 545' using a nitrogen inlet pressure 1,000 mm. mercury above the outlet pressure, which was atmospheric. The A values for the substances were calculated and are shown in Fig. 1, where A_1 refers to 'Apiezon L', A_2 to 'Reoplex 400', polyester (electron donor) and A_3 to 1,3,5-trinitrobenzene (electron acceptor). Substances with low polarity have high values of A_1; $1/A_1$ is approximately proportional to the dielectric constant of the substances chromatographed. Compounds with a protonic function (electron acceptors) have high values of A_2 and substances which can act as electron donors have high values of A_3. Thus each compound has a position on the graph governed by its electron acceptor–donor properties and the group of points for each homologous series of compounds lie on a line pointing towards the 'Apiezon L' apex.

This method, together with the use of the three individual retention values, is being applied to the identification of the components of coal tar and should prove useful in the identification of the degradation products of other substances of low volatility. The method should prove useful in studying the electron donor and acceptor properties of volatile substances and of non-volatile liquids used as stationary phases. Further applications may be possible in interpreting and predicting the course of organic substitution reactions which are governed by the electron distribution in the reacting molecules.

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(*Reprinted from Nature, Vol.* 188, *No.* 4755, *pp.* 1021–1022.
December 17, 1960)

Commonwealth of Australia
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION
Reprinted from: "Journal of Chromatography"
Vol. 10, No. 3, pp. 284-293 (1963)

THE ROLE OF THE STATIONARY PHASE IN GAS CHROMATOGRAPHY

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INTRODUCTION

The large number of stationary-phase liquids described in the literature and offered for sale by suppliers is bewildering to the gas chromatographer. The choice of a suitable stationary phase for a given separation of volatile compounds can be facilitated by a study of the balance of intermolecular forces between the solute and solvent. A qualitative prediction of the retention behaviour of a solute on a given phase can be made using the vapour pressure of the solute and the classification of liquids first proposed by EWELL, HARRISON AND BERG[1]. This has been discussed in some detail by KEULEMANS[2], AMBROSE AND AMBROSE[3] and HARDY AND POLLARD[4].

In gas chromatography, apart from the vapour pressure of the solute, the most important single factor governing the magnitude of the solute retention on a stationary phase is the nett electron donor–acceptor interaction between solute and solvent. The most common example of this is hydrogen-bond formation. The electron donor–acceptor properties of both solute and stationary-phase liquid can be used as a basis for a quantitative classification of phases and as a basis for a method of identification of unknown volatile compounds by gas chromatography.

MOLECULAR STRUCTURE AND INTERMOLECULAR INTERACTIONS

First we must consider briefly the structure of the molecules, their intermolecular interactions and the factors which govern the specific retention volume of a solute. Non-polar molecules in gas chromatography are confined mainly to gases and saturated hydrocarbons. Polar molecules contain one or more polar atoms or groups together with a neutral or non-polar part, usually saturated hydrocarbon chains. The polar part may be the strongly electronegative atoms F, O or N or electron attracting groups, *e.g.* $-NO_2$, $-C{\equiv}N$, $-CF_3$ or electron repelling groups such as $-NMe_2$, $-CH_3$, $-CMe_3$, $-OMe$. It is the type and number of polar groups in a molecule relative to the size of the neutral part which determines the polarity or distribution of electrons on the different parts of the molecule. If the molecule contains double bonds with their mobile π-electrons this allows electron attracting or repelling groups to transmit their effects further through the hydrocarbon part of the molecule than is possible with saturated hydrocarbon chains. Most polar molecules can act as electron donors or acceptors or both, given the required environment, but usually one effect is predominant. It is the concentration of electrons or the electron-cloud density which governs the potential donor or acceptor property of the molecule.

In compounds which form hydrogen bonds with electron donors the proton, because of its small size, can present a concentrated area of effective positive charge (low electron density) close to a donor molecule which has an area of high electron density. For example: chloroform has a low concentration of excess electrons spread over the three chlorine atoms leaving a concentrated deficit of electrons on the proton. The compound 1-nitropropane has an excess of electrons on the nitro group and a deficit of electrons on the α-methylene group while the remaining part of the alkyl chain is substantially neutral. The amino hydrogen atoms of primary and secondary amines act as acceptor sites while the nitrogen of tertiary amines act as donors. In aromatic compounds there can be an excess or deficit of π-electrons on each side of the ring depending on whether the substituent groups are electron repelling or attracting. In aromatic compounds both the π-electron atmosphere of the ring and the substituent groups can act as donor or acceptor sites. Steric hindrance may also play an important part in the availability of donor or acceptor sites. For example: the work of FITZGERALD[5,6] shows that 2,6-dimethylphenol has a ~~larger~~ smaller retention volume than the close boiling 3-methylphenol on the donor-type phase diaminodiphenyl sulphone and 2,6-dimethylpyridine has a ~~larger~~ smaller retention volume than the close boiling 3-methylpyridine on the acceptor-type phase tris-(2-cyanoethyl)-nitromethane.

THE FACTORS GOVERNING THE RETENTION VOLUME

Now let us consider the factors governing the retention volume. If ideal behaviour is assumed in the gas phase the partial pressure of a solute 1 above a solution in solvent 2 at temperature T° K is given by:

$$p_1 = Py_1 = x_1 \gamma_1 p^\circ{}_1$$

where x_1 and y_1 are the mole fractions of solute 1 in the liquid and vapour respectively, P is the total pressure, $p^\circ{}_1$ is the vapour pressure of solute 1 at T °K and γ_1 is the activity coefficient of component 1 (referred to the standard state of pure liquid solute at the same temperature and pressure). The partition coefficient K has been defined[3] as:

$$K = \frac{x_1}{y_1} \cdot \frac{n_s}{n_m} = \frac{P}{\gamma^\infty{}_1 p^\circ{}_1} \cdot \frac{n_s}{n_m} = \frac{n_s RT}{\gamma^\infty{}_1 p^\circ{}_1}$$

where n_s and n_m are the moles per ml in the stationary phase and mobile phase respectively and γ^∞ refers to infinite dilution. The specific retention volume per gram of stationary phase V_g is given by[3]:

$$V_g = \frac{K\ 273}{\rho_L\ T}$$

where ρ_L is the density of the stationary phase at the column temperature T. Then:

$$V_g = \frac{273\ R}{M_L} \cdot \frac{1}{\gamma^\infty{}_1 p^\circ{}_1}$$

where M_L is the molecular weight of the stationary-phase liquid. The absolute retention volume V is given by:

$$V = \frac{NRT}{\gamma^{\infty}{}_1 p^{\circ}{}_1}$$

where N is the number of moles of stationary phase on the column and T is the temperature at which the volumetric flowrate is expressed.

For ideal solutions $\gamma^{\infty} = 1$ and V_g is inversely proportional to the vapour pressure of the compound. However, in gas chromatography there is usually a large molecular size difference between the volatile component and the stationary phase so, even when these are both normal paraffins, there is a small negative deviation from Raoult's law due to entropy effects. This is of the form[7]:

$$\log \gamma^{\infty} = D(n_1 - n_2)^2$$

where n_1 and n_2 are the number of carbon atoms in the solute and solvent and D is a constant having a negative value.

Many volatile compounds and stationary phases form non-ideal solutions so that V_g is controlled by both p° and γ^{∞} and for a given p°, V_g is controlled by the value of γ^{∞}.

The value of γ^{∞} is determined by the balance of intermolecular forces between the molecules of solute 1 and stationary-phase liquid 2. For solutions where excess entropy effects are small we have:

$$\log \gamma^{\infty} = k\,(E_{11} + E_{22} - 2E_{12})$$

where E is the energy of interaction between the molecules. High values of E may be due to dipole, induced dipole and electron donor–acceptor interactions. Let us consider three circumstances.

(1) E_{11} *predominant.* Here the solute has a high positive value of $\log \gamma$ and therefore a small retention volume relative to a compound of the same boiling point which forms an ideal solution. For example: associated compounds such as nitromethane and methanol on the non-polar phase Apiezon L. (This is equivalent to saying that at the high temperature and low concentration in the liquid phase these compounds are much less associated than in the pure liquid state and would therefore have a much higher "effective" p°.)

(2) E_{22} *predominant.* The solute has a high positive value of $\log \gamma$ and therefore a smaller retention volume than a compound of the same boiling point which forms an ideal solution, *e.g.* saturated hydrocarbons on a glycerol phase.

(3) E_{12} *predominant.* Here electron donor–acceptor interaction between the solute and solvent leads to a negative value of $\log \gamma$ and thus to long retention times, *e.g.* 1,1,2-trichloroethane on Reoplex 400 or primary amines on polyethylene glycol.

PIEROTTI *et al.*[8] have studied and correlated the value of γ^{∞} for a wide range of solutes and solvents.

The effects of these intermolecular interactions are often larger at lower temperatures.

CLASSIFICATION OF STATIONARY PHASES

An approximate measure of the electron donor or acceptor properties of a stationary phase can be obtained from the ratio of the retention volumes of two compounds of about the same boiling point, one an acceptor and one a donor. Table I shows examples of this method based on retention data measured at 125° C on a number of phases using the apparatus and methods described by BROWN[9]. A high value of the ratio indicates a donor-type phase while a low value indicates an acceptor-type. The selectivity of a given phase for a particular separation has been determined by BAYER[10] who uses the ratio of retentions of two homologous series corrected to identical boiling point as a selectivity coefficient. A similar approach has been used by HUEBNER[11] who used the retention ratio of methanol to alkane to determine the "polarity index" of surface active agents.

TABLE I

ACCEPTOR/DONOR RETENTION RATIOS ON PHASES

*Phase**	*Ratio of retention volumes (125° C)*				
	$\frac{CHCl_3}{CCl_4}$	$\frac{CHCl_2\,CH_2Cl}{Dioxane}$	$\frac{Cyclohexanol}{Cyclohexanone}$	$\frac{Pyrrole}{Pyridine}$	$\frac{Aniline}{NMe_2\text{-}aniline}$
REO	1.66	1.32	1.17	—	2.52
XF 1150	1.65	1.64	—	2.14	1.79
DGS	1.10	1.26	—	1.73	2.88
APL	0.665	1.74	0.981	0.676	0.48
m-Bis	0.890	1.32	—	0.862	0.70
ZONYL	0.925	0.595	—	0.435	0.91
FCP	0.874	0.572	0.022	0.700	0.705
QF 1	0.840	0.986	—	0.714	0.706
AROCLOR	0.636	0.720	—	0.705	0.507
TNB	1.25	0.568	0.490	—	1.01

* The phases are identified under Fig. 1

The use of the V_g of only two compounds, donor and acceptor, to determine the properties of a stationary phases does not give much information about the relative polarity of the phase and does not permit one to distinguish readily between a non-polar phase and one which has both donor and acceptor properties. If, however, three test compounds are used, one non-polar, one an acceptor and one a donor it is possible to determine the relative polarity of the phase as well as its donor or acceptor potential. If V_n, V_a and V_d are the retention volumes of the non-polar, the acceptor and donor compounds on the phase we can calculate the "retention fractions".

$$F_n = V_n/(V_n + V_a + V_d)$$

and similarly F_a and F_d and these can be plotted on a triangular graph. The retention volumes of *n*-decane, 1,1,2-trichloroethane and dioxane were measured on a number of phases at 125° and the retention fractions calculated to give the classification of phases shown in Fig. 1. The non-polar phases are close to the *n*-decane apex and have high values of F_n and the polar phases have low values of F_n. The acceptor-type phases are towards the dioxane apex and have a high value of F_d and a low value of F_a, while the donor-type phases are towards the trichloroethane apex and have a high value of F_a and a low value of F_d.

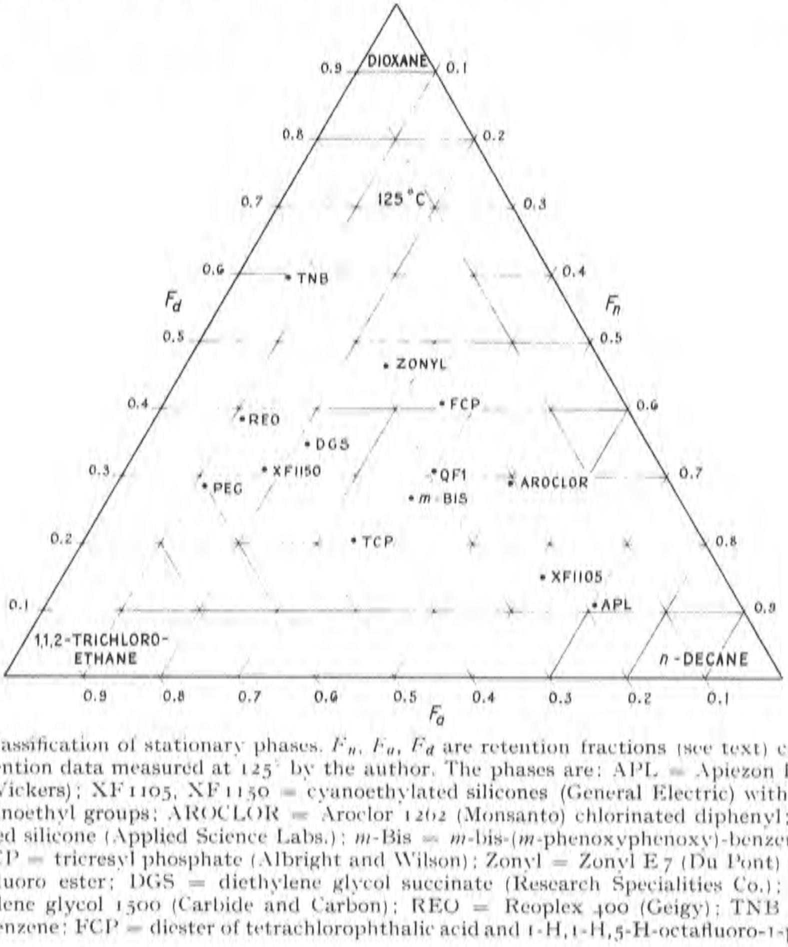

Fig. 1. Classification of stationary phases. F_n, F_a, F_d are retention fractions (see text) calculated from retention data measured at 125° by the author. The phases are: APL = Apiezon L (Metropolitan, Vickers); XF 1105, XF 1150 = cyanoethylated silicones (General Electric) with 5% and 50% cyanoethyl groups; AROCLOR = Aroclor 1262 (Monsanto) chlorinated diphenyl; QF 1 = fluorinated silicone (Applied Science Labs.); *m*-Bis = *m*-bis-(*m*-phenoxyphenoxy)-benzene (Eastman); TCP = tricresyl phosphate (Albright and Wilson); Zonyl = Zonyl E 7 (Du Pont) pyromellitic perfluoro ester; DGS = diethylene glycol succinate (Research Specialities Co.); PEG = polyethylene glycol 1500 (Carbide and Carbon); REO = Reoplex 400 (Geigy); TNB = 1,3,5-trinitrobenzene; FCP = diester of tetrachlorophthalic acid and 1-H,1-H,5-H-octafluoro-1-pentanol.

Similarly, using the retention data of McNAIR[12], TENNEY[13] and BROWN[9] for *n*-hexane, ethanol and 2-butanone at 100° C we have the classification of the phases shown in Fig. 2. The position on the triangular graph for a given phase is determined by the choice of the three test compounds and these can be varied to suit a particular problem. The "functional group retention ratio" to be described below can be used with advantage instead of the retention volume of a single compound in the classification of phases by this method.

The number of donor-type phases available to the gas chromatographer is adequate, but there are few strong acceptor-type phases suitable for use over a range of temperature. Many strong acceptor compounds have a rigid molecular structure which gives them melting points close to a temperature where they have an appreciable vapour pressure. The compound di-*n*-butyl tetrachlorophthalate is a useful weak acceptor-type phase (Fig. 2) but it has sufficient alkyl content to give appreciable retention values for aliphatic hydrocarbons. If this compound could be modified by replacing the butyl groups by more strongly electron withdrawing non-hydrocarbon groups a more polar and more strongly acceptor-type phase should be obtained. The diester of tetrachlorophthalic acid with 1-H,1-H,5-H-octafluoro-1-pentanol was made and on testing proved to be a much stronger acceptor than the butyl ester as can be seen from Fig. 2. This stable fluoroester is a liquid at room temperature and has a boiling point of 180° C/0.6 mm Hg.

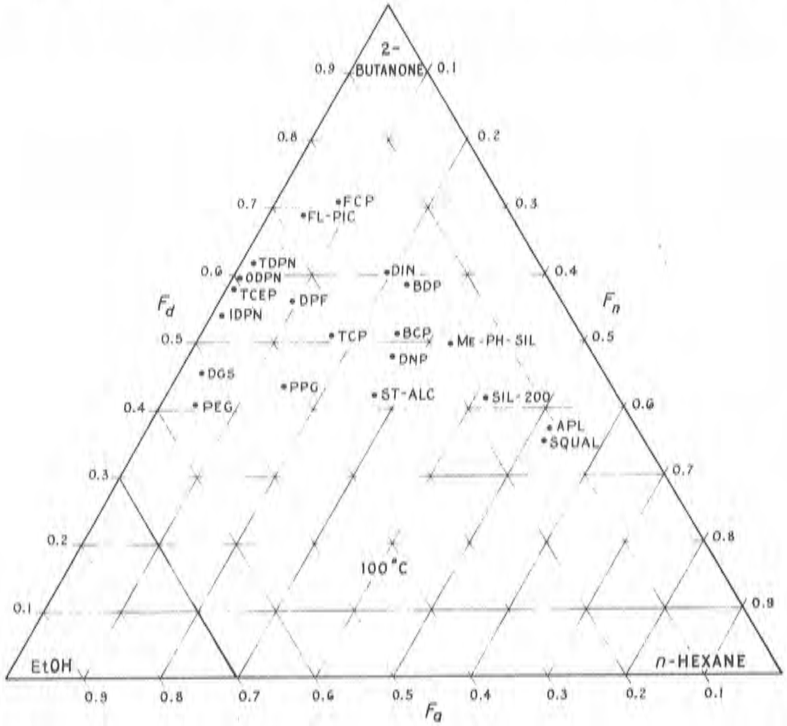

Fig. 2. Classification of stationary phases. F_n, F_a, F_d are retention fractions (see text) calculated from the retention data at 100° C and 67° C of Brown[9], McNair[12], Tenney[13], and Raupp[14]. The phases are: APL = Apiezon L; SQUAL = squalane; Sil-200 = Silicone DC-200; Me-Ph-Sil = methylphenyl silicone (General Electric 81705); St-alc = stearyl alcohol; DNP = dinonyl phthalate; BCP = di-*n*-butyl tetrachlorophthalate; BDP = benzyldiphenyl, DIN = di-*n*-octyl ester of 4,4-dinitrodiphenic acid; TCP = tricresyl phosphate; PEG = polyethylene glycol; PPG = polypropylene glycol; DGS = diethylene glycol succinate; DPF = diphenyl formamide; IDPN = iminodipropionitrile; ODPN = oxydipropionitrile; TDPN = thiodipropionitrile; TCEP = 1,2,3-tris-(2-cyanoethyl)-propane; FL-PIC = fluorene picrate; FCP = diester of tetrachlorophthalic acid and 1-H, 1-H, 5-H-octafluoro-1-pentanol.

IDENTIFICATION OF ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY

If we reverse the procedure just described for the classification of phases and run a number of compounds on three selected phases, one neutral, one an acceptor and one a donor and plot the three "affinity fractions" analogous to the "retention fractions" on a triangular diagram we have a method for studying the donor–acceptor properties of the volatile compounds. In an earlier communication[15] the author proposed this method for the identification of compounds by gas chromatography. From Fig. 1 of the earlier communication and from Fig. 3 of this paper which is based on data of HORNING *et al.*[16] it can be seen that the position on the graph is governed by the relative strength of molecular interaction of the donor, acceptor and neutral parts of the molecules with the stationary-phase liquids, the position of a given compound is fixed for 3 given phases and the position of a member of a homologous series depends on the length of the hydrocarbon chain.

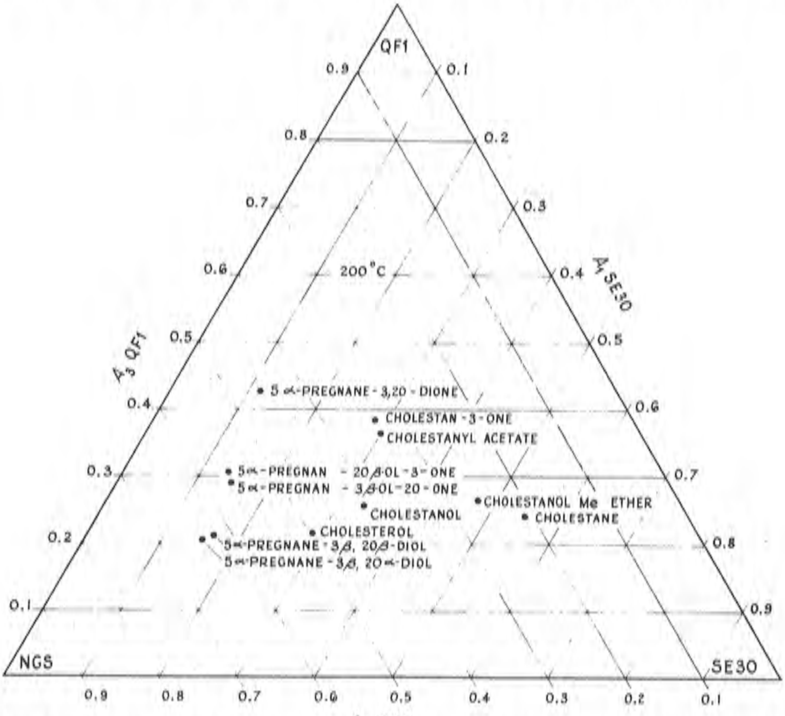

Fig. 3. Identification of steroids. A_1, A_2, A_3 affinity fractions (see BROWN[15]) from the data of HORNING *et al.*[16]. Phases: SE 30 = silicone; NGS = neopentyl glycol succinate; QF 1 = fluorinated silicone.

The value of this method of identifying volatile compounds by gas chromatography would be improved considerably if the effect of hydrocarbon chain length on the retention volume could be eliminated and we could study the behaviour of the functional groups alone. This can be done by taking the ratio or log of the ratio of V_g of a compound RX containing the functional group X to the V_g of a suitable homomorph hydrocarbon, *e.g.* V_g *n*-hexanol/V_g *n*-hexane or nitrobenzene/benzene. For a homologous series of compounds containing the same functional group we should expect this to be a constant at a given temperature as the graphs of log V_g against carbon number for two homologous series are often almost parallel straight lines. Values of the "functional group retention ratio", V_g RX/V_g RH for a number of different homologous series on various phases are shown in Table II. These were calculated from the data of BROWN[9], MCNAIR[12] and RAUPP[14] using extrapolation of the plot of V_g RH against carbon number to obtain values for V_g of the two lower hydrocarbon homomorphs. It can be seen that the functional group retention ratios are constant to within the accuracy of the experimental data. The choice of homomorph hydrocarbon can be made to suit the problem; for example, the homomorph for 2-pentanone could be *n*-pentane or *n*-propane if the functional group is taken as $-CO-CH_3$, or for the study of the acceptor interactions of chloroform with donor phases the homomorph could be taken as fluorotrichloromethane. The best choice is probably the hydrocarbon having the same carbon skeleton or the same number of carbon atoms as the compound containing the functional group. In measuring these ratios for compounds containing functional groups which interact strongly with the stationary phase the retention volumes of the homomorph hydrocarbons may be too small to be measured with sufficient accuracy and it is recommended that these be determined from a log V_g against carbon number graph for the higher members of the series.

TABLE II

FUNCTIONAL GROUP RETENTION RATIOS

*Phase**	*DIN*	*APL*	*FL-PIC*	*DNP*	*SQUAL*	*ADOL-40*		
Temp.(C°)	*100*	*100*	*100*	153	153	*153*	*153*	*153*
Group	*>C=O*	*>C=O*	*-OH*	*-OH*	*-OH*	*-OH*	*-Br*	*-Cl*
Carbon No. 3	—	—	87	8.9	3.4	15.0	11.0	6.25
4	—	—	81	9.8	3.8	15.6	11.0	6.32
5	11.3	2.97	84	9.5	3.8	15.6	10.8	6.28
6	11.3	3.04	86	8.9	3.9	15.5	10.4	6.15
7	11.1	2.92	—	8.6	4.0	14.9	—	—
8	10.7	2.98	—	—	3.9	15.0	—	—

* These data were calculated from the data of BROWN[9], MCNAIR[12] and RAUPP[14]. The phases are identified under Fig. 2. Adol-40 is 9,10-octadecen-1,12-diol.

The functional group retention ratio for a few aromatic compounds has been determined by BORER[17] using benzene as the homomorph. A similar approach has been employed by CLAYTON[18] with steroids. EVANS AND SMITH[19] have used *n*-nonane as a universal homomorph and KOVATS[20] a more complicated function of retention volumes which he named the Retention Index and which EVANS AND SMITH[19] state is, "100 times the carbon number of a hypothetical hydrocarbon having the same retention as the unknown". SWOBODA[21] goes one step further and uses the difference between KOVATS' Index for a compound and for its homomorph. Another method for the identification of unknown compounds from retention data has been proposed recently by MERRITT AND WALSH[22] using the ratio of retention volumes of the unknown on two carefully chosen phases.

Let us return to the functional group retention ratio. The value of this ratio for a given homologous series is a measure of the interaction of the functional group with the stationary phase. In fact $-\underline{RT \ln RX/RH}$ is the nett free energy change ΔG on the transfer of one mole of a compound RX from the vapour at one atmosphere

$-RT \cdot \ln V_g RX/V_g RH$

in the mobile phase to solution at a low given concentration in the stationary phase plus that for removal of one mole of the homomorph from the stationary phase to the mobile phase under the same conditions. Values of the functional group retention ratio or ΔG, measured on one or more stationary phases, are very useful for the identification of unknown compounds. This easily measured thermodynamic quantity which is a quantitative measure of functional group to phase interaction can be divided into its enthalpy and entropy terms by measuring its temperature dependence.

By using the values of the functional group retention ratio on three carefully selected phases it is possible to plot the group retention fractions derived from them on a triangular graph which shows only one point for each class of compounds. Fig. 4 is such a graph based on the data of BROWN[9], MCNAIR[12] and RAUPP[14]. This method can be employed for the identification of unknown compounds provided that a method is available for transforming the unknown compound into its unknown homomorph so that this can also be gas chromatographed on the same three phases. This degradation has been done by micro vapour-phase hydrogenation for a number of oxygen, nitrogen and sulphur compounds by workers at the Bartlesville, U.S. Bureau of Mines Research Laboratories[23, 24].

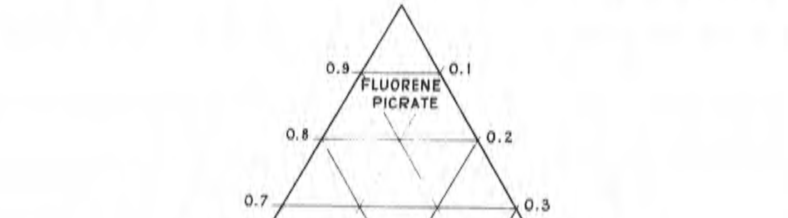

Fig. 4. Identification of homologous series of compounds with various functional groups. G_1, G_2, G_3 group retention fractions (see text) calculated from the data at 100°C of BROWN[9], MCNAIR[12] and RAUPP[14]; R = alkyl group; φ = phenyl group; PEG = polyethylene glycol.

When the donor–acceptor interaction between a polar solute and a polar phase is not too high we find that the free energy change $\Delta G = \underline{-RT \ln \text{RX/RH}}$ is a constant

$-RT \ln V_{gRX}/V_{gRH}$

for a given homologous series on a given phase over a range of column temperatures. However, if the specific donor–acceptor interaction is large there is a difference in orientational freedom on the phase between the polar compound and its homomorph leading to a change in entropy and this gives a variation of ΔG with temperature. For very strong interactions this may lead to variation in entropy and thus in ΔG with the length of the hydrocarbon part of the polar molecule.

SUMMARY

The molecular structure of volatile solutes and stationary-phase solvents, their molecular interactions, and the factors governing the magnitude of the retention volumes are briefly discussed.

A method is described for the classification of stationary phases into types according to their polarity and behaviour as electron donors or acceptors by measuring the retention volumes of three selected compounds on each phase.

A similar method is described for the identification of unknown compounds from their retention data on three carefully selected phases. This method uses the "functional group retention ratio", a quantitative measure of the interaction of the functional group in an homologous series of polar compounds with the stationary-phase liquids, to identify the functional group of the unknown compound.

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THE
ANALYSIS AND PREPARATION OF "GLACIAL METAPHOSPHORIC ACID"

By

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Reprinted from "The Australian Chemical Institute Journal and Proceedings." Vol. 9, *No.* 9, *Sept.*, 1942.

Ramsay, Ware Publishing Pty. Ltd., 117-129 King Street, Melbourne.

THE ANALYSIS AND PREPARATION OF "GLACIAL METAPHOSPHORIC ACID."

By IAN BROWN, B.Sc., A.A.C.I.

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Summary

Analysis of various samples of reagent metaphosphoric acid indicates that the usual concentration of metaphosphoric acid is between 35 and 50 per cent., the accompanying materials being orthophosphoric acid, 0.3-3.9 per cent.; pyrophosphoric acid, 23-33 per cent., and sodium oxide approximately 18 per cent., with between 6-10 per cent. of combined water.

A method for the volumetric analysis for such materials is discussed in detail.

The course of the conversion of orthophosphoric acid-sodium orthophosphate mixtures to material approximating closely to reagent metaphosphoric acid was studied and a method suitable for the preparation of this material in the laboratory is described.

The course of hydrolysis of the "metaphosphoric acid" when in solution was studied under a number of conditions.

The work outlined in this communication was undertaken to investigate the feasibility of the laboratory production of "Glacial Metaphosphoric Acid," as this reagent has assumed considerable importance in biochemical analyses and is at times difficult to obtain.

1. Composition of Samples of Reagent Glacial Metaphosphoric Acid.

The literature indicates that reagent metaphosphoric acid obtainable on the market contains sodium phosphates and some ortho- and pyrophosphoric acids as impurities. Bettendorf (1888).

Several samples from various manufacturers were analysed with the following results:—

Sample	% Meta- P_2O_5	% Ortho- P_2O_5	% Pyro- P_2O_5	% Na_2O	% Combined H_2O
Merck	34.9	3.9	32.9	18.1	9.1
Schering Kahlbaum	30.9	4.5	35.7	18.2	9.5
Baker	49.8	0.3	23.2	18.3	6.9

Two other samples that had been in stock for a long time, which were encrusted with a semi-crystalline efflorescence, were analysed, the efflorescent material and the clear inner portion being treated separately.

Sample	% Meta-P_2O_5	% Ortho-P_2O_5	% Pyro-P_2O_5	% Na_2O	% Combined H_2O
A.*	18.4	7.1	47.9	11.0	14.0
A†	0	58.8	9.9	10.8	21.3
B*	40.0	4.0	31.8	11.7	11.4
B†	0	61.0	7.3	10.4	21.7

* = clear inner portion. † = semi-crystalline efflorescence.

2. Method of Estimation

The methods of analysis have been reviewed recently by Gerber and Miles (1938, 1941), who have employed colorimetric pH titration methods for the determination of ortho-, pyro-, and metaphosphoric acids, and of their sodium salts. The procedure employed was based essentially on the work of the above authors.

For the volumetric determination, meta-, pyro-, and orthophosphoric acids are considered as mono-, di-, and tri-basic acids which are estimated by titration with sodium hydroxide in three stages, the end-points of which are distinguished by colorimetric pH measurements.

In titration with NaOH to pH 4.4, the following reactions are involved:—

$HPO_3 + NaOH = NaPO_3 + H_2O$

$H_4P_2O_7 + 2NaOH = Na_2H_2P_2O_7 + 2H_2O$

$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$

and on titration to pH 8.8 the following reactions are involved:—

$Na_2H_2P_2O_7 + 2NaOH = Na_4P_2O_7 + 2H_2O$

$NaH_2PO_4 + NaOH = Na_2HPO_4 + H_2O$

The ionisation constants of the phosphoric acids at 18°C. (Abbott and Bray, 1909) are:—

Orthophosphoric acid $K_1 = 1.1 \times 10^{-2}$

$K_2 = 1.95 \times 10^{-7}$

Pyrophosphoric acid $K_2 = 1.1 \times 10^{-2}$

$K_4 = 3.6 \times 10^{-9}$

The ionisation constant of metaphosphoric acid is probably of the order of 1×10^{-3}.

The addition of excess silver nitrate liberates the third hydrogen atom of the orthophosphoric acid as HNO_3, thus:

$NaPO_3 + AgNO_3 = AgPO_3 + NaNO_3$

$Na_4P_2O_7 + 4AgNO_3 = Ag_4P_2O_7 + 4NaNO_3$

$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$

The HNO_3 may then be titrated as a strong acid.

The P_2O_5 equivalents of the three acids are computed by two successive subtractions.

In practice the above procedure is altered. Two aliquots are titrated, one with bromocresol green as the indicator to a provisional reaction of pH 4.4, and the other with thymol blue to pH 8.8, in the presence of excess sodium chloride, this salt being added to reduce hydrolysis and to bring the equivalence points for the titration to $Na_4P_2O_7$ and Na_2HPO_4 into closer proximity. After the bromocresol green end-point has been reached, excess silver nitrate is added, and the liberated nitric acid is titrated using methyl red as indicator.

The end-points of pH 4.4 and pH 8.8 mentioned above are both provisional. They depend on the ratio of ortho- and pyrophosphoric acids present in the mixture, as the equivalence points of the pyro-salts are not in perfect agreement with those of the ortho-salts. These are respectively:—

NaH_2PO_4	.... pH 4.6	Na_2HPO_4	... pH 8.5
$Na_2H_2P_2O_7$	... pH 4.4	$Na_4P_2O_7$	... pH 9.1

When the approximate proportions of ortho- and pyrophosphoric acids have been determined, the appropriate end-points may be chosen from the data of Gerber and Miles (1938).

This procedure is suitable only in the absence of other weak acids or weak bases, whose buffer action would interfere with the titrations. The presence of strong acids and bases however does not interfere with the values obtained for ortho- and pyrophosphoric acids, but obviously the bromocresol green titration does not then represent the total P_2O_5 content. This may be found under such circumstances by the titration of an aliquot of the solution after complete hydrolysis to orthophosphoric acid by boiling with dilute HNO_3.

In the presence of a large quantity of sodium salts it is necessary to adjust the sample to a more acid reaction than pH 4.2 by the addition of a known quantity of standard nitric acid prior to making it up to the required volume. The acid added at this stage is taken into account in subsequent calculations as the "acid equivalent."

If samples contain large quantities of sodium it is sometimes necessary to remove the carbonates present by aeration of the solution after the addition of acid.

In this study, where great accuracy was not essential and where the orthophosphoric acid was present in small quantities, pH 4.2 and pH 9.1 were chosen as end points for most of the titrations.

The method assumes that polymers of HPO_3 titrate in solution as HPO_3 and that the complex polyphosphates (Andress and Wüst, 1938; and Schwartz and Munter, 1942), which are intermediate in composition between HPO_3 and $H_4P_2O_7$ behave as mixtures of these acids.

3. Procedure

(*i*) *The reagents*:

(a) Standard NaOH (carbonate free) 0.1409 normal, 1 ml. = 0.01 g. P_2O_5.
(b) Silver nitrate 0.85 N. (144 g. per litre).
(c) Bromocresol green 0.4% (in equivalent quantity of NaOH).
(d) Thymol blue 0.4% (in equivalent quantity of NaOH).
(e) Methyl red 0.2% in 60% ethyl alcohol.

(*ii*) *Solution of the sample*:

Between 1 and 2 g. of the sample (containing between 0.7 and 1.5 g. of P_2O_5) is accurately weighed and dissolved in 50 ml. of ice-cold water, with mechanical stirring, and diluted to 100 ml. The aliquots, 25 ml., should be titrated as soon as possible.

(*iii*) *The titrations:*

The titrations were carried out by the method of Gerber and Miles (loc. cit.) with the following exceptions:—

(a) The end-points were determined by comparison of the titration flask with similar flasks containing standardised buffers of the appropriate pH and the same quantity of indicator.

(b) Except in the case of the methyl red titration, smaller quantities of indicator were found to be convenient, i.e., 0.1 ml. of bromocresol green and 0.25 ml. of thymol blue were employed.

(c) With samples containing sodium phosphates, the total P_2O_5 was found by titration after hydrolysis. The reaction of the cooled acid solution was adjusted to pH 4.2 and, after the addition of excess silver nitrate, it was titrated, using methyl red, until the pink colour of the supernatant liquid was just discharged.

4. Calculation of the Composition from the Titrations.

When sodium salts are present together with the free acids, as, for example, in the "Reagent Metaphosphoric Acid" as it is marketed, the quantity of P_2O_5 existing as meta-, pyro- and ortho-acid and the quantity of sodium may be calculated by the following method which is derived from the titration figures and the chemical equations considered above. In the example set out, a 25 ml. aliquot contained 0.3675 g. of the mixture.

Weight of sample in 25 ml. aliquot = 0.3675 g.

	Groups represented	Millilitres standard alkali	x Factors	= % composition
MRT/2	o+p+m	26.4		
TB		60.9		
BCG		47.0		
MR		15.4		
AE		36.2		
(TB-BCG)	o+p	13.9		
By difference	m	12.5	x $\frac{1}{0.3675}$	= 34.1% meta P_2O_5
MR-(TB-BCG)	o	1.5	x $\frac{1}{0.3675}$	= 4.1% ortho P_2O_5
By difference	p	12.4	x $\frac{1}{0.3675}$	= 33.9% pyro P_2O_5
$\frac{MRT}{2}$+BCG-AE	Na	15.6	x $\frac{0.4368}{0.3675}$	= 18.5% Na_2O
MR + BCG-AE	combined H_2O	26.2	x $\frac{0.1269}{0.3675}$	= 9.1% combined H_2O
				= 99.7% Total

In the above, the figures in the third column opposite TB, MR and BCG represent the number of ml. of 0.1409 N alkali required to bring a 25 ml. aliquot to the end-point in the thymol blue, methyl red, and bromocresol green titrations, respectively. AE is the "acid equivalent," i.e., the number of ml. of standard alkali equivalent to the N/2 nitric acid added to each aliquot. The total P_2O_5 value is derived from the methyl red titration after hydrolysis; 1 ml. of standard alkali is equivalent to 0.005 g. P_2O_5. Hence the term MRT/2.

In samples which contain only the phosphoric acids, the method is reduced to that of Gerber and Miles (1938).

5. Preparation of Metaphosphoric Acid.

The preparation of metaphosphoric acid by heating orthophosphoric acid is complicated by a number of factors. The changes which take place are complex—Copson, Gordon, and Baskervill (1942), Easterwood (1942), Holt and Meyers (1911 and 1913), Pascal and Réchid (1933), Réchid (1933), and Tredwell and Leutwyler (1937)—and the composition of the product depends on the temperature, time and rate of heating, rate of subsequent cooling, the presence of metal phosphates, etc. Technical complications are also encountered in the choice of vessels in which the reaction may be carried out. Platinum, silver nickel, stainless steel, Pyrex glass, silica, etc., are all seriously attacked by the hot acid and so cannot be utilised for the purpose.

Following the suggestion of Graham (1833) gold vessels were employed in these studies. This material was found to be entirely satisfactory.

When orthophosphoric acid is heated, the acid boils and most of the free water passes off. Fuming commences when the transformation to the pyro-acid has almost reached a maximum. At this stage the melt becomes progressively more viscous as the pyro- is transformed to the meta-acid.

Samples withdrawn at the earlier stages are very deliquescent and readily soluble. They contain appreciable quantities of the pyro-acid. Further heating results in a harder product which, while still deliquescent, is not as readily soluble. The approximate composition then is 50% meta- and 25% pyro- P_2O_5.

Continued heating past this point results in a brittle glasslike deliquescent solid which, in water, decrepitates noisily forming a turbid suspension that dissolves slowly. Further heating results finally in an almost insoluble non-deliquescent glass.

The dehydration proceeds until the P_2O_5 content of the product reaches about 78% (HPO_3 requires 88.7%), and then this material apparently volatilises unchanged.

When sodium phosphates are present in the melt, some polyphosphates, intermediate between pyro- and metaphosphates, are formed. The changes are hastened and solid products are produced more easily than in the absence of sodium. The solid forms are probably polymers of metaphosphoric acid. Holt and Meyers (1911) and Réchid (1933).

6. Experimental Preparations.

A series of lots of 300 ml. of 89% orthophosphoric acid containing varying amounts of sodium, added as strong caustic soda, were heated in a gold beaker of 500 ml. capacity directly over a Fisher burner; samples of about 1 g. were removed from time to time for analysis. In some preparations the temperature of the melt was taken periodically.

The details of the individual lots are as follows:—

Run I. (Fig. I.) 300 ml. of 89% orthophosphoric acid was heated carefully until boiling ceased and then more strongly.

Run II. (Fig. II.) A mixture of 250 ml. of 89% acid and 14 ml. of 16.8 N NaOH were heated as in Run I.

Run III. (Fig. III.) As for Run II., but 50 ml. of 16.9 N NaOH added before heating.

Run IV. (Fig. IV.) As for previous runs, but 100 ml. of NaOH used.

The effects of increasing concentrations of sodium in the mixture may be seen from the foregoing figures.

The changes from ortho- to pyro- and pyro- to metaphosphate are obviously hastened, and a readily soluble product of high meta-: pyro- ratio, which may be cast into sticks, is formed more easily.

It is essential to control the heating if reproducible results are desired.

The effect of temperature on a series of batches of a mixture of orthophosphoric acid and trisodium orthophosphate, yielding about 16% Na_2O in the final product, was investigated. Batches of the mixture were heated to boiling and the temperature allowed to rise to 300°, 325°, and 350°C. respectively. At these levels the heating was regulated to maintain the temperature until the desired product was obtained.

The final method for the laboratory preparation was determined from the analytical data derived from these runs.

7. Laboratory Preparation of Glacial Metaphosphoric Acid.

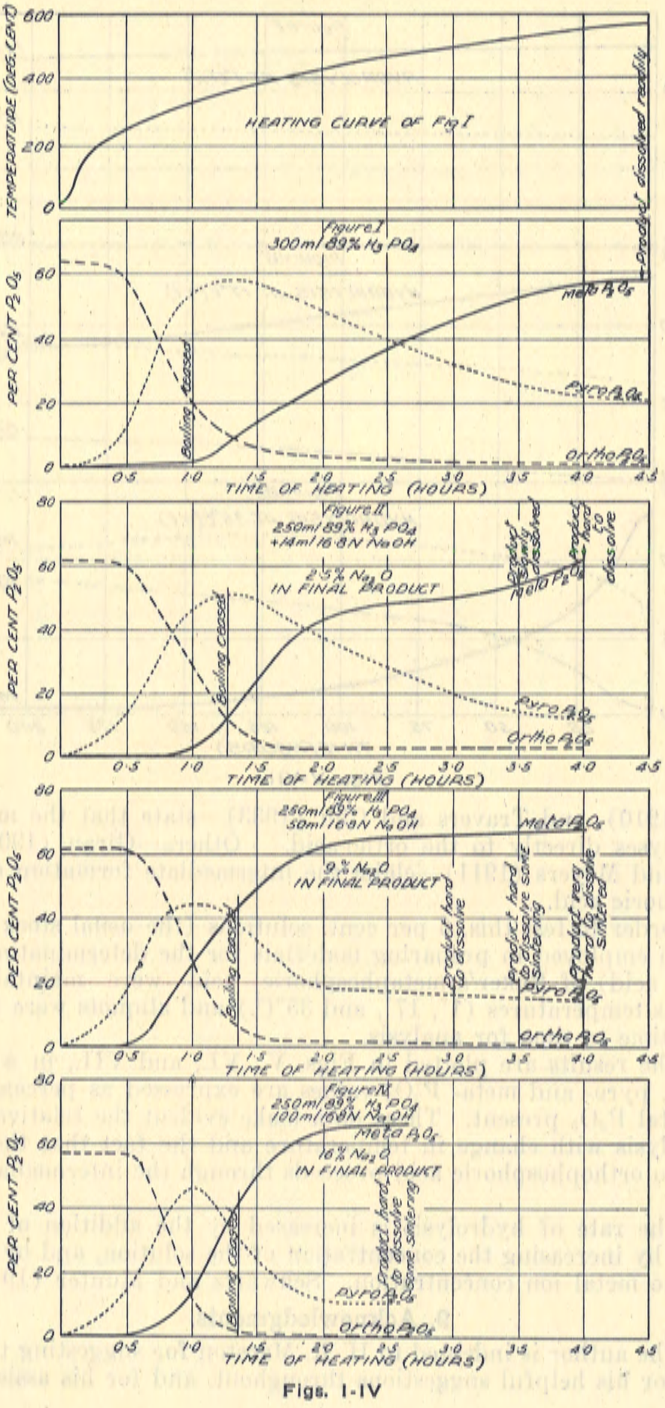
A mixture of 280 g. of 89% orthophosphoric acid and 150 g. of trisodium orthophosphate (8.4 moles of H_2O) is heated in a gold vessel. The rate of heating is controlled so that the temperature of the mixture follows the heating curve (Fig. VIII.). This entails rapid heating to boiling point, and subsequent steady boiling until a temperature of 300°C. is reached. The heat is then controlled so that the temperature of 350°C. is reached in one and a half hours after heating began. This temperature is maintained for a further 1.5 hours. At this stage the product is poured into a cold chromium-plated iron mould.

About 290 g. of clear glass-like sticks of the following composition is obtained: 52% meta- P_2O_5, 23% pyro- P_2O_5, 16% Na_2O, 8% combined water.

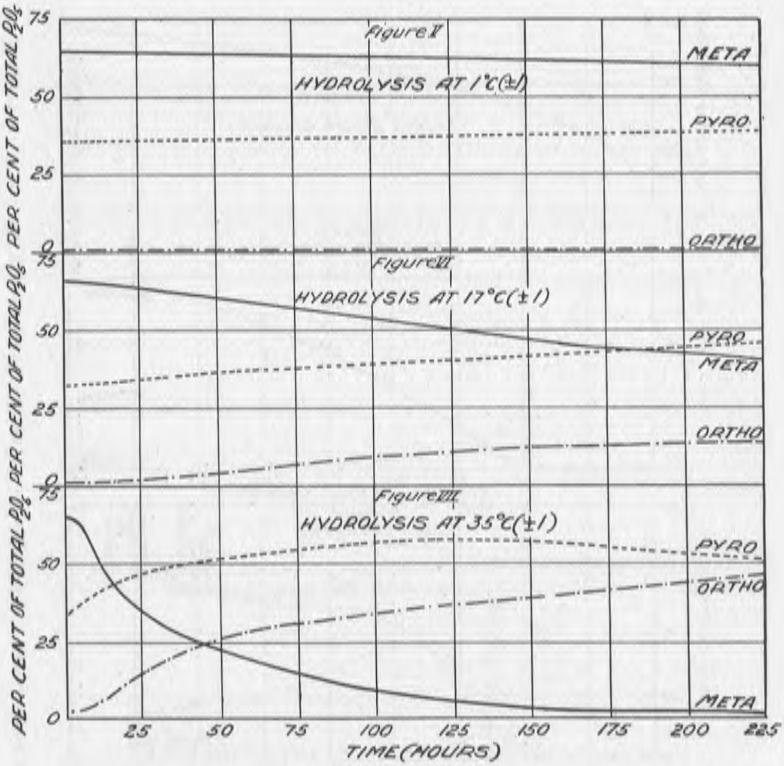
This material dissolves readily and keeps well if stored at once in well stoppered bottles, and may be considered high quality reagent "Glacial Metaphosphoric Acid."

8. Hydrolysis of Metaphosphoric Acid.

Two distinct courses have been proposed for the hydrolysis of metaphosphoric acid solutions. Some authors—Sabatier (1888), Bala-


TEMPERATURE (DEG. CENT)
600
400
200
0
HEATING CURVE OF Fig I
Product dissolved readily
Figure I
300 ml 89% H_3PO_4
PER CENT P_2O_5
60
40
20
0
Boiling ceased
Meta P_2O_5
Pyro P_2O_5
Ortho P_2O_5
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
TIME OF HEATING (HOURS)
80
Figure II
250 ml 89% H_3PO_4
+14 ml 16·8N NaOH
2·5% Na_2O
IN FINAL PRODUCT
Boiling ceased
Product slightly dissolved
Product hard to dissolve
Meta P_2O_5
Pyro P_2O_5
Ortho P_2O_5
TIME OF HEATING (HOURS)
Figure III
250 ml 89% H_3PO_4
50 ml 16·8N NaOH
9% Na_2O
IN FINAL PRODUCT
Meta P_2O_5
Boiling ceased
Product hard to dissolve
Product hard to dissolve some sintering
Product very hard to dissolve sintered
Pyro P_2O_5
Ortho P_2O_5
TIME OF HEATING (HOURS)
Figure IV
250 ml 89% H_3PO_4
100 ml 16·8N NaOH
Meta P_2O_5
16% Na_2O
IN FINAL PRODUCT
Boiling ceased
Product hard to dissolve some sintering
Pyro P_2O_5
Ortho P_2O_5
TIME OF HEATING (HOURS)

Figs. I-IV



Figs. V-VII

reff (1910), and Travers and Chu (1933)—state that the meta-acid hydrolyses directly to the ortho-acid. Others—Giran (1903), and Holt and Meyers (1911)—claim the intermediate formation of pyrophosphoric acid.

In order to test this, 6 per cent. solutions (the usual stock concentration employed in preparing materials for the determination of ascorbic acid) of Baker's metaphosphoric acid were maintained at various temperatures (1°, 17°, and 35°C.) and aliquots were removed from time to time for analysis.

The results are plotted in Figs. V., VI., and VII., in which the ortho-, pyro- and meta- P_2O_5 values are expressed as percentages of the total P_2O_5 present. These data make evident the relative rate of hydrolysis with change in temperature and the fact that the hydrolysis to orthophosphoric acid proceeds through the intermediate pyro-stage.

The rate of hydrolysis is increased by the addition of mineral acids, by increasing the concentration of the solution, and by increasing the metal ion concentration. Schwartz and Munter (1942).

9. Acknowledgments.

The author is indebted to H. R. Marston for suggesting the problem, for his helpful suggestions throughout, and for his assistance in

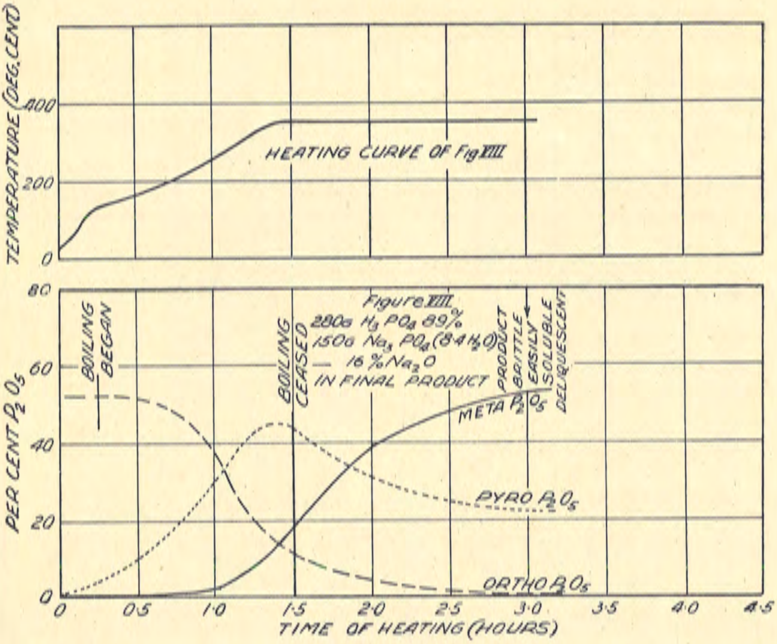


Fig. VIII

preparing the manuscript. He is grateful also to G. W. Bussell for preparing the figures, to W. R. Wood for technical assistance, and to his colleagues J. W. H. Lugg, A. B. Beck, and D. W. Dewey, for suggestions and help during the course of the work.

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[*Reprint from the Journal of the Council for Scientific and Industrial Research, Vol.* 20, *No.* 2, *May*, 1947.]

Furfural: A Pilot Plant Investigation of Its Production from Australian Raw Materials

By I. Brown, B.Sc. (Hons.), E. F. Symons,* and B. W. Wilson, M.Sc.**

Summary.

A pilot plant investigation of a single-stage digestion process for the production of furfural from oat-hulls and maize-cores is described. The variations in yield obtained over a wide range of operating conditions are given, together with the data necessary for the design of full-scale digestion equipment.

A critical study of the recovery of furfural from the digestion products by distillation is described and the necessary data are given for the design of column condensers.

The cost of production of furfural in Australia from oat-hulls was found to be approximately 1s. per pound, based on a plant designed for the production of 200 tons of furfural per year.

1. Introduction

The purpose of the work described in this paper was to collect and summarize previously published data on the manufacture of furfural and to design and operate a pilot plant suitable for the production of furfural from Australian agricultural waste materials. Sufficient data were obtained to permit the rational design of a large-scale plant to suit Australian conditions and to permit a preliminary estimation of production costs.

Furfural is produced in aqueous solution by the steam distillation under pressure in the presence of a catalyst, of a wide variety of agricultural wastes such as oat-hulls, maize-cores, and other cellulosic materials and is recovered from the distillate by fractional distillation. The earliest commercial development of this process occurred in the United States of America where attempts (1-7) were made to derive useful products, in particular furfural, from maize-cores and later from oat-hulls (8). A pilot plant investigation by La Forge and Mains (9) showed that the industrial production of furfural was economically feasible, and work on the distillation of furfural solutions by Mains (10, 11, 12) greatly facilitated the development of the commercial production of furfural. The industry developed rapidly after the introduction of a process for refining lubricating oils (13) in which furfural is used as a selective solvent. The design and operation of plants developed during this period has been described by Killeffer (14) and Brownlee (15). In contrast to the development of American processes, European industry has favoured processes in which furfural is produced in conjunction with pulp or alcohol (16, 17, 18). Recently this type of process has been re-investigated in America (19) with a view to the simultaneous production of furfural and alcohol from agricultural wastes.

The main difference between these processes is in the methods employed for digestion. In the American process the pentosan hydrolysis and the dehydration of pentoses to furfural are carried out

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in a single stage using high pressure or superheated steam. The European processes employ a two-stage digestion consisting of a low temperature pentosan hydrolysis followed by the dehydration of the pentoses at elevated temperature after their separation from the cellulosic material. Both types of digestion can be carried out batchwise or continuously.

In selecting a suitable digestion process for pilot plant development, continuous methods were eliminated because of the probable small demand for furfural in Australia, and the use of superheated steam was avoided because of the expected difficulties of agitating and discharging the semi-solid mass from the digester. The process selected for investigation was the single-stage digestion and steam distillation of the pentosan-containing material at elevated pressure in the presence of dilute sulphuric acid. Also, some aspects of a two-stage process were investigated by Wilson*.

Furfural can be obtained from any pentosan-containing material; the most favoured materials for its production are oat-hulls and maize-cores, although such diverse materials as rice-hulls, flax-shives, straw, and wood have been used (20). A survey of the potential raw materials in Australia which took into account their pentosan content and probable costs, led to the choice of oat-hulls as the main raw material for this investigation, because in Australia oats are milled at centres close to existing chemical industries while maize is milled at country centres.

The major use of furfural is as a cheap solvent and particularly as a selective solvent in the refining of lubricating oils, but its chief uses in Australia are as a substitute for formaldehyde in phenol formaldehyde resins and as a solvent in the paint and coatings industries.

For convenience in presentation the description of the work has been divided into the following sections:—

The Process Study of the Digestion.
The Pilot Plant Investigation of the Digestion.
The Recovery of Furfural from the Digestion Product.
The Cost of Furfural Production.

2. The Process Study

Before designing the pilot plant it was necessary to have some knowledge of the relative importance of the variables of the digestion process, and, in particular, it was necessary to know the limits within which the pilot plant would be required to operate.

These variables were as follows:—

1. Pressure and temperature of operation.
2. Catalyst concentration.
3. Period of digestion.
4. Steam throughput.
5. Liquid/solid ratio.
6. Type and degree of agitation.

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* This *Journal*, p. 258.

Some of this information was available in the literature, but to determine the remainder and to verify published results for Australian raw materials a study was undertaken in equipment available at the time.

(i) The process equipment.

The digester used for the process study was a copper-lined, mild steel, steam-jacketted unit designed to operate at pressures up to 200 lb./sq. in. The digester, which was 24 inches in diameter by 24 inches deep, was fitted with a slow-speed paddle-type stirrer, a filling opening, vapour outlet line, waste discharge valve, and all necessary pressure gauges and safety valves. Live steam was introduced just above the waste discharge valve and the furfural laden vapour was passed through the vapour outlet valve and an orifice-type flowmeter to a copper condenser. The condensate was collected in a copper tank mounted on platform scales.

(ii) The operating procedure.

The digester was charged with 60 lb. of air-dry oat-hulls and the required quantities of water and sulphuric acid. Steam was introduced into both the digester and the jacket and the required digestion pressure was obtained in about five minutes. To prevent excessive condensation of the live steam in the digester, the jacket pressure was adjusted to exceed the digestion pressure by 25 lb./sq. in. throughout the running and blowing-down periods.

The vapour outlet valve was adjusted to give the required condensate rate and the digestion pressure was maintained constant by controlling the live steam input. On completion of the digestion the digester pressure was reduced to atmospheric over a period of 30 to 60 minutes and the spent material discharged. Samples of the aqueous condensate were taken at intervals during the digestion and subsequently analysed to determine the rate of furfural production; the total product was sampled to determine the over-all yield.

(iii) Analytical methods.

Furfural.—The furfural content of aqueous furfural solutions was determined by a modification of the method of Hughes and Acree (21).

About 150 g. of crushed ice, or sufficient to maintain the temperature of the solution at 0°C. during the titration, is placed in a 500 ml. iodine flask and a 25 ml. aliquot of the furfural solution containing from 50 to 100 mg. of furfural added. To this mixture is added 25·00 ml. of decinormal potassium bromate solution containing 50 g. per litre of potassium bromide, the ice-cold mixture is quickly acidified with 17 ml. of concentrated hydrochloric acid, and the stoppered flask is shaken and allowed to stand for from five to seven minutes with occasional shaking. After the addition of 10 ml. of an aqueous solution of potassium iodide containing 150 g. per litre, the mixture is titrated with decinormal sodium thiosulphate. One ml. of decinormal potassium bromate is equivalent to 0·00480 g. of furfural.

The method was checked using solutions made from furfural carefully purified by the method of Evans and Aylesworth (22) and the results compared with those obtained using the gravimetric thiobarbituric acid method of Mackney and Reynolds (23). The results of the comparison are shown in Table 1.

TABLE 1.—A COMPARISON OF ANALYTICAL METHODS FOR FURFURAL.

Mg. Furfural per Aliquot.	Weight Percentage of Furfural.			Error in Bromate Estimation.
	As Weighed.	Gravimetric Method.	Bromate Method.	
				%
10·36	1·036	1·045	1·092 ± 0·112	± 10
27·00	2·695	2·610	2·736 ± 0·138	± 5·4
51·80	1·036	1·045	1·047 ± 0·011	± 1·0
67·38	2·695	2·610	2·710 ± 0·025	± 0·92

The errors shown for the bromate method represent the errors due to those of the burette readings made in the standardization of the solutions and in the analysis.

These results show that the bromate method has an accuracy of 1 per cent. when using synthetic solutions of furfural containing at least 50 mg. per 25 ml. aliquot.

Solid raw materials were analysed for furfural by distilling samples with 12 per cent. hydrochloric acid (24) and determining the furfural content of the distillate by the bromate method.

(iv) The study of the process variables.

An indication of the optimum operating conditions for the production of furfural from both oat-hulls and maize-cores was obtained from a series of experiments in which the effect of each of the process variables was studied over a wide range.

The results of this process study are shown in Figs. 1 and 2 and indicate that the best yield of furfural from oat-hulls is obtained when the operating conditions are in the following ranges:—

Catalyst concentration, 1·0 to 1·5 lb. of 93 per cent. H_2SO_4/100 lb. dilute acid.

Working pressure, 120 to 140 lb./sq. in. (gauge).

Liquid/solid ratio, 0·5 to 2·0.

Steam throughput, exceeding 65 lb./(hr.) (100 lb. oat-hulls).

The optimum period of digestion was found to be from 3 to 4 hours at working pressure.

The results obtained with maize-cores were substantially the same.

Throughout this work the raw materials were weighed in an air-dry condition as they were received from storage under cover and all yields are expressed on the air-dry basis. The best percentage recoveries of furfural from oat-hulls and maize-cores were 57·2 and 52·5 respectively, indicating that factors other than these operating conditions play an important part in determining the yield of furfural. These limiting factors are discussed in an accompanying paper.

PROCESS STUDY WITH OAT-HULLS.

Furfural yield in 3 hour runs.

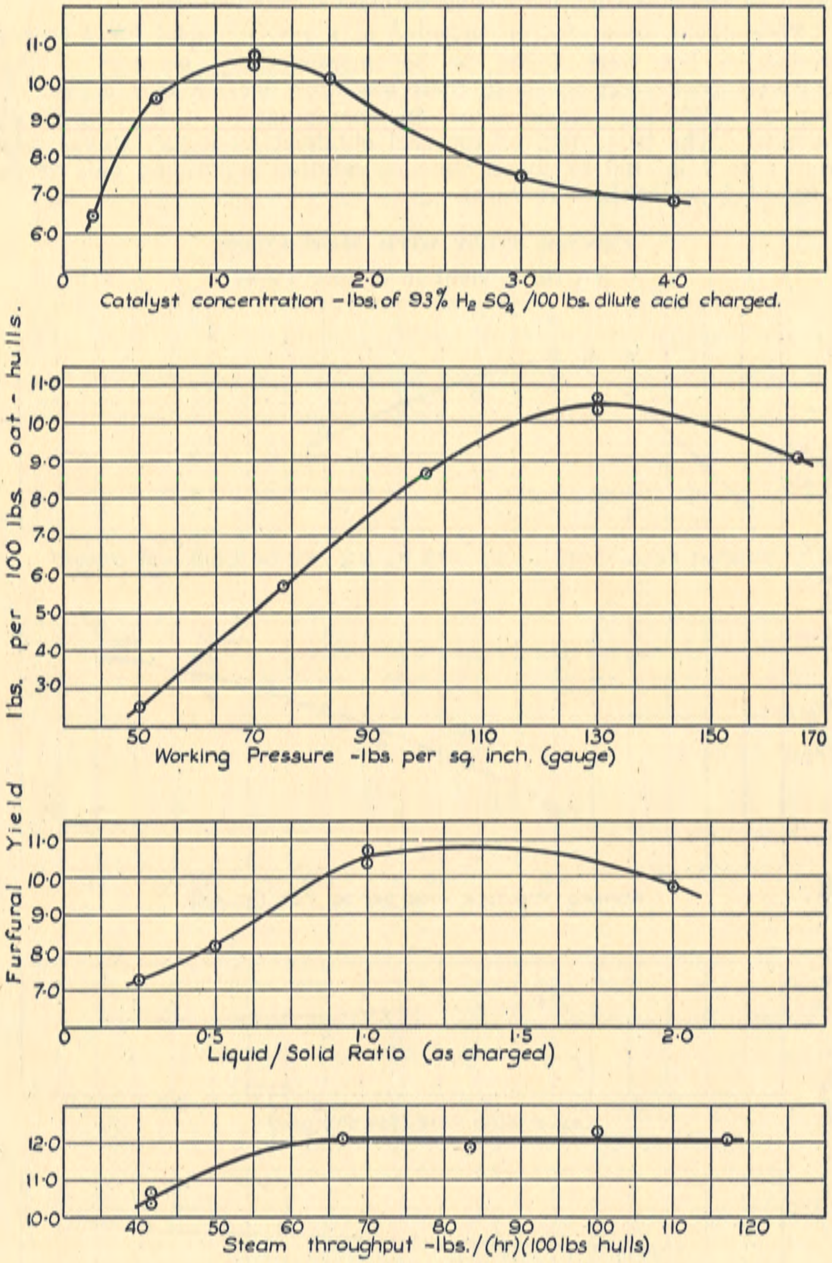

FIG. 1.

Under the optimum conditions for furfural production from oat-hulls 1·4 lb. of acids (expressed as acetic) were produced per 100 lb. of raw material at a concentration of 0·72 per cent. in the condensate, while the corresponding figures for maize-cores were 2·25 lb./100 at a concentration of 0·6 per cent. The quantity of acetic acid was found to increase with increasing catalyst concentration.

Flax shives were also investigated as a raw material for furfural production but were found to be unsatisfactory because of the relatively poor yield obtained, their low bulk density of 7 lb./cu. ft. and the difficulty encountered in manipulating this long-fibred material. The best yield of furfural obtained from flax shives was from 6 to 7 lb./100 lb. in an aqueous solution containing only from 1·0 to 1·5 per cent. of furfural.

PROCESS STUDY WITH MAIZE-CORES.
Furfural yield in 3 hour runs.

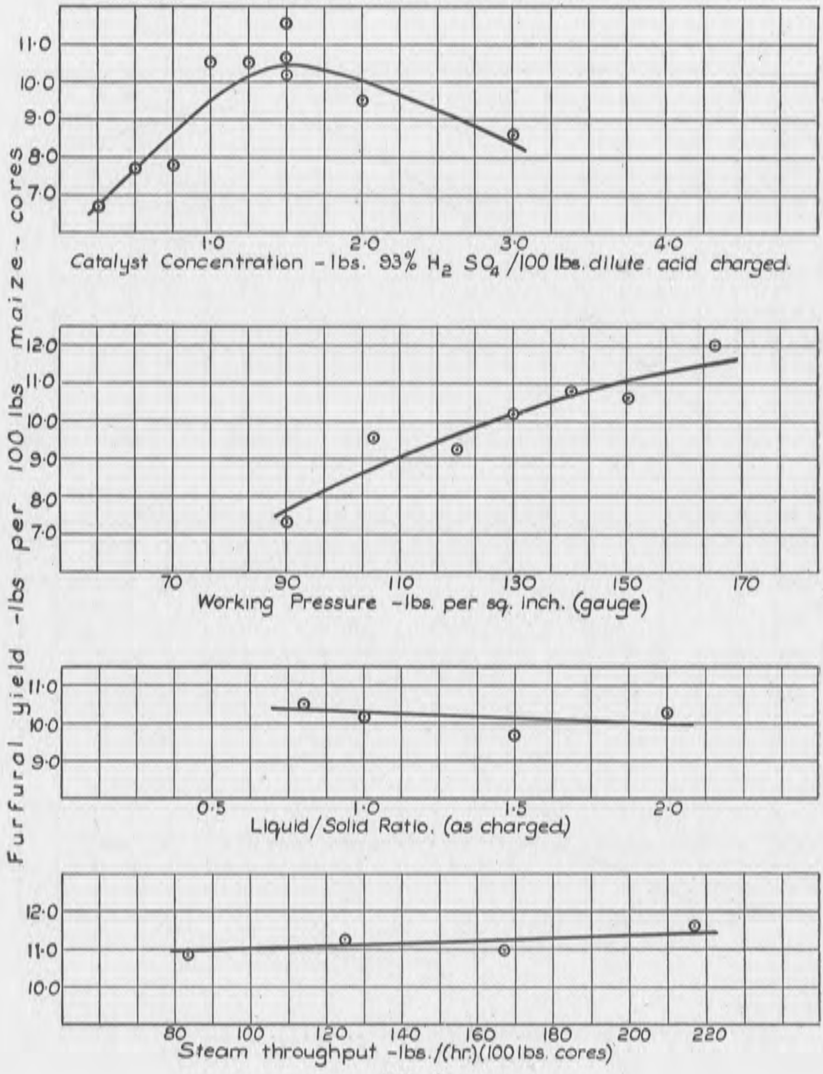

FIG. 2.

(v) The determination of additional data for pilot plant design.

Experience gained during the process study showed that it would be essential to control accurately the flowrate of live steam to the digester and the amount of indirect heat supplied, to maintain a constant liquid/solid ratio throughout the digestion period. It was also found to be essential to provide agitation, to increase the depth : diameter ratio of the digester because of the considerable decrease in the bulk of the raw material in the early stages of the digestion, and to provide a filter for the removal of wax from the condensate.

3. The Pilot Plant Investigation

(i) The pilot plant.

The pilot plant digester and auxiliary equipment, which is illustrated in Plate 1, was designed for the digestion of 300 lb. of oat-hulls per batch and was arranged on three levels. The uppermost level housed the mild steel charging hopper of 30 cubic feet capacity, a 50-gallon copper dilute acid tank, and the condenser which was a horizontal, four-pass, floating-head unit with fifteen ½-in. diameter, 13-gauge copper tubes per pass. The central operating level housed the digester, the instrument panel, the 180 gallon capacity copper condensate tank mounted on platform scales, and a condensate filter. Two copper condensate storage tanks each of 230 gallons capacity were mounted below the operating level and a mobile rectangular mild steel tank of 32 cubic feet capacity was provided at ground level for the removal of the residue discharged from the digester.

The vertical cylindrical digester, 5 feet long and 2 ft. 6 in. in diameter, which was fabricated from ⅜-in. mild steel plate, was provided with a 3-in. bronze gate valve for discharging, a live steam inlet, and a footstep bearing for the stirrer shaft. The flanged dished cover, which had an 8-in. diameter filling opening, a central stirrer mounting, and a 2-in diameter vapour outlet, was attached to the digester body with forty ¾-in. diameter high tensile steel bolts. The body and cover were lined with 10-gauge copper which proved satisfactory throughout this work. Indirect heating was provided by a steam coil of ten turns of 1-in. diameter copper tube spaced at 1¾-in. centres and mounted 2 inches from the walls of the digester. The stirrer consisted of three pairs of bronze paddle blades rotating at 32 r.p.m. and driven through a reduction gear by a 3-h.p. electric motor.

All control valves and measuring instruments were situated on the instrument panel. The live steam entering the digester was measured with an orifice flowmeter actuating an electrically indicating mercury manometer. The vapour flow from the digester was controlled from an orifice flowmeter but was measured by direct weighing of the condensate. Pressure, both in the digester and in the steam coil, was determined by calibrated pressure gauges, the volume of condenser-water by a calibrated positive displacement water meter, and the stirrer power consumption by a kilowatt-hour meter.

(ii) Method of operation.

The digester was charged with 300 lb. of raw material and the required quantity of dilute acid. Live steam was admitted at the rate of 300 lb./hour to sweep air from the digester through the filling opening, the digester was then closed and the live steam rate adjusted to permit the attainment of working pressure in from 45 to 60 minutes. Stirring was commenced when the digester pressure reached 40 to 50 lb./sq. in. and, just before the working pressure was reached, the steam pressure in the heating coil was adjusted to exceed the working pressure by 15 lb./sq. in. The live steam inlet and vapour outlet valves were then adjusted to give the desired rate of steam throughput and, during the digestion period, the working pressure was maintained constant by the adjustment of the steam pressure in the heating coil.

At the conclusion of the digestion period the live steam valve was closed and the rate of vapour discharge increased to about 300 lb./hour to reduce the digester pressure to atmospheric in 30 minutes.

Readings of gauges and meters were recorded at five minute intervals and condensate samples were taken when required. The total condensate was weighed and sampled and then allowed to cool overnight before filtering and storing for subsequent distillation.

(iii) Experimental results from the pilot plant investigation.

(*a*) *The Effect of Variation of Operating Conditions on the Yield of Furfural.*

The experimental results obtained with oat-hulls in runs of three hours duration at working pressure are shown in Table 2 and the results obtained with maize-cores in similar runs are shown in Table 3. These results indicate the variation in yield of furfural which may be expected by varying the conditions of digestion. Results obtained with rice-hulls, hardwood sawdust, and flax shives are compared with those for oat-hulls and maize-cores in Table 4. The operating conditions used in these latter experiments were not necessarily the optimum ones for each material.

(*b*) *The Effect of the Period of Digestion on the Yield and Concentration of Furfural.*

The digestion period can be divided into three parts, the period required to achieve the working pressure, the period at the working pressure, and the period required to reduce the working pressure to atmospheric or the " blow-down " period.

The results of runs of different duration, using oat-hulls and maize-cores, and having the condensate from the working period and blow-down period collected separately, are shown in Table 5 and in Figs. 3 and 4.

The furfural concentration in the vapour from the digester throughout a typical five-hour run and during the " blow-down " period of a three and four-hour run is shown in Fig. 5.

(*c*) *The Use of Sodium Bisulphate as Catalyst.*

It has been suggested (25) that the addition of metallic salts to the digestion mixture might increase the yield of furfural due to their tendency to increase the critical solution temperature of furfural-water mixtures.

Some runs were carried out using sulphuric acid as the catalyst with and without the addition of an equivalent quantity of sodium sulphate. The results of these runs showed that the addition of the

TABLE 2.—RESULTS OBTAINED IN THREE-HOUR RUNS WITH OAT-HULLS.

Run Number.	Catalyst Concentration Percentage H_2SO_4.	Working Pressure lb./sq. in.	Liquid/Solid Ratio as Charged.	Steam Throughput lb./(hr.) (100 lb.).	Furfural.	
					Condensate Concentration Percentage.	Yield lb./100 lb.
B 27	1·0	130	1·5	66·7	3·80	9·9
B 18	1·25	,,	,,	,,	4·00	10·4
B 20	,,	,,	,,	,,	3·90	10·4
B 60	,,	,,	,,	,,	4·15	10·5
B 37	1·5	,,	,,	,,	4·15	10·9
B 66	,,	,,	,,	,,	3·62	9·9
B 85	,,	,,	,,	,,	3·92	9·9
B 87	,,	,,	,,	,,	4·46	11·3
B 39	1·75	,,	,,	,,	3·73	9·3
B 41	1·25	110	,,	,,	3·70	9·5
B 61	,,	,,	,,	,,	4·06	10·1
B 35	,,	120	,,	,,	3·95	9·8
B 36	,,	,,	,,	,,	3·98	9·6
B 55	,,	,,	,,	,,	4·25	10·5
B 56	,,	,,	,,	,,	4·26	11·2
B 57	,,	,,	,,	,,	4·25	10·6
B 18	,,	130	,,	,,	4·00	10·4
B 20	,,	,,	,,	,,	3·90	10·4
B 60	,,	,,	,,	,,	4·15	10·5
B 43	,,	140	,,	,,	3·80	9·6
B 48	,,	,,	,,	,,	3·90	9·9
B 50	,,	,,	,,	,,	3·70	9·6
B 53	,,	,,	,,	,,	4·15	10·8
B 54	,,	,,	,,	,,	3·87	10·1
B 58	,,	,,	,,	,,	4·15	10·8
B 59	,,	,,	,,	,,	4·00	10·5
B 44	,,	150	,,	,,	3·70	9·7
B 46	,,	,,	,,	,,	3·74	10·6
B 51	,,	,,	,,	,,	3·87	10·5
B 52	,,	,,	,,	,,	3·80	10·2
B 34	,,	130	1·25	,,	4·20	10·5
B 18	,,	,,	1·50	,,	4·0	10·4
B 20	,,	,,	1·50	,,	3·9	10·4
B 71	,,	,,	1·75	,,	3·7	9·9
B 94	,,	,,	1·75	,,	3·8	9·8
B 30	,,	,,	1·50	58·4	4·28	9·6
B 29	,,	,,	,,	61·6	4·05	10·0
B 18	,,	,,	,,	66·7	4·00	10·4
B 20	,,	,,	,,	,,	3·90	10·4
B 60	,,	,,	,,	,,	3·80	9·9
B 61	,,	,,	,,	,,	4·15	10·9
B 22	,,	,,	,,	75·0	3·65	10·7
B 25	,,	,,	,,	,,	3·75	10·5
B 26	,,	,,	,,	,,	3·60	10·7
B 21	,,	,,	,,	83·4	3·25	10·2

TABLE 3.—RESULTS OBTAINED IN THREE-HOUR RUNS WITH MAIZE-CORES.

Run Number.	Catalyst Concentration Percentage H_2SO_4.	Working Pressure lb./sq. in.	Liquid/Solid Ratio as Charged.	Steam Throughput lb./(hr.) (100 lb.).	Furfural.	
					Condensate Concentration Percentage.	Yield lb./100 lb.
B 112	0·5	130	1·5	66·7	3·22	7·9
B 111	1·0	,,	,,	,,	3·67	9·4
B 109	1·25	,,	,,	,,	3·48	9·0
B 108	1·50	,,	,,	,,	3·14	8·4
B 129	1·50	,,	,,	,,	3·32	8·4
B 110	1·75	,,	,,	,,	2·64	6·9
B 121	1·50	110	,,	,,	3·41	8·0
B 120	,,	120	,,	,,	3·48	8·1
B 108	,,	130	,,	,,	3·14	8·4
B 129	,,	130	,,	,,	3·32	8·4
B 123	,,	140	,,	,,	3·08	7·3
B 122	,,	150	,,	,,	2·96	7·3
B 113	1·5	130	1·0	,,	2·65	6·2
B 108	,,	,,	1·5	,,	3·14	8·4
B 129	,,	,,	1·5	,,	3·32	8·4
B 114	,,	,,	2·0	,,	2·61	7·2
B 115	,,	,,	1·5	50·0	2·90	5·6
B 116	,,	,,	,,	58·4	3·05	6·6
B 108	,,	,,	,,	66·7	3·14	8·4
B 129	,,	,,	,,	66·7	3·32	8·4
B 119	,,	,,	,,	75·0	3·29	8·4
B 118	,,	,,	,,	83·4	3·03	8·5

TABLE 4.—RESULTS OBTAINED WITH VARIOUS RAW MATERIALS.

Raw Materials and Run Number.	Raw Material.			Operating Conditions.*		Total Furfural Content of Products lb./100 lb.			Yield lb./100 lb.	Percentage Recovery.
	Bulk Density lb./cu. ft.	Contents lb./100 lb.		Catalyst Concentration Percentage H_2SO_4.	Steam Throughput lb./(hr.)(100 lb.).	Liquid Residue.	Solid Residue.	Condensate.		
		Furfural.	Moisture.							
Oat-hulls B 104 ..	13·2	19·0	9·9	1·5	66·7	0·32	0·78	3·60	9·2	48·5
Maize-cores B 129 ..	11·5	20·3	6·1	1·5	66·7	0·29	0·47	3·32	8·4	41·2
Rice-hulls B 131 ..	8·7	9·8	9·2	1·0	70·0	0·19	0·40	1·74	5·0	51·5
Hardwood sawdust B 133 ..	13·0	7·0	10·8	1·0	50·0	0·10	0·25	1·28	2·9	41·4
Flax shives A 123 ..	7·0	14·0	..	1·5	73·0	..	..	1·44	7·2	51·4

* These runs were 3-hour runs made at a working pressure of 130 lb./sq. in. and with a liquid/solid ratio of 1·5.

Oat-hulls: Variation of furfural yield with digestion time.

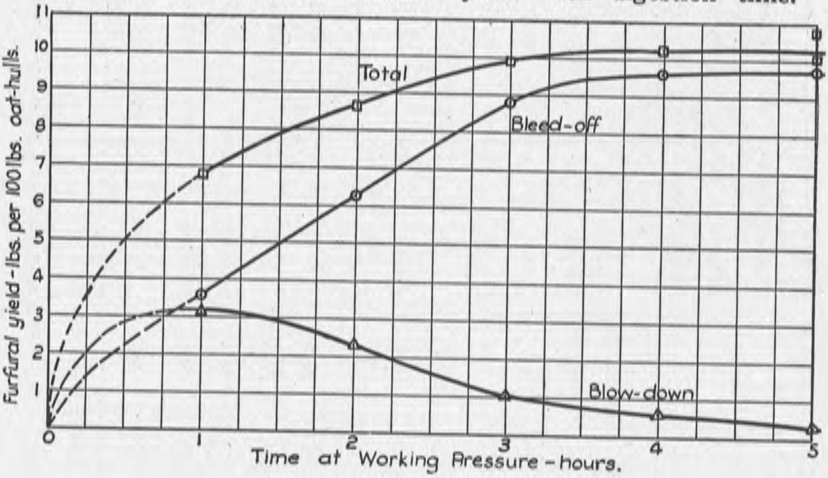

FIG. 3.

Maize-cores: Variation of furfural yield with digestion time.

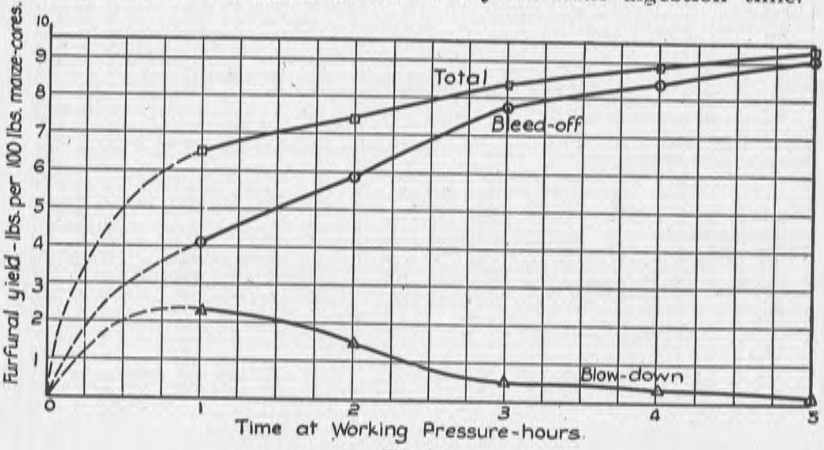

FIG. 4.

Oat-hulls: Variation of furfural concentration with time.

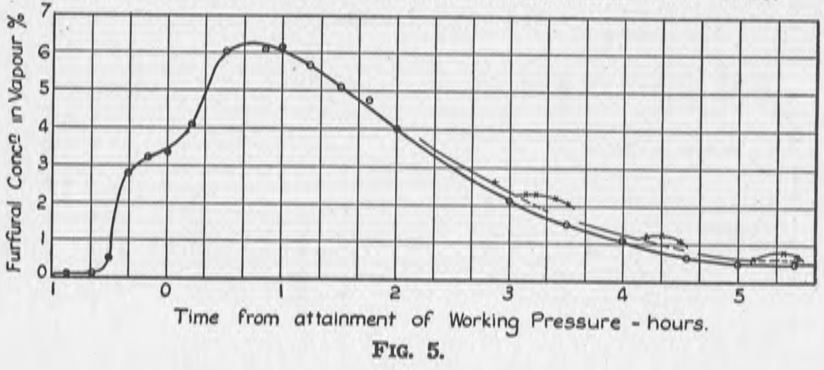

FIG. 5.

TABLE 5.—EFFECT OF DURATION OF DIGESTION ON YIELD OF FURFURAL‡.

Raw Material.	Run Number.	Time at Working Pressure.	Product from Period at Working Pressure.			Product from Blow-Down Period.			Yield.	Furfural Concentration.		Lb. Steam Used per Lb. Furfural.*
			Total.	Furfural.		Total.	Furfural.			At End of Blow-down.	In Total Product.	
		hrs.	lb.	%	lb.	lb.	%	lb.	lb./100 lb.	%	%	
Oat-hulls ..	B 89	1	205	5·27	10·8	155	6·03	9·35	6·7	5·49	5·59	27·3
	B 92	2	392	4·77	18·7	161	4·50	7·25	8·7	4·15	4·68	28·9
	B 66	3	660	4·00	26·4	160	2·05	3·28	9·9	2·00	3·62	32·0
	B 91	4	799	3·60	28·8	159	1·15	1·83	10·2	1·15	3·20	37·6
	B 90	5	1,004	2·90	29·1	147	0·59	0·87	10·0	0·58	2·60	45·0
Maize-cores ..	B 128	1	200	6·12	12·2	169	4·24	7·16	6·5	6·40†	5·25	28·4
	B 134	2	408	4·30	17·6	156	2·98	4·64	7·4	3·50	3·93	33·6
	B 129	3	630	3·70	23·3	128	1·38	1·76	8·4	1·47	3·32	37·9
	B 126	4	797	3·18	25·3	165	0·85	1·40	8·9	0·88	2·78	43·1
	B 124	5	1,016	2·69	27·4	141	0·41	0·58	9·3	0·58	2·42	48·3

* Steam used /lb. furfural calculated on the basis of 200 lb./hr. plus 350 lb. required to heat charge to working pressure.

† For maize-cores these concentrations were at end of working period not at end of blow-down.

‡ The operating conditions used in these runs for oat-hulls and maize-cores were:—Working pressure 130 lb./sq. in., catalyst concentration 1·5 per cent., liquid/solid ratio 1·5, steam throughput 66·7 lb./(hr.) (100 lb. raw materials).

sodium sulphate gave a slight increase (0·5 to 1 lb./100 lb. hulls) in furfural yield over the range of concentration from 1·45 to 4·35 lb. of sodium sulphate per 100 lb. of solution.

Although these tests were not comprehensive they showed that sodium bisulphate could be used as a catalyst, but its advantage over sulphuric acid was not great.

(iv) Discussion of results.

(a) *Catalyst Concentration.*

The best yield of furfural was obtained from oat-hulls, under the conditions specified, with a catalyst concentration of from 1·25 to 1·5 per cent., while a slightly lower concentration of from 1·0 to 1·25 per cent. was the most satisfactory for maize-cores. At a lower catalyst concentration a lower yield was obtained and some difficulty was experienced in discharging the spent mass from the digester, while higher concentrations gave a lower yield, due to increased decomposition of furfural and the intermediate pentoses.

(b) *Working Pressure.*

There was no gain in the yield of furfural from either oat-hulls or maize-cores by increasing the working pressure above 130 lb./sq. in. The use of higher pressures was undesirable as the yield of furfural was decreased owing to an increase in rate of formation of undesirable by-products and to the longer time required to reach working pressure. The use of lower pressures with correspondingly higher catalyst concentrations did not give any improvement in the furfural yield.

(c) *Steam Throughput.*

The yield of furfural from both oat-hulls and maize-cores increased slowly as the steam throughput was increased to about 70 lb./(hr.) (100 lb. raw material) and then remained substantially constant. The use of higher throughputs served only to increase dilution of the aqueous furfural.

(d) *Liquid/Solid Ratio.*

Variation of this factor did not greatly affect the yield of furfural. The best yields of furfural were obtained at a liquid/solid ratio of from 1·25 to 1·5 as charged; values lower than 1·0 produced a thick digestion mixture which was difficult to stir and discharge from the digester, while values higher than 1·75 resulted in increased steam consumption.

(e) *The Period of Digestion.*

The results obtained with oat-hulls indicated that there was no advantage in extending the digestion period beyond three hours and that the period required to reach working pressure should not exceed 30 to 40 minutes. In those cases where the digestion period was extended to five hours the quantity of furfural produced during the fourth and fifth hours was small in relation to the quantity of steam used. Actually almost equal yields of furfural were obtained for the three-hour digestion because of the greater quantity of furfural then produced during the " blow-down " period.

The results of the runs with maize-cores showed the same trend, but indicated that a slightly longer digestion period was an advantage.

In the shorter runs the low yield was due to incomplete stripping of furfural, while in the longer runs the stripping of the furfural was virtually complete.

(v) The optimum conditions for the production of furfural.

The optimum conditions for the production of furfural from oat-hulls and maize-cores in the plant described in this paper are detailed in Table 6.

There was no indication that further alterations in these variables would increase the yield of furfural.

TABLE 6.—THE OPTIMUM CONDITIONS FOR THE PRODUCTION OF FURFURAL.

—	Oat-hulls.	Maize-cores.
Catalyst Concentration	1·25–1·50 per cent. ..	1·0–1·25 per cent.
Working Pressure	120–130 lb./sq. in. ..	120–130 lb./sq. in.
Liquid/Solid Ratio	1·25 to 1·50 ..	1·4 to 1·6
Steam Throughput	65–75 lb./(hr.) (100 lb.)	65–70 lb./(hr.) (100 lb.)
Time of Digestion—		
To Working Pressure ..	30–40 minutes ..	30–40 minutes
At Working Pressure ..	3–4 hours	3–4 hours
Blow-down	30–45 minutes ..	30–45 minutes

(vi) Additional data necessary for the design of digestion plant.

In addition to the determination of the range of operating conditions under which a satisfactory yield of furfural can be obtained, these experiments provided some of the data necessary for the design of larger plant.

Further pilot-plant runs were made to obtain other data necessary for the design of larger digestion equipment.

(a) *The Digester Shape.*

The optimum shape of digester required for carrying out this process depends on the depth of charge necessary to ensure efficient stripping of the furfural by the live steam and on the relationship between digester diameter and power requirements for stirring.

The effect of charge depth and steam throughput on the rate of stripping of furfural was determined in a series of runs in which the steam throughout and the charge depth was varied and in which samples of the condensate were taken hourly to determine the rate of furfural stripping.

TABLE 7.—THE EFFECT OF CHARGE DEPTH AND STEAM THROUGHPUT ON STRIPPING OF FURFURAL.

Run Number.*	Working Depth (feet).	Steam Throughput lb./(hr.) (100 lb. Hulls)	Furfural Stripping Rate lb./(hr.) (100 lb. Hulls) at—			Lb. Steam Used /lb. Furfural Stripped at—			Total Furfural Yield lb./ 100 lb. Hulls.	Total Steam Used / Total Furfural Yield
			1st Hour.	2nd Hour.	3rd Hour.	1st Hour.	2nd Hour.	3rd Hour.		
B 78	2·4	108	4·64	2·71	1·18	23·3	39·8	91·4	11·0	29·5
B 141	2·6	90·0	4·50	2·76	1·31	20·0	32·3	68·7	9·85	27·4
B 142	2·6	90·0	4·63	2·70	1·27	19·5	33·4	70·9	9·81	27·5
B 143	3·2	90·0	4·74	2·62	..	19·0	34·4	..	9·45	28·6
B 144	3·2	90·0	4·79	2·65	..	18·8	34·0	..	9·90	27·3
B 76	3·4	72·0	4·09	2·88	1·69	17·6	25·0	42·6	9·84	21·9
B 75	3·8	74·7	4·20	2·92	1·64	17·8	25·6	45·6	9·83	22·8
B 82	4·8	66·0	3·76	2·74	1·58	17·6	24·1	41·8	9·36	21·0

* These runs were made with a working pressure of 130 lb./sq. in., a liquid/solid ratio of 1·5 and a catalyst concentration of 1·5 per cent.

Since the conversion of pentosan to furfural was complete after the first hour* of the digestion period, subsequent changes in the furfural vapour concentration were dependent only on the rate of stripping.

Results of these tests, shown in Table 7, indicate that a substantially constant value is obtained for the ratio of steam used to furfural stripped when the charge depth exceeds 3·5 feet. Therefore a digester of similar shape to that used in the pilot plant would be suitable for larger scale production although a slightly smaller diameter/height ratio would be preferable from the construction and stirrer power requirement aspects.

(*b*) *Stirring Requirements.*

The effect of stirring on the yield of furfural from oat-hulls was determined from a series of tests, the results of which are shown in Table 8.

TABLE 8.—THE EFFECT OF STIRRING ON FURFURAL YIELD.

Run Number.	Stirrer.	Steam Throughput lb./(hr.)(100 lb.).	Furfural.	
			Condensate Concentration Percentage.	Yield lb./100 lb. Oat-hulls.
B 95	Off	66·7	3·12	7·8
B 97	"	83·4	2·93	7·8
B 98	"	88·0	2·64	8·4
B 18	On	66·7	4·00	10·4
B 20	"	66·7	3·90	10·4

These results showed that stirring was necessary and that the agitating effect of the live steam was small, even at relatively high throughputs. The principal function of the stirrer was to overcome the channelling of the steam. The power consumption of the stirrer at various stages during the digestion is shown in Table 9.

These results showed that the stirrer power requirements were substantially the same for all the raw materials used and that there was a rapid drop in the power consumption during the early stages of the digestion. As no significant loss in yield was obtained when the stirrer was started just before the working pressure was reached, stirring in the early stages would be unnecessary in a production plant.

(*c*) *Digester Condenser Requirements.*

(1) *Pilot plant condenser.*—Preliminary runs with the pilot plant indicated that the over-all heat transfer coefficient for the condensation of the aqueous digestion product was much smaller than that for steam because a substantial quantity of wax from the product was deposited on the condenser tubes, giving a low vapour-side film coefficient which was, in this case, the controlling factor in the heat transfer.

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* This *Journal*, p. 258.

Material and heat balances were made over the pilot plant condenser after the plant had been in operation for some time and the wax deposit had reached a maximum to enable the combined vapour-side film and fouling coefficient to be calculated for use in the design of condensers for a larger furfural plant.

TABLE 9.—THE STIRRER POWER REQUIREMENTS.

Raw Material	Oat-hulls.			Maize-cores.	Hardwood Sawdust.	Rice-hulls.
Run Number	B 102	B 103	B 130	B 126	B 133	B 131
Digester pressure at which stirrer started (lb./sq. in.) ..	Start	60	130	110	70	80
	watts.	watts.	watts.	watts.	watts.	watts.
Stage of Digestion—						
Dry oat-hulls ..	2,160	..	..	..	..	..
Wet oat-hulls ..	2,268	..	..	..	..	..
Pressure—						
1 lb./sq. in. ..	1,435	..	..	..	..	..
60 lb./sq. in. ..	600	1,812	..	..	..	..
130 lb./sq. in. ..	370	550	468	468	504	486
After 1 hr. at W.P.	330	360	432	320	396	360
,, 2 hrs. at W.P.	310	340	360	320	396	360
,, 3 hrs. at W.P.	310	330	300	320	396	324
Total power consumption K.W.H. per run	2·24	1·60	1·20	1·17	1·35	1·28

Accurate calculated values of the vapour-side film coefficient for condensation could not be obtained from the experimental data on the pilot plant condenser, as this four water-pass unit acted as a de-superheater and cooler as well as a condenser. Approximate values could be calculated, however, by assuming single pass operation and first determining the relative tube areas required for de-superheating, condensing, and cooling.

Under favourable operating conditions, with a water exit temperature of about 200°F., the vapour-side film coefficient for condensation of dilute furfural vapour from the digester was found to be of the order of 200 ± 50 B.T.U./(hr.) (sq. ft.) (deg. F.).

(2) *The effect of partial wax removal.*—Runs were also made with an experimental, horizontal, single-tube condenser to determine the effect of partial wax removal by de-superheating the vapour before condensing it. The experimental unit was operated with vapour from a normal digestion, starting with a clean tube and proceeding until constant fouling conditions were obtained as shown by the vapour-side film coefficient remaining substantially constant for subsequent runs.

There was an initial rise in the value of the vapour-side film coefficient from 1220 ± 50 B.T.U./(hr.) (sq. ft.) (deg. F.) to 1430 ± 65 which was probably due to the promotion of dropwise condensation by a thin wax film on the tube surface. This was followed by a rapid fouling of the tube and a simultaneous fall in the value of the film coefficient to 800 ± 30 B.T.U./(hr.) (sq. ft.) (deg. F.) at which value it remained substantially constant.

(d) The Effect of Indirect Heating.

A steam coil was used to provide indirect heating in the pilot plant to compensate for heat losses and to maintain the liquid level constant during the digestion. The use of indirect steam was found to have no appreciable effect on the yield of furfural and would be unnecessary in a larger production unit.

(e) Material Balance Runs.

Material balances were made when operating with oat-hulls under the following operating conditions: working pressure 130 lb./sq. in., catalyst concentration 1·5 per cent., liquid/solid ratio 1·5 and a steam throughput 66·7 lb./(hr.) (100 lb. hulls), with a blow-up time of 52-60 minutes, digestion time of three hours, a blow-down time of 30-35 minutes, and a high water velocity through the condenser to prevent furfural loss from the condensate. The condenser water consumption was calculated on the basis of a water temperature rise of 140 deg. F. and a condensate exit temperature of 210° F. Results are shown in Table 10. The " lignin " values were determined as percentage insoluble in 72 per cent. sulphuric acid (26).

These material balance figures showed clearly what takes place during the digestion process and indicated the quantities of raw materials and utilities required for furfural production. The increase in the " lignin " content of the solid material was due to tarry decomposition products. The wax in the product was found to contain 95 per cent. of fatty acids consisting chiefly of palmitic and oleic acids.

4. The Recovery of Furfural from the Digestion Product

Furfural is most readily recovered from the aqueous solutions obtained from the digestion process by means of distillation, although the solvent extraction methods which have been described (27, 28, 29) may prove more economical for more dilute solutions.

Distillation methods are attractive economically because of the enrichment which occurs when the azeotrope, containing 35 per cent. furfural, separates on cooling into two layers, the lower of which contains 95 per cent. furfural at atmospheric temperature. Pure furfural can be obtained by subsequent distillation of the 95 per cent. product under reduced pressure.

(i) The distillation of aqueous furfural solutions.

The distillation of aqueous furfural solutions has been described by La Forge and Mains (9) and equipment for this separation employing both vapour and liquid feeds has been described (14, 15, 30).

The aqueous furfural solutions obtained from the digestion process normally contain from 2 to 5 per cent. furfural, 0·5 to 1·5 per cent. acids (chiefly acetic) and about 0·05 per cent. of volatiles (chiefly methanol). When the mixture is continuously distilled in a suitable column the furfural water azeotrope, containing 35·0 per cent. furfural and boiling at 208°F., is obtained as a two-phase distillate

TABLE 10.—RESULTS OF MATERIAL BALANCE DIGESTIONS.

Charge.								Steam.					Condensate.					
Run Number.	Water.	93% H_2SO_4.	Oat-hulls.	" Lignin " in Hulls.	" Lignin "	Potential Furfural in Hulls.	Potential Furfural.	Blow-up.	Run.	Coil.	Total.	Stirrer Power Consumption.*	Weight.	Furfural.	Acetic Acid.	Furfural.	Acetic Acid.	Water.
	lb.	lb.	lb.	%	lb.	%	lb.	lb.	lb.	lb.	lb.	kw. hrs.	lb.	%	%	lb.	lb.	lb.
B 102	450	6·75	300	..	..	19·1	57·2	350	603	195	1,148	2·24	761	3·62	0·68	27·6	5·2	728
B 103	450	6·75	300	9·73	29·2	19·0	56·9	350	602	210	1,162	1·67	754	3·65	0·70	27·5	5·3	721
B 104	450	6·75	300	9·73	29·2	19·3	58·0	350	603	201	1,154	1·86	765	3·60	0·65	27·6	5·0	732

* In Run B 102 the stirrer was on from start, in other runs from when digester pressure was 60 lb./sq. in.

Run Number.	Wax in Product.	Total Residue.	Liquid Residue.			Solid Residue.							Requirements for Digestion per lb. Furfural.				
			Wt.	Potential Furfural.	Furfural.	Wet Wt.	Dry Wt.	" Lignin."	Potential Furfural.	" Lignin."	Potential Furfural.	Water.	Steam.	Water.	Power.	Oat-hulls.	93% H_2SO_4.
	lb.	lb.	lb.	%	lb.	lb.	lb.	%	%	lb.	lb.	lb.	lb.	lb.*	kw. hr.	lb.	lb.
B 102	1·25	902	572	0·45	2·5	330	175	..	0·38	..	0·67	155	41·6	217	0·081	10·9	0·25
B 103	..	913	522	0·34	1·9	391	171	49·3	0·78	84·4	1·3	220	42·3	217	0·061	10·9	0·25
B 104	..	894	595	0·30	1·8	299	154	50·4	0·79	77·5	1·2	145	41·8	217	0·063	10·9	0·25

* 200 lb. condenser water and 17 lb. charge water.

which when cooled to 72°F. gives layers consisting of solutions containing 95 and 8·4 per cent. furfural. The aqueous layers can be returned to a suitable point in the column above the feed inlet, but if this is done, it is necessary to remove the volatiles which would otherwise accumulate in the upper part of the column and in the decanter and thereby increase the mutual solubility of the two layers. Almost all the acetic acid is contained in the aqueous waste from the column.

(*a*) *Distillation Column Design Methods.*

(1) *Mains method.*—The only method described for the design of distillation equipment specifically for the recovery of furfural from its aqueous solutions is that of Mains (12) who extended the method of Lewis (31) to take into account the additional liquid feed returned to the column from a continuous decanter.

(2) *The application of McCabe-Thiele method to the distillation of furfural solutions.*—The graphical McCabe-Thiele (32) method was applied to the design of furfural distillation equipment to determine its usefulness for this system, as the Mains method is tedious. A comparison of results obtained by the two methods is shown in Table 11. The calculations in the McCabe-Thiele method were made using the vapour-liquid equilibrium data of Mains (10) and the assumptions that the waste composition was 2 per cent. of that of the feed, that closed steam heating was employed, that the feed, reflux, and decant entered the column as liquids at their boiling points, and that the operation was under conditions of constant molal overflow. The last-mentioned assumption was justified as the molal latent heats of vaporization of furfural and water at their boiling points are 18,580 and 17,460 B.T.U./lb. mole respectively.

TABLE 11.—A COMPARISON OF MCCABE–THIELE AND MAINS METHODS OF COLUMN DESIGN.

Feed Wt. Percentage Furfural.	Reflux Ratio at Top of Column.	Number of Theoretical Plates Required.					
		Lower Section.		Middle Section.*		Upper Section.	
		McCabe.	Mains.	McCabe.	Mains.	McCabe.	Mains.
1	8	>12	..	1·7	..	1·7	..
	7	..	8·5	..	0·6	..	1·8
2	5	5·7	..	1·2	..	1·7	..
	4	7·1	5·7	1·2	0·5	1·7	1·8
	3	11	11	1·6	0·5	1·7	1·8
	2·5	high	19	2·1	0·7	1·7	1·8
3	4	4·5	2·8	0·9	0·3	1·7	1·8
	3	5·3	3·9	1·0	0·3	1·7	1·8
	2	10	..	1·3	..	1·7	..
	1·5	high	16	2·2	1·0	1·8	1·8
4	4	3·9	1·9	0·4	0·2	1·7	1·8
	3	4·4	2·3	0·6	0·2	1·7	1·8
	2	5·7	..	0·8	..	1·8	..
	1·5	7·6	5·8	1·0	0·4	1·8	1·8

* Between feed inlet and decant return.

When live steam heating is employed, additional plates are required in the stripping section of the column. This additional requirement was calculated by the McCabe-Thiele method, assuming one mole of steam used per mole of furfural solution vaporized; and was found to be from 0·2 to 0·4 theoretical plates depending on the ratio of the liquid to vapour flowrates in the stripping section.

(3) *Experimental distillation of furfural solutions.*—Furfural was recovered from the digestion product by distillation either in a 6-in. diameter column packed with ½-in. Raschig rings or in an 8-in. diameter bubble-cap column.

Short trial runs at various reflux ratios with the packed column using a 3·5 per cent. furfural feed showed the H.E.T.P. to be approximately 24 inches based on the number of theoretical plates determined by the McCabe-Thiele method. This high value was due to the high vapour velocities which were about 85 per cent. of the flooding velocity.

The results of four preliminary experiments with the bubble-cap unit operated as a stripping column by the method of Koffolt (33) with a 1·0 per cent. furfural solution as feed and with a waste containing 0·02 per cent. furfural enabled the approximate number of theoretical plates required at various liquid/vapour ratios to be calculated; as shown in Table 12.

TABLE 12.—EXPERIMENTAL RESULTS WITH BUBBLE-CAP COLUMN.

Run Number.	Liquid/Vapour Ratio.	Number of Theoretical Plates.		
		Experimental.	Calculated.	
			McCabe-Thiele.	Mains.
S-7	4·76	10	6·8	4·0
S-4	4·67	9	6·4	3·7
S-5	4·27	6	5·7	3·0
S-6	3·91	5	5·0	2·5

These results indicate that the McCabe-Thiele method is more satisfactory for the design of furfural distillation equipment than the method used by Mains. It is intended to continue work on certain aspects of the distillation of furfural-water mixtures.

(b) *A Comparison of Liquid and Vapour Feed to the Column.*

The use of the digestion product as a direct vapour feed to the column has been employed (14, 15) as an alternative to the condensed product as a liquid feed. A comparison of these two methods was made to determine their relative advantages.

(1) *The comparison for saturated vapour.*—The minimum reflux ratio and the number of theoretical plates at various higher reflux ratios were calculated by the McCabe-Thiele method for both liquid feeds at the boiling point and saturated vapour feeds containing from

3 to 8 per cent. furfural, using live steam and a waste furfural concentration of 1·6 per cent. of that in the feed. From these results suitable reflux ratios were chosen for each feed concentration such that the total number of theoretical plates required was approximately eight. The essential difference between the two methods is that the minimum reflux for vapour feed is from 9·3 to 13·6 times that for liquid feed, owing to the large and relatively sudden change in slope of the equilibrium curve and to the low mole fraction of furfural in the feed.

Material balances were then calculated on the basis of 10 lb. mol./hour passing through the decanter. For these calculations it was assumed that the vapour from the digester was stripped of its wax before passing to the digester condenser or vapour feed column and also that the live steam used in the digester was equal in quantity to the water in the feed to the columns. The condenser water requirements were calculated on a basis of a water temperature rise of 130 deg. F., and the condenser surface areas were determined on a basis of a water velocity of 5 ft./sec. and vapour-side film coefficients of 800 and 1,300 B.T.U./(hr.) (sq. ft.) (deg. F.) for the digester and column condensers respectively.

The column diameters were determined by the method of Bain and Hougen (34) assuming water as the working substance, 1-in. rings as packing and an operating vapour velocity of 70 per cent. of the flooding velocity. The packed volumes were calculated using an H.E.T.P. of 24 inches.

The results of this comparison are shown in Table 13.

(2) *The effect of superheated vapour on the comparison.*—If the vapour from the digester is superheated to the extent of 70 deg. F., the water requirements for the digester condenser in the case of liquid feed would be increased by 3·6 per cent. and the surface area by 17 per cent. This degree of superheating, in the case of a vapour feed, would change the required reflux ratio for a given number of plates by only 5 per cent., would reduce the column steam requirements by 3·5 per cent., and the effect on the required column diameter would be small.

In a liquid-fed column, equipment for the removal of wax from the digester vapour before its condensation is unnecessary provided adequate condenser capacity is installed. Thus, the cost of a wax stripper for the vapour-fed column is counterbalanced by the cost of additional condenser surface area for the liquid-fed column. The additional digester condenser capacity required can be seen in Table 14.

(3) *Conclusions.*—These calculations show that the use of vapour feed slightly decreases the steam and condenser water consumption, decreases the necessary condenser surface area, but increases the diameter of the distillation column and requires the careful removal of waxy materials with an additional scrubbing column. On a basis of cost there would be little difference between the two methods; the liquid-fed unit would be preferable because of its greater flexibility and ease of operation.

TABLE 13.—COMPARISON OF REQUIREMENTS FOR LIQUID AND VAPOUR FEED TO COLUMN.

Concentration of Furfural in Feed.	Minimum Reflux Ratio.		Working Reflux Ratio.		Theoretical Plates req.				Steam Required—lb./hr.					Condenser Surface Area sq. ft.			
					Upper Sections.		Lower Section.		Digester.	Column.		Total.		Digester.	Column.	Total.	
	L.	V.	L.	V.	L.	V.	L.	V.	L. and V.	L.	V.	L.	V.	L.	L.	L.	V.
Wt. %																	
3	1·50	14·2	3·0	15·0	2·7	3·6	5·7	5·7	2,400	720	460	3,120	2,860	95·5	22·4	118	86
4	0·95	10·2	2·0	12·0	2·5	3·4	6·1	4·2	1,800	540	530	2,340	2,330	71·8	16·1	88	70
5	0·80	7·9	1·5	9·0	2·4	3·4	5·6	4·7	1,420	450	360	1,870	1,780	57·2	13·4	71	54
6	0·50	6·5	1·5	7·0	2·3	3·5	5·4	5·5	1,160	450	260	1,610	1,420	47·8	13·4	61	43
7	0·40	5·4	1·0	6·0	2·0	3·2	4·7	4·4	990	360	250	1,350	1,240	41·0	10·8	52	38
8	0·33	4·5	1·0	5·0	2·0	3·2	5·0	4·2	840	360	210	1,200	1,050	34·4	10·8	45	32

Concentration of Furfural in Feed.	Condenser Water—gal./hr.				Column Diameters—in.				Packed Volume—cu. ft. of 1-in. Rings.					
	Digester.	Column.	Total.		Upper Sections.		Lower Section.		Upper Sections.		Lower Section.		Total.	
	L.	L.	L.	V.	L.	V.	L.	V.	L.	V.	L.	V.	L.	V.
Wt. %														
3	1,850	544	2,390	2,160	13·5	27·0	13·8	11·0	5·4	28·8	11·9	7·5	17·3	36·3
4	1,390	405	1,795	1,760	11·7	24·4	12·0	11·9	3·7	22·0	9·5	6·5	13·2	28·5
5	1,110	338	1,450	1,350	10·7	21·3	10·8	9·8	3·0	17·0	7·3	5·0	10·3	22·0
6	925	338	1,260	1,090	10·7	19·2	10·8	8·3	2·9	14·3	6·7	4·0	9·6	18·3
7	795	270	1,070	950	9·6	17·9	9·8	8·2	2·0	11·0	4·9	3·2	6·9	14·2
8	670	270	940	810	9·6	16·6	9·8	7·5	2·0	9·5	5·2	2·6	7·2	12·1

TABLE 14.—THE EFFECT OF WAX REMOVAL ON CONDENSER REQUIREMENTS FOR LIQUID FEED.

Furfural Concentration in Feed.	Surface Area of Digester Condenser (sq. ft.).	
	Wax Removed (h_s = 800).	Wax Not Removed (h_s = 200).
3 per cent.	95·5	266
4 "	71·8	200
5 "	57·2	159
6 "	47·8	133
7 "	41·0	114
8 "	34·4	96

h_s = vapour-side film coefficient (including fouling).

(*c*) *Hot Versus Cold Decantation.*

A considerable reduction in cooler surface area and cooling water can be realized by decanting in two stages. The 35 per cent. distillate is first decanted at 210°F. to yield a decant containing 18·4 per cent. furfural which is returned to the column and a 84 per cent. product which is cooled to atmospheric temperature and again decanted. The quantity of 8 per cent. decant from this second operation is small and it can be returned cold to the column without effecting its operation.

(*d*) *Removal of the Volatiles.*

The nature of the more volatile by-products from oat-hulls was deduced from the boiling points and refractive indices of fractions obtained on distillation of samples from the column decanter and from the vent of the digester condenser. These deductions were confirmed by measuring the melting points of prepared derivatives. The relative proportion of the substances identified was estimated from the distillation curve to be as follows:—

Substance Identified.	Approximate Proportion by Volume.
	%
Methanol	80
Acetone	15
Acetaldehyde	2
Furane	2
Methyl furanes	1

The actual quantity of volatiles present in the digestion product is of the order of 0·05 per cent. The volatiles must be removed at some stage in the process to prevent their accumulation in the upper part of the column and in the decanter. Three methods for their removal have been described: the separation of the volatiles from the vapour by partial condensation(9), separation by partial condensation with decantation (14, 15), and stripping of the volatiles from the aqueous decanter layer in a small auxiliary column before returning the dilute furfural solution to the main column (30). The latter method is the most satisfactory and could be used with either a hot or a cold decanter to yield impure methanol as a by-product.

(ii) Drying of 95 per cent. furfural.

The 95 per cent. furfural must be dried with a minimum of exposure to heat and this can be done conveniently in a small column operating under reduced pressure.

The number of theoretical plates required to dry 95 per cent. furfural to 99·9 per cent. product with a distillate of 35 per cent. furfural was determined by the McCabe-Thiele method, using the atmospheric pressure equilibrium data of Mains as no data were available at reduced pressures. The calculated number of theoretical plates found would therefore be slightly high. These results are shown in Table 15.

TABLE 15.

Reflux Ratio.	Number of Theoretical Plates Required.		
	Rectifying Section.	Stripping Section.	Total.
5	1·5	2·5	4·0
3	1·5	3·0	4·5
2	1·5	3·5	5·0

(iii) Condenser requirements for the distillation column.

The vapour-side film coefficient for the condensation of the furfural-water azeotrope, with a concentration of 35 per cent. furfural, was calculated from data obtained from runs with the small experimental single-tube heat exchanger mentioned previously. In these runs a small quantity of the vapour was condensed in a subsidiary condenser to ensure the use of the full tube surface in the experimental unit.

It was found that, when the furfural concentration was slightly below 35 per cent., the condensation was filmwise with droplets of a furfural rich layer on the water-rich film. As the furfural concentration was increased there was a well-defined change to semi-dropwise condensation with small patches of two-phase condensate about ⅛ in. by ¼ in. separated by smaller, apparently bare patches. This change in the type of condensation was accompanied by a significant increase in the vapour-side film coefficient.

The results of these experiments are shown in Table 16. The furfural content of the streams from experimental and auxiliary condensers indicate the composition of the condensing vapour. The probable errors shown in the last column and the absolute errors were calculated by the usual methods (35), assuming an accuracy in all temperature measurements of ± 1·0°F. and that the error in the water flow rate was covered by an error of ± 4 seconds in the time measurement. The absolute errors were found to be from 2·48 to 2·50 times the probable errors.

TABLE 16.—HEAT TRANSFER COEFFICIENTS FOR CONDENSATION OF FURFURAL-WATER AZEOTROPE.

Run Number	—	D-7.	D-8.	D-10.	D-11.
Water temperature rise	Deg. F. ..	45·1	50·1	45·7	54·3
Water velocity ..	Ft./sec. ..	2·08	2·08	2·08	2·08
Logarithmic-mean temp. difference	Deg. F. ..	120·7	121·2	121·9	116·6
Over-all coefficient U	B.T.U./(hr.) (sq. ft.) (deg. F.)	340	375	343	423
Water-side film coefficient h_w	B.T.U./(hr.) (sq. ft.) (deg. F.)	622	617	620	632
Absolute percentage error in h_s	.. ..	13·6	20·0	13·8	38·8
Probable percentage error in h_s	.. ..	5·45	8·04	5·61	15·6
Type of condensation	.. ..	filmwise	semi-dropwise	filmwise	semi-dropwise
Percentage furfural in condensate	Main ..	34·0	35·8	28·3	36·0
	Excess ..	34·9	34·7	30·5	35·0
Vapour-side film coefficient h_s	B.T.U./(hr.) (sq. ft.) (deg. F.)	1,300±70	2,080±170	1,340±70	4,350±680

5. Cost of Furfural Production

(i) The demand for furfural in Australia.

The annual consumption of furfural during the last few years has been estimated to be from 10 to 30 tons, used chiefly for modifying phenolic resins. The probable annual demand for plastics manufacture in the near future has been estimated to be from 50 to 100 tons; a maximum of 50 tons as a modifier for phenolic resins and from 10 to 50 tons for the manufacture of phenol-furfural resins. For every 100 lb. of the furfural resin made, 55 lb. each of phenol and furfural would be required as compared with 90 lb. of phenol and 7½ gallons of 40 per cent. formaldehyde. For the raw material costs of these two types of resin to be the same, the wholesale cost of furfural would be 1s. 9d. per lb. calculated on the present costs of phenol at 1s. 6d. per lb. and formalin at 6s. per gallon. If a local supply of furfural was available, additional quantities would be used for the manufacture of derivatives and for use as solvents.

TABLE 17.—LOCATION OF RAW MATERIALS IN AUSTRALIA.

Raw Materials.	State.	Source of Information.	Tons Raw Material Per Year.	Equivalent as Furfural Tons Per Year.	Location of Milling Plants.
Oat-hulls	Victoria	Government Statist	3,500	350	All in Melbourne—several plants
	New South Wales	Various manufacturers	4,500	450	All in Sydney—several plants
Maize-cores	Atherton Tableland, Queensland	Queensland Department of Agriculture	2,700	270	At one centre
	Rest of Queensland	Queensland Department of Agriculture	15,400	1,540	On individual farms
	New South Wales	Year Book	9,700	970	Probably on farms
	Victoria	Maize Marketing Board	800	80	On individual farms
Cottonseed hulls	Queensland	Queensland Department of Agriculture	1,000	95	At one mill
Rice-hulls	New South Wales	Government Statist	3,750	225	90 per cent. milled in Sydney
	Victoria	Various manufacturers	1,700	102	All in Melbourne
Flax-shives	Victoria	.. ..	3,500	245	At various centres
	South Australia	.. ..	2,500	175	At various centres

In addition to these raw materials, a large quantity of bagasse is available in Queensland and New South Wales with a furfural yield of about 8·5 lb./100 and also vast quantities of wood waste are available with a furfural yield of from 2 to 3 lb./100.

(ii) Availability of raw materials.

The quantities of raw materials available in various states based on average values for the years 1940 to 1945, are shown in Table 17. States with production of less than 1,000 tons of individual raw materials are not listed and the figures are only approximate as considerable seasonal variation occurs.

This survey showed that sufficient high grade raw material was available at each of a number of individual centres to supply Australian furfural requirements for some years.

No attempt has been made to determine cost of raw materials other than that of oat-hulls, which at the time of writing was £1 14s. per ton at mills in Melbourne. The supply and cost of the higher grade raw materials would vary with the season and also with the demand for them as stock feed, especially in dry seasons. The cost of other raw materials is probably appreciably less than that of oat-hulls.

(iii) Cost of production.

(*a*) *Design of Plant for Costing Furfural Production.*

The present minimum economic scale for furfural production in Australia by methods similar to that investigated is probably of the order of from 100 to 200 tons per year. For the purpose of determining the cost of production from oat-hulls, a plant was designed for a production of 200 short tons per year (400,000 lb.). Details of this plant are given in Table 18, in which the numbers refer to items on the flow sheet.* The plant design was based on the operation of three eight-hour shifts per day for 250 days per year assuming a yield of 10 lb. per 100 lb. of air-dry hulls and an average furfural concentration of 4 per cent. in the digestion product.

(1) *The digestion equipment.*—A digester similar to that used in the pilot plant work to be employed and operated with a working pressure of 130 lb./sq. in., a catalyst concentration of 1·25 per cent., a liquid/solid ratio of 1·5, and a steam throughput of 66·7 lb./(hr.)(100 lb. hulls). The five-hour operating cycle to be divided as follows: charging, 15 mins.; blow-up to working pressure, 30 mins.; at working pressure, 180 mins.; blow-down, 60 min.; and discharge, 15 mins.

(2) *The distillation equipment.*—The 4 per cent. furfural solution from the digester to be concentrated in a continuous, packed column with hot liquid feed and employing a hot decanter and operating with live steam, at a reflux ratio of 1·1 (equivalent to 2·0 with a cold decanter) and with waste furfural concentration of 0·03 per cent.

The 95 per cent. product from this column to be dried to 99·9 per cent. in a continuous packed column operating with closed steam at a 28-in. vacuum (50 mm./Hg.) and at a reflux ratio of 5·0.

The volatiles to be removed in a small packed column from the aqueous stream from the hot decanter before its return to the main column.

The distillation columns were designed by the McCabe-Thiele method (32) using 30 inches for the H.E.T.P. of 1-in. Raschig rings

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* See folder at end of *Journal*.

TABLE 18.—DETAILS OF PLANT DESIGNED FOR COSTING FURFURAL PRODUCTION.

Number.*	Item.	Size.	Type.	Dimensions.	Materials.	Requirements.		
						Steam lb./day.	Cooling Water gal./day.	Power kw. hr./day.
1	Hull storage	160,000 cu. ft.	Silo	..	Concrete	..	..	..
2	Hull elevator	250 cu. ft./hr.	Pneumatic	..	Mild steel	..	..	8
3	Hull hopper	250 cu. ft.	..	9′ x 9′ x 9′	,,	..	..	..
4	Strong acid tank	50 gal.	Cylindrical	2′ ϕ x 2′6″	,,	..	..	..
5	Dilute acid charge tank	500 gal.	,,	4′ ϕ x 6′6″	Copper	..	..	..
6	Digester	250 cu. ft.	Vertical	5′ ϕ x 16′	Mild steel copper lined	40,450	..	80
7	Residue storage tank	400 cu. ft.	Cylindrical	9′ ϕ x 5′	Mild steel	..	..	..
8	Residue transport tank	150 cu. ft.	Rectangular	6′ x 5′ x 5′	,,	..	..	..
9	Digester condenser	2,200 lb. vapour/hr.	4-pass, floating head	300 sq. ft.	Copper	..	31,280	..
10	Aqueous furfural storage tanks	2,000 gal. each (2)	Cylindrical	6′ ϕ x 11′6″	Mild steel copper lined	..	..	..
11	Wax filters	50 gal. each (2)	Sand and pebbles	2′ ϕ x 2′6″	Copper	..	..	..
12	Column feed pumps	2,000 lb./hr. 60 ft. head each (2)	Centrifugal	..	Bronze	..	..	24
13	Feed heater	2,000 lb./hr. 130 deg. F.	4-pass, floating head	15 sq. ft.	Copper	5,430	..	..
14	Concentration column	1,700 lb./hr. feed	Packed	1′ ϕ x 28′	Mild steel copper lined	11,450	..	..
15	Column condenser	666 lb. vapour/hr.	4-pass, floating head	22 sq. ft.	Copper	..	8,620	..
16	Reflux divider	..	Weir	..	Bronze	..	..	..
17	Hot decanter	60 gal.	Automatic	2′ ϕ x 3′	Copper	..	..	..
18	Volatiles column	237 lb./hr. feed	Packed	3″ ϕ x 4′	,,	240	250	..
19	Strong furfural cooler	90 lb./hr., 135 deg. F.	Concentric tube	3 lengths, 3′ of $\frac{3}{8}''$ in $\frac{3}{4}''$	,,	..	1,310	..
20	Cold decanter	10 gal.	Automatic	1′ ϕ x 2′	,,	..	..	..
21	Drying column	70 lb./hr. feed	Packed	5″ ϕ x 6′	,,	600	..	..
22	Drying column condenser	40 lb./hr. vapour	2 pass	3·2 sq. ft.	,,	..	2,700	..
23	Distillate receivers	20 gal. each (2)	Cylindrical	1′6″ ϕ x 2′	,,	..	..	..
24	Return pump	50 lb./hr., 60 ft. head	Gear	..	Bronze		..	1
25	Product cooler	70 lb./hr., 110 deg. F.	Concentric tube	3 lengths of 4′ $\frac{3}{8}''$ in $\frac{3}{4}''$	Copper	.	166	..
26	Product filter	5 sq. ft.	Cylindrical	1′ ϕ x 2′	,,	..	..	..
27	Product receivers	80 gal. each (2)	,,	2′ ϕ x 4′	Mild steel	..	..	..
28	Vacuum pump	28″ Vac. 50 c.f.m.	Hytor (2-stage)	..	Bronze	..	..	48
29	Methanol receiver	10 gal.	Cylindrical	1′ ϕ x 2′	Copper	..	..	..

* The numbers refer to items illustrated in folder at end of Journal.

and 12 inches for that of ⅜-in. rings, while the column diameters were determined by the method of Bain and Hougen (34) assuming operation at 70 per cent. of the flooding velocity.

(3) *Condensers and coolers.*—The size and construction of these units and their water requirements were determined on the basis of water temperature rises of from 70° to 200°F. for the digester and big column condensers, from 70° to 90°F. for the drying column, and from 70° to 80°F. for the coolers. Liquid-side coefficients were calculated by the expression

$$h_w = 150\ (1 + 0{\cdot}011t)\ v^{0\cdot8}/D^{0\cdot2}$$

where t is the average liquid temperature, v its velocity in ft./sec. and D the inside tube diameter in inches. The vapour-side film coefficients used were those determined from the pilot plant study, namely 200 B.T.U./(hr.) (sq. ft.) (deg. F.) for condensation and 50 for de-superheating in the digester condenser, 1,300 for the column condensers, and 3,000 for steam in the feed heater.

(4) *Cost of the plant.*—The cost of items of plant equipment was determined unit by unit as carefully as possible from a consideration of the cost of materials, probable cost of their fabrication, and cost of instruments, motors, &c., all at rates prevailing at the time of writing.

Digester residue disposal costs were estimated on the basis of provision of equipment for removal of half the volume of residue as water from each batch and the carting by motor truck of the remainder during one shift.

The cost of the plant grouped into units was as follows:—

Digestion unit	£1,300
Distillation unit	900
Hull storage and handling ..	3,300
Tanks and fittings	1,100
Residue handling equipment ..	1,450
Pipes and fittings	700
Erection and installation ..	1,000
Instruments	550
Design costs	500
Total	£10,800

A figure of £11,000 was taken as the plant cost.

(*b*) *Cost of Production.*

Details of the items contributing to the production cost are shown in Table 19. The cost of production was first determined on the basis of the plant being an adjunct to an existing plant with adequate excess boiler capacity and then the additional cost of boiler facilities was determined for its operation as an individual plant.

TABLE 19.—DETAILS OF COST OF FURFURAL PRODUCTION.*

Item.	Quantity Per Day.	Bulk Cost.	Cost/Unit (pence).	Units/lb. Furfural.	Cost/lb. Furfural (pence).	Percentage of Total Cost Including Boiler.
Oat-hulls	7·21 tons	£1 14s. per ton	0·183 per lb.	10·11	1·853	16·7
Steam	58,200 lb.	5s. per 1,000 lb.	0·06 per lb.	36·35	2·181	19·6
Water-cooling	44,300 gal.	6d. per 1,000 gal.	0·006 per gal.	27·70	0·166	1·5
Water-charge	2,400 gal.	6d. per 1,000 gal.	0·006 per gal.	1·50	0·009	0·1
Sulphuric acid (94 per cent.)	303 lb.	£9 16s. 6d. per ton	1·05 per lb.	0·189	0·198	1·8
Electric power	161 kw. hr.	0·98d. per kw. hr.	0·98 per kw. hr.	0·101	0·099	0·9
Labour—						
Process workers	6 (2 per shift)	£6 10s. per week			1·170	28·4
Labourers	6 (2 per shift)	£5 10s. per week			0·990	
Truck driver	1	£6 10s. per week			0·195	
Fitters	2	£7 10s. per week			0·450	
Technical control	1	£12 per week			0·360	
Depreciation on £11,000 at 10 per cent.	£4·4				0·660	14·9
Interest on £11,000 at 5 per cent.	£2·2				0·330	
Maintenance on £11,000 at 10 per cent.	£4·4				0·660	
Running costs of waste disposal truck	65 miles	1s. per mile			0·488	4·4
Containers—200 returnable drums, life 2 years	3 (44 gal.)	£3 each			0·180	1·6
Total without boiler					9·989	89·9
Boiler installation—depreciation on £6,000 at 10 per cent.	£2·4				0·360	3·2
Interest on £6,000 at 5 per cent.	£1·2				0·180	1·6
Boiler attendants	3 (1 per shift)	£6 10s. per week			0·585	5·3
Boiler costs					1·125	10·1
Total with boiler					11·114	100

* On a basis of 200 short tons of furfural per annum.

The cost figures and material and energy requirements per pound of furfural which are shown in Table 19 form a suitable basis on which the cost of furfural production may be calculated for a wide range of conditions.

From these results it can be seen that the cost of producing furfural in Australia from oat-hulls would be unlikely to exceed 11d. per pound, exclusive of overhead charges, as compared with the present price of approximately 1s. 4d. for imported furfural in ton lots, duty paid, on wharf in Sydney.

6. General Conclusions

The pilot plant investigation of the production of furfural from oat-hulls and maize-cores has shown that these Australian raw materials are satisfactory, has enabled the optimum production conditions to be defined and has supplied data necessary for the design of larger furfural digestion equipment.

The study of the recovery of furfural from its aqueous solutions by distillation has shown the McCabe-Thiele method to be suitable for the design of furfural distillation equipment and has enabled a choice to be made of equipment required for this separation.

The estimate made of the cost of furfural production from oat-hulls has shown Australian production of this substance on a scale of 200 tons per annum to be economically feasible provided the cost of raw material and overhead charges are not excessive.

7. Acknowledgments

The authors thank all those who helped with this project, particularly Mr. D. R. Zeidler of the Chemical Engineering Section for his advice throughout the work and assistance with the preparation of the manuscript; and Dr. H. H. Hatt and Mr. R. G. Curtis for the preliminary survey of the literature and for the laboratory work which preceded the pilot plant investigation.

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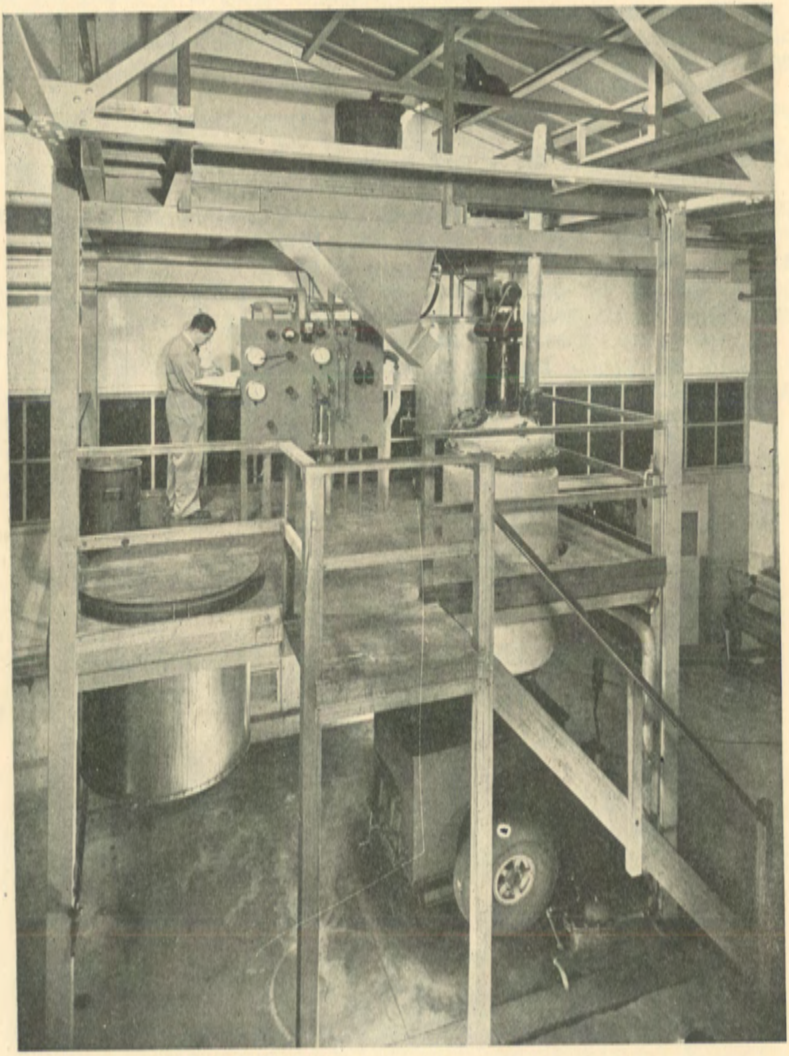
PLATE 1

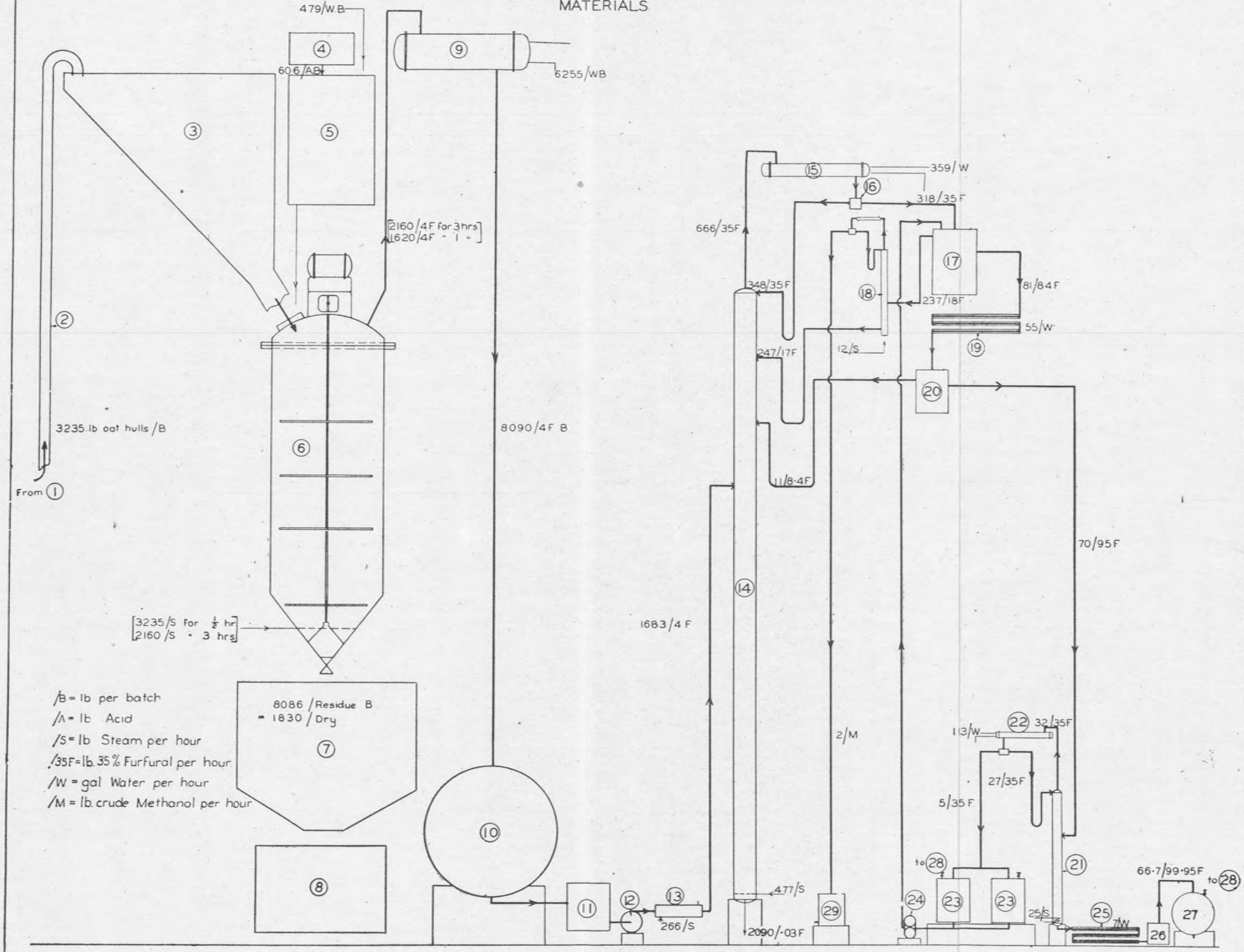
Furfural: A Pilot Plant Investigation of Its Production from Australian Raw Materials. (See page 225.)



Furfural pilot plant digester and auxiliary equipment.

FURFURAL

A PILOT PLANT INVESTIGATION OF ITS PRODUCTION FROM AUSTRALIAN RAW MATERIALS



FLOW SHEET OF PLANT DESIGNED FOR COSTING FURFURAL PRODUCTION. [FOR KEY-SEE TABLE 18. P. 253.]

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J. J. Gourley,
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