THE FREE ENERGY OF SOME ORGANIC SUBSTANCES IN ORGANIC SOLVENTS.

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CONTENTS.

INTRODUCTION.

The phenomenon of solubility has engaged the attention of scientists for many years, yet because of its wide and complex nature, no single theory has been advanced to account adequately for the behaviour of all solutions. During last century empirical laws were formulated by Henry and Raoult, Raoult's being subsequently used as the basis for expansion in theories of solubility.

Henry (Phil. Trans., 29, 1803; Gilb. Ann., 20, 147, 1805) studied the solubility of gases in liquids, and found that the concentration of gas dissolved by a given volume of solvent was proportional to its partial pressure above the solution. This may be expressed as:-

$$\frac{p\ (\text{gas})}{c\ (\text{gas})} = \text{constant} \qquad (1)$$

In very dilute solutions the various ways (mol fraction, weight and volume concentrations) of expressing concentrations are nearly proportional to each other. If we use the mol fraction, we may write Henry's law as:-

$$\frac{p_2}{N_2} = K_2 \qquad (2)$$

where p_2 = partial pressure of gas,

N_2 = its mol fraction in liquid,

K_2 = Henry's law constant.

Raoult (Compt. rend., 104, 1430, 1887; Z. physik. Chem., 2, 353, 1888) found that the fractional lowering of the vapour pressure of a solvent by the addition of an involatile solute was equal to the mol fraction of the solute at low concentrations; i. e.,

$$\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = N_2 \qquad (3)$$

where p_1° = vapour pressure of the pure solvent,

p_1 = vapour pressure of the solution,

N_2 = mol fraction of the solute.

or since $N_2 = 1 - N_1$

$$p_1/p_1^{\circ} = N_1 \qquad (4)$$

where N_1 = mol fraction of solvent.

A similar expression viz.,

$$\frac{p_2}{p_2^{\circ}} = N_2 \qquad (5)$$

applies to solutions containing a large percentage of the solute.

Zawidski (Z. physik. Chem., 35, 129, 1900) later found, that for certain binary solutions, this relation held for both components over the whole range of concentrations.

Provided the mol fractions are properly evaluated, it can be shown that Raoult's law is universally true for the solvent when the concentration of the solute is very small, and it follows from thermodynamical principles, that if Raoult's law is true under these conditions, Henry's law is also valid, (Butler's Fundamentals of Chemical Thermodynamics, Volume II, page 83) i.e. when Raoult's law holds for the solvent in dilute solution, Henry's law holds for the solute in dilute solution and vice versa. However, Raoult's law does not necessarily hold over the whole range of concentrations. As in the theoretical treatment of gases, an ideal was postulated, and G. N. Lewis (J.A.C.S., 30, 668, 1908), discussing the validity of Raoult's law, proposed that such ideal solutions would obey the law implicitly over the whole range of composition from $N_2 = 1$ to $N_2 = 0$. Then by comparison of (2) and (5) it is evident that the constant of Henry's law is $K_2 = p_2^o$. This however, is only true in comparatively few cases. In the majority of systems deviations from Raoult's law occur, and the Henry's law constant (i.e. the ratio of pressure to mol fraction in a very dilute solution) does not coincide with the vapour pressure of the pure liquid. Thus for dilute solutions Henry's law is the general law, which is certainly true if the solution is sufficiently dilute. The identification of Henry's law constant with p_2^o, as is required by the extended application of Raoult's law, is a special case which is only valid for ideal solutions.

Generally it may be said that the necessary condition for the validity of Raoult's law is that the energy and nature of the interaction of the solute molecule with its surrounding molecules shall be the same in the solution as in the pure liquid. In general this can only be satisfied when a solvent molecule may be replaced by a solute molecule without any change of volume, and when the energy of interaction of solvent and solute molecules is the same as that between two solute molecules. Hildebrand (Solubility, pages 60-62) has stated as the conditions for the validity of Raoult's law, that there shall be (1) no heat effect (2) no volume change, when the pure liquids are mixed. While these conditions are no doubt necessary, they are probably not in all cases sufficient to ensure the validity of Raoult's law. Large heat effects and thus large deviations can be expected when solute and solvent differ considerably in polar character.

The problem of deviations from Raoult's law was first approached as the probable result of interactions, which might be either chemical or physical in nature, between the molecules present in the solution.

Dolezak (Z. physik. Chem., 64, 727, 1908; etc.) was the first to treat deviations as a result of chemical combinations between the components or association of one or both components. His work, though extended over many years, has met with severe criticism, chiefly because of the elasticity of his assumptions, and because in several cases they have led to the assumption of association in liquids which, according to all other criteria, are entirely normal or unassociated. In certain systems chemical combination between the components of the solution undoubtedly is the cause of deviations from ideality as has been shown by Kendall and co-workers on the solvation effect upon the solubility of solids: (Kendall, Davidson & Adler, J.A.C.S., 43, 1481, 1921).

On the physical side van der Waals (Z. physik. Chem., 5, 133, 1890) has attempted to account for the deviations in terms of the cohesive forces between the molecules, similar to those he had postulated in deducing his pressure-volume isotherms for gases. Van Laar modified his equations slightly: (ibid., 72, 723, 1910; 83, 599, 1913). From the work of these authors and others the principal conclusion reached is, that the total vapour pressure of a solution should vary linearly with the mol fraction, only when the component liquids have equal critical pressures. Since the critical pressure, in terms of the van der Waals' theory, is given by the equation $P_c = 8a/27b^2$, and since b is closely related to V, the molal volume, the critical pressure should be closely related to a/V^2, the internal pressure.

After Rothmund (Z. physik. Chem., 26, 489, 1898) had indicated a relation between the dialectric constant and solubility in some aqueous solutions, Walden (ibid., 66, 409, 1909) pointed out the approximate parallelism between the dialectric constants and the internal pressures, forming the qualitative rule for the relative solubilities of various liquids in water, that the smaller the difference in internal pressures the greater the mutual solubility. It is only when substances of low polarity are considered, that Walden's conclusions are valid, as in water the solubility of a liquid seems to be governed chiefly by its polarity, so that as far as water is concerned Rothmund's generalisation is probably nearer the truth. Walden's is probably the first statement of the internal pressure theory of solubility, more commonly associated with Hildebrand: (J.A.C.S., 38, 1452, 1916). If the internal pressures of the two liquids are the same, then in a solution each molecule may be under the same forces as in its pure liquid. The vapour pressure is determined merely by the proportion of the two molecules present, but if the internal pressures are different, deviations from Raoult's law may occur. For such systems in which the components are as far as possible non polar, Hildebrand (J.A.C.S., 51, 66, 1929) proposed the equation:-

$$\bar{F}_2 - \bar{F}_2^o = RT \log N_2 - \beta N_1^2 \qquad (6)$$

where $\bar{F}_2$ = molar free energy in the solution,

$\overline{F}_2^{\,o}$ = the molar free energy in the pure liquid,

N_1 & N_2 = mol fraction of respective components,

β = a constant for a given mixture and temperature.

The constant β, Hildebrand has suggested should be proportional to the difference in internal pressures of the two components. The equation has shown good agreement with the vapour pressures and solubilities of a large number of solutions, which he terms 'regular solutions', characterised by absence of chemical and orienting effects. As these intermolecular forces might be expected to be a function of the volume of the solution, and therefore of the spatial distribution of the molecules in the liquids, Hildebrand and Wood (J. Chem. Physics, 1, 817, 1933) have derived the equation:-

$$\overline{F}_2 - \overline{F}_2^{\,o} = RT \log N_2 + A_{12}\, v_1^{\,2} \qquad (7)$$

where $A_{12} = V_2\left\{(E_2/V_2)^{\frac{1}{2}} - (E_1/V_1)^{\frac{1}{2}}\right\}^2$

v_1 = volume fraction of component 1,

E_1 & E_2 = the cohesive energies,

V_1 & V_2 = volume per mol of the pure solvents.

Excellent agreement has been shown in some systems, in which the molecular structure of the components was known. If the molecular volumes are equal, the two equations (6) and (7) become identical. The constants β and A_{12} are a measure of how far the system departs from ideal behaviour.

The close parallelism between the mutual solubility of liquids and their interfacial energy has long been recognised, but owing to the orientation of molecules at macroscopic interfaces, (Harkins, Brown and Davies, J.A.C.S., 39, 354, 1917) the observed interfacial energy cannot be taken as a measure of the forces acting over the whole surface of the molecules in solution. This parallelism is the foundation of Langmuir's 'principle of independent surface action', (Coll. Symp. Mono., 3, 48, 1925), according to which the potential energy of a molecule in a liquid is composed additively of the interactions at the different parts of the interface between the molecule and its surroundings. To test the equations which Langmuir derived in his theory, Smyth and Engel (J.A.C.S., 51, 2646, 1929) determined the partial vapour pressures of a number of binary solutions, and showed a general qualitative agreement, but quantitatively there were large deviations, which they attributed to the effect of dipole moments in the molecules. Approximate confirmation of this principle was also found in the case of the vapour pressures and solubilities of the lower n-aliphatic alcohols in aqueous solution by Butler: (Butler, Thomson and Maclennan, J.C.S., 674, 1933).

In the general treatment of solubility, substances have been divided roughly into electrolytes and non-electrolytes, the aqueous solution of the former showing a marked increase in the amount of current allowed to pass between two oppositely charged electrodes in the solution. Considerable progress has been made in the treatment of such electrolytic solutions by considering the electrical or 'long range' forces between the charged ions. Born (Z. physik. Chem., 1, 45, 1920) showed that the electrical energy involved in changing the surroundings of a charged ion was:-

$$F_e = \frac{\varepsilon^2}{2r}\left(\frac{1}{D_1} - \frac{1}{D_2}\right) \qquad (8)$$

where ε & r = charge and radius of ion,

D_1 & D_2 = dialectric constant of the two media.

This equation gives support to the parallelism between dialectric constants and solubility first noticed by Rothmund (loc. cit.).

In aqueous solutions these long range ionic forces are no doubt of major importance, but in other solvents of low dialectric constant in which free ions cannot exist, other forces of a similar origin may be important. An electrical field will be set up round a molecule when the individual charges of its component parts are unsymetrically arranged, and attempts have been made on similar lines to those of Born to calculate the energy of transfer of such molecules, known as dipoles, quadrupoles etc., according to their degree of complexity, to nonpolar solvents. Martin (Phil. Mag., 8, 550, 1929), taking as his model two charged spheres in contact, showed that the electrostatic energy of transferring a dipole from a vacuum to a medium of dialectric constant D, is given by:-

$$F_e = \frac{\mu^2}{3a^3}\left(1 - \frac{1}{D}\right) \qquad (9)$$

where μ = dipole moment,

a = radius of the molecule.

Using a slightly different model of a rigid sphere, in which the distance apart of the two electrical centres forming the dipole is infinitely small compared with the radius of the sphere, a model which he believes is more susceptible to mathematical treatment, Bell (Trans. Far. Soc., <u>27</u>, 797, 1931) derived a similar equation:-

$$F_e = \frac{\mu^2}{3a^3}\left(\frac{D-1}{2D+1}\right) \qquad (10)$$

The relative solubilities of polar compounds in non polar solvents should then be closely associated with the magnitude of the dipole moment and the radius, yet in only a few of the systems investigated has qualitative agreement been found.

The most important recent advance has been the theoretical calculation of the interaction of the van der Waals' 'short range' forces between two atoms by London (Z. physik. Chem., <u>63</u>, 245, 1930), who has shown that these forces are chiefly due to an interaction between short period electronic vibrations. These forces are certainly of great importance in non polar solutions, but in the case of polar substances the long range dipole forces cannot be overlooked.

The interactions which govern solubility can now be summarised as:-

(1) the van der Waals or dispersion forces, the approximate value of which for any two atoms has been calculated by London,

(2) the interaction of dipoles with each other or with polarisable molecules,

(3) the interaction of ions with each other, with dipoles or polarisable molecules,

(4) the interaction of two molecules involving compound formation by the mutual sharing of electrons.

The importance of each factor depends on the system considered.

<u>THERMODYNAMICAL THEORY</u>: The following theoretical treatment of binary solutions was involved in the calculation of results from the experimental work of this research.

(a) The partial molar free energy of a solute 2 in a binary solution, in which benzene, let us say, is the solvent, can be expressed by:-

$$\overline{F}_2 = F_2^{o} + RT \log p_2/p_2^{o} \qquad (11)$$

where F_2^{o} = molar free energy in pure liquid,

p_2 = partial vapour pressure of solute,

p_2^{o} = vapour pressure of pure solute at the same temperature.

but $p_2/p_2^o = f_2 N_2$

where f_2 = activity coefficient (introduced to compensate divergences from Raoult's law - as stated in this way it equals unity in the pure liquid),

N_2 = mol fraction of solute.

Hence by substituting an equation (11)

$$\overline{F}_2 = F_2^o + RT \log f_2 N_2 \qquad (12)$$

In very dilute solutions, when it can be assumed that the molecules of the solute are not appreciably associated, the partial molar free energy can be written as a function of the concentration:-

$$\overline{F}_2 = (\overline{F}_2^o)_B + RT \log N_2 \qquad (13)$$

where $(\overline{F}_2^o)_B$ = standard molar free energy in the dilute benzene solution.

If f_2^o is the activity coefficient in this dilute solution, then by combining equations (12) and (13)

$$(\overline{F}_2^o)_B - F_2^o = RT \log f_2^o \qquad (14)$$

This expression, which can be called the 'energy of dilution', gives a measure of the energy required to isolate 1 mol of solute molecules individually and surround each of them with benzene molecules.

(b) When a solution is in equilibrium with its vapour, the partial molar free energy of each component is the same for both phases. Again consider a benzene solution.

In Liquid Phase: The partial molar free energy of the solute in the dilute solution considered is:-

$$(\overline{F}_2)_S = (\overline{F}_2^{\,o})_B + RT \log N_2$$

In Gaseous Phase: The energy relations in the gaseous phase are given by:-

$$(\overline{F}_2)_G = (F_2^{\,o})_G + RT \log p_2 \qquad (15)$$

where $(\overline{F}_2)_G$ = partial molar free energy of the solute in the gaseous phase,

$(F_2^{\,o})_G$ = molar free energy of the solute in the gaseous phase at unit pressure (1 mm. Hg),

p_2 = partial vapour pressure of solute.

But since $(\overline{F}_2)_S = (\overline{F}_2)_G$

$$(\overline{F}_2^{\,o})_B + RT \log N_2 = (\overline{F}_2^{\,o})_G + RT \log p_2$$

or $$(\overline{F}_2^{\,o})_B - (\overline{F}_2^{\,o})_G = RT \log p_2/N_2 \qquad (16)$$

The ratio p_2/N_2 is in effect the limiting value at small concentrations of the solute between the vapour and the solvent, and is analogous to the Henry's law constant. $RT \log p/N$ can be called the 'energy of solvation', in contra-distinction to the expression previously obtained, and represents the amount of energy required to bring 1 mol of solute molecules individually from the gaseous phase at unit pressure into solution in the pure solvent.

This quantity is better adapted for theoretical interpretation, as its standard of reference is the solute in its vapour phase at unit pressure; the previous expression involves the consideration of the solute as a pure liquid, itself a complex state.

<u>OBJECT of EXPERIMENTS</u>: Although a very large number of systems have been studied, very little systematic work on the partial vapour pressures of binary solutions has been carried out, which permits the comparison of closely related solutes in the same or different solvents. This work has been devoted to the measurement of the energy values of a number of organic substances in organic solvents. The factors governing the free energy of solution are two-fold:-

(1) those acting in dilute solutions, in which there is no interaction between solute molecules,

(2) additional factors in more concentrated solutions, where this interaction cannot be ignored.

These factors are separated thermodynamically by expressing the partial molar free energy of a solute as:-

$$\overline{F}_2 = (\overline{F}_2{}^{o})_S + RT \log f_2 N_2 \qquad (17)$$

where $(\overline{F}_2{}^{o})_S$ = standard molar free energy - constant for a given solvent,

and f_2 = activity coefficient, which represents the variation of the free energy with the concentration (in so far as it differs from $(\overline{F}_2{}^{o})_S + RT \log N_2$). Expressed in this way it equals unity when the mol fraction N_2 approaches 0.

More attention has been given to the

variation of the activity coefficients with concentration than to the elucidation of the factors governing $(\overline{F}_2^{\,o})_S$. Of the factors determining solubility, the later is usually the more important term, particularly in the case of slightly soluble substances. Since this quantity depends only on the interactions between the solute molecule and the solvent molecules in its vicinity, it presents a more favourable case for theoretical interpretation.

EXPERIMENTAL METHODS: The problem of making the necessary measurements for the calculation of the energy values can be approached in two ways.

(1) By observing the variation of free energy with concentration. Thus previous workers in this laboratory (Butler, Thomson and Maclennan, loc. cit.) investigated the vapour pressure relations of the lower aliphatic alcohols in aqueous solution over the whole range of concentrations, and in addition to showing the variation of activity coefficient with concentration, they were able to calculate the value of the coefficient at infinite dilution by extrapolation of the curves, log f_2 against N_1, and hence the energy of dilution. With only the energy of dilution as objective, the investigation would, in this method, be limited to the observation of a few points on the vapour pressure concentration curves, in comparatively dilute solutions, but this

would involve too much time to allow a large number of systems to be investigated.

(2) By identifying the activity coefficient of very dilute solutions with that at infinite dilution. That this is permissable is readily seen from the $\log f_2 - N_1$ curves. This method involves only one measurement, and as rapidity was desirable, it was realised at the start that operations would have to be confined to the lowest concentrations that were workable. The 'air bubbling' method as used by Butler, Thomson and Maclennan, (loc. cit.), even for a single measurement, did not lend itself to rapidity, so several simpler methods were thought out and tried.

I. Distribution Ratio Method: When equilibrium has been established in a three component system, in which two of the components are immiscible liquids, the free energy of the third components is the same in each of these liquids. To take a concrete example we shall refer to the distribution of a solute between benzene and water.

The partial molar free energy of the solute in the two layers is:-

Benzene layer.

$$\overline{F}_2 = (\overline{F}_2{}^{o})_B + RT \log (N_2)_B$$

where $(\overline{F}_2{}^{o})_B$ = standard molar free energy in an infinitely dilute benzene solution,

$(N_2)_B$ = mol fraction of solute in benzene layer.

Water layer.

$$\overline{F}_2 = (\overline{F}_2{}^o)_W + RT \log (N_2)_W$$

where $(\overline{F}_2{}^o)_W$ = standard molar free energy in an infinitely dilute aqueous solution,

$(N_2)_W$ = mol fraction of solute in water layer.

Combining these equations we have:-

$$(\overline{F}_2{}^o)_W - (\overline{F}_2{}^o)_B = RT \log {(N_2)_B}/{(N_2)_W} \qquad (18)$$

$(N_2)_B/(N_2)_W$ is the distribution ratio of the solute between benzene and water, so if this could be found at very small concentrations, the energy values of all the lower aliphatic alcohols from C_1-C_8, calculated in water by Butler, Thomson and Maclennan, could be found in a number of organic solvents, such as benzene, carbon tetrachloride etc., immiscible with water. Considerable time was spent in an attempt to find the distribution ratio of ethyl alcohol between benzene and water at low concentrations at 25°, but the difficulties which arose in connection with

(1) ensured complete equilibrium between the two layers,

(2) the evolution of a reliable and rapid method of analysis,

proved insuperable. The first entailed suitable agitation in a thermostat, without the minutest loss of liquid. The difficulty of analysis by interferometric methods arose from the fact that all standard solutions were necessarily three component systems, which complicated their preparation and detracted from their reliability. Viscometric methods were also tried but found unsuitable.

Attempts were now made to find the partial vapour pressures at low concentrations directly, and hence the energy values.

II. A method used successfully by Bell (J.C.S., 2905, 1932) to find the partial vapour pressure of water in dilute organic solutions was tried. As used by Bell an excess of a salt hydrate pair (Na_2SO_4, $10\ H_2O + Na_2SO_4$) of known vapour pressure was shaken with a quantity of solvent for some time until equilibrium had been established between dissolved water and the water of crystalisation. Analysis gave the concentration of the solution.

Crystals of $CaCl_2$, $3C_2H_5OH$, as proved by analysis, were prepared and thoroughly agitated with varying amounts of benzene in a thermostat at 25°, but consistent values in the analysis of solutions could not be obtained owing probably to

(1) difficulty of preparing crystals absolutely free from moisture and adhering alcohol,

(2) an anomalous behaviour of the three component system, alcohol, calcium chloride, benzene.

III. Finally an air bubbling method, as used by Butler, Thomson and Maclennan, was found to be suitable, when a slight modification of the equations involved was made.

The partial vapour pressure of the solute in a dilute binary solution can be found from the following equations.

If n_1 and n_2 are the concentrations in mols % of the components over the solution, and p_1, p_2 their partial vapour pressures, then if the vapours are ideal

$$p_2/p_1 = n_2/n_1$$

Since, however, the solution is very dilute Raoult's law will hold for the solvent, so that

$$p_1 = p_1{}^o \times N_1$$

where $p_1{}^o$ = vapour pressure of the pure solvent at the same temperature,

N_1 = its mol fraction.

Combining these equations

$$p_2 = n_2/n_1 \times p_1{}^o \times N_1 \qquad (19)$$

n_2/n_1 can be found by analysis of the condensate that is procured by passing a slow stream of air or nitrogen through a solution of known composition, and condensing the vapour taken up by the nitrogen stream in a freezing mixture. N_1 is known from the composition of the standard solution and p_1^o from tables.

EXPERIMENTAL.

I. PURIFICATION of MATERIALS.

Temperatures have been corrected for stem errors in thermometers and reduced to 760mm..

(a) SOLUTES.

(1) METHYL ALCOHOL: The recognised impurities in commercial methyl alcohol are acetone, formaldehyde, and water. By the method outlined in Allan's Commercial Organic Analysis, Volume I, page 109, acetone was found to be present to the extent of about ·1% by weight. The acetone was converted into iodoform by adding a solution of 25 grams iodine in 1 litre methyl alcohol, in successive small quantities, to 500 ccs. N NaOH, which was constantly shaken. The solution was kept over night and the precipitated iodoform then removed by filtration: dissolved iodoform was hydrolysed by refluxing under an eight bulb rectifying column until the smell was absent, and the mixture then fractionally distilled. Three fractionations brought the boiling range within ·5°C. Using precautions against contamination, such as calcium chloride tube to the receiver, tin foil covering to all corks, the last trace of water was removed by refluxing under a column over aluminium amalgam, (Hartley and Raikes, J.C.S., <u>127</u>, 524, 1925), for four hours and again distilled. The bulk of the distillate came over within ·1°. This was stored in a coloured winchester to prevent photochemical de-

decomposition and a rubber cap tied tightly over the stopper. When tested with mercuric cyanide, dissolved in 6 N NaOH, for aldehyde and ketone, (Hartley and Raikes, loc. cit.), there was no reaction.

b.p. 64·58 - 64·67°/760·4 mm.   64·61°/760 mm.

(2) ETHYL ALCOHOL: The standard method for the purification of commercial absolute alcohol as used by Danner, (J.A.C.S., 44, 2832, 1922), was adopted. The alcohol was kept over freshly burned lime in a firmly stoppered flask for a week, and agitated at frequent intervals to ensure uniform contact with the lime. It was now refluxed for eight hours and finally fractionated using an eight bulb column, the middle portion only, boiling within a suitable range, being retained. It was stored in a tightly stoppered brown winchester, further protection from contamination with the atmosphere being ensured by a rubber cap.

Throughout the whole of the purification, all corks were lined with tin foil to avoid direct contact with the alcohol, either in the liquid or vapour phase, and during refluxing and distillation moisture from the atmosphere was excluded by a calcium chloride tube.

b.p. 78·53 - 78·60°/761·6 mm.   78·52°/760 mm.

(3) PROPYL ALCOHOL: The chief impurities in commercial propyl alcohol are allyl alcohol and water. Allyl alcohol cannot be removed by

fractionation, since its boiling point is so close to that of propyl alcohol. To make fractionation practicable, the allyl alcohol was converted into a higher boiling derivative, dibromo-propyl alcohol, by treatment with a suitable quantity of bromine, which was determined by titrating a sample of the propyl alcohol with potassium bromide-bromate solution. The slight excess of bromine reacts only slowly with the propyl alcohol forming bromo-propionaldehyde, which has also a high boiling point. After standing over night the propyl alcohol was fractionated and that fraction distilling from 96 - 98° collected. This fraction was dried over freshly burned lime for a week with frequent shaking, refluxed for ten hours, and again fractionated, the middle third being collected.

b.p. 96·40 - 96·80°/747·2 mm. 96·96°/760 mm.

(4) <u>n-BUTYL ALCOHOL</u>: This was a B.D.H. product and the only impurity seemed to be a trace of water. It was dried over freshly burned lime, refluxed and fractionated, the middle portion being retained.

b.p. 117·58 - 117·70°/747·65 mm. 118·06°/760 mm.

(5) <u>n-PROPYL CHLORIDE</u>: (B.D.H.) This was dried over calcium chloride and fractionated, the whole coming over within 1°. The middle fraction with a boiling range of ·2° was stored in a coloured bottle.

b.p. 45·60 - 45·80°/752·7 mm. 45·99°/760 mm.

(6) n-PROPYL BROMIDE: (B.D.H.) This received exactly the same treatment as the chloride.

b.p. 70·70 - 70·75°/752·5 mm. 71·05°/760 mm.

(7) n-PROPYL IODIDE: (B.D.H.) This was washed with a dilute solution of NaOH to remove traces of iodine, then with water, and subsequently dried over calcium chloride. The middle portion with a small boiling range, from a fractionation, was colourless, and to avoid photochemical decomposition, it was stored in a coloured bottle wrapped in black paper.

b.p. 100·90 - 101·10°/751·0 mm. 101·42°/760 mm.

(8) n-BUTYL CHLORIDE: (B.D.H.) This was dried over calcium chloride for a few days, refluxed and fractionated, and the middle fraction stored in a coloured bottle.

b.p. 77·00 - 77·50°/752·3 mm. 77·59°/760 mm.

(9) n-BUTYL BROMIDE: (B.D.H.) This was treated in exactly the same manner as the chloride.

b.p. 101·00 - 101·30°/750·6 mm. 101·58°/760 mm.

(10) n-BUTYL IODIDE: (B.D.H.) This was coloured with traces of free iodine. To remove this it was washed twice with NaOH, then several times with distilled water, and allowed to dry for a few days over anhydrous potassium carbonate. To avoid decomposition, which occurs to some extent

at the normal boiling point, the iodide was fractionated under diminished pressure, the middle portion being retained and stored in a coloured bottle wrapped in black paper.

b.p. 127·15°/759·3 mm. 127·18°/760 mm.

(11) <u>n-BUTYL NITRITE</u>: (B.D.H.) This was dried over calcium chloride for a day or two, and fractionated under diminished pressure, as a test carried out with a small portion seemed to indicate slight decomposition at the normal boiling point.

b.p. 75·80°/759·3 mm. 75·83°/760 mm.

(12) <u>CHLOROFORM</u>: A Macfarlane & Co., (B.P.) product. This was shaken with concentrated sulphuric acid for $\frac{1}{4}$ hour to remove alcohol, washed with NaOH and water. After drying over anhydrous potassium carbonate it was fractionated.

b.p. 60·70 - 60·90°/748·0 mm. 61·30°/760 mm.

(13) <u>METHYLENE CHLORIDE</u>: (B.D.H.) This was washed with water, dried over calcium chloride and fractionated.

b.p. 38·80 - 39·00°/738·1 mm. 39·90°/760 mm.

(b) <u>SOLVENTS</u>.

(1) <u>BENZENE</u>: (B.D.H.) Extra Pure Benzene for molecular weight determinations, guaranteed free from thiophene, was used. It was dried over freshly burned lime, fractionally distilled and then

fractionally frozen three times.

b.p. 79·95 - 80·04°/761·6 mm. 79·93°/760 mm.

(2) CARBON TETRACHLORIDE: Sulphur Free carbon tetrachloride, dried over lime, on fractional distillation, came over in bulk within a very restricted range of temperature.

b.p. 76·20 - 76·30°/753·7 mm. 76·52°/760 mm.

(3) CYCLO HEXANE: (B.D.H.) Spectroscopically pure cyclo hexane was dried and fractionally distilled.

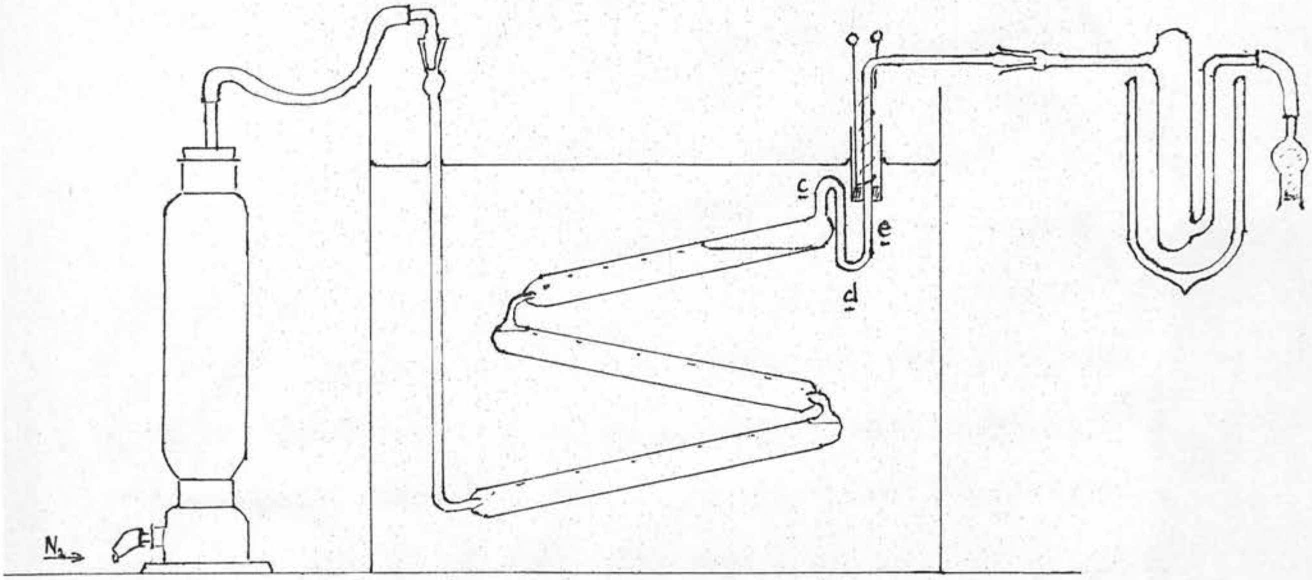
b.p. 80·10 - 80·30°/750·2 mm. 80·58°/760 mm.

As indicated later in the results, 'blank' experiments in the apparatus under the usual conditions were carried out on all three solvents in the purified state and untreated condition, and as no appreciable difference was observed in the concentration of the two condensates, the solvents were used without treatment.

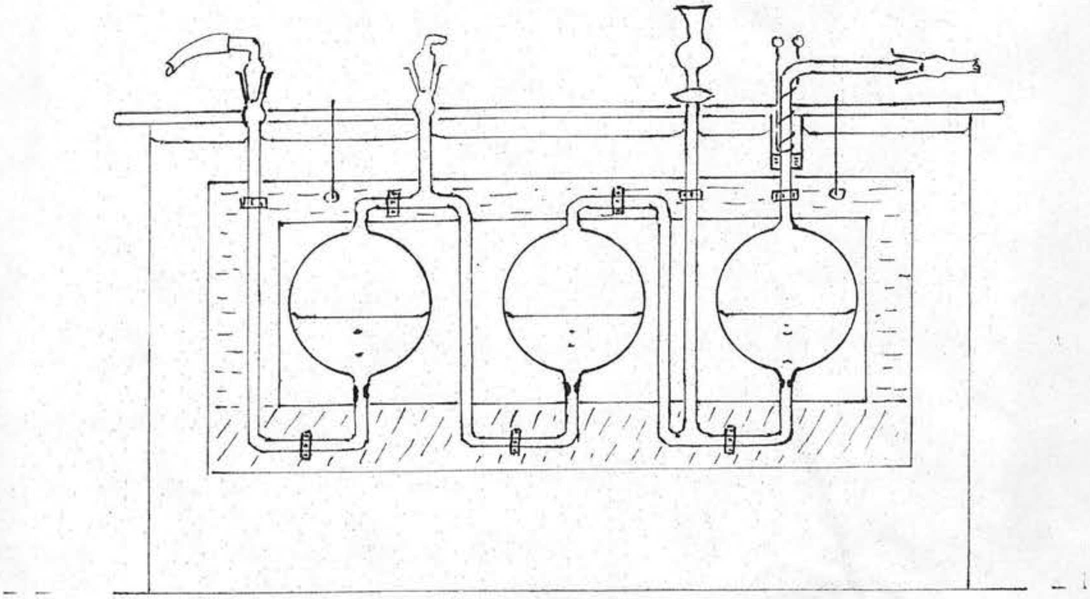
II. APPARATUS.

After some preliminary work on very dilute solutions of ethyl alcohol and benzene, of the order of ·1 mols %, with the 'S' type of bubbler, used by previous workers in this laboratory, it was deemed necessary, owing to the inconsistency of the results, to introduce some modifications, which would ensure complete saturation at these low

Fig. 1 (a) 'S' BUBBLER.



(b) 'BULB' BUBBLER.



concentrations. The alterations, besides improving enormously the reproducibility of the results, made manipulation of the apparatus much easier and more efficient. When, however, vapour pressure measurements were transferred to some of the derivatives of the alcohols and other liquids, which were not so liable to association, and could therefore be used at higher concentrations, which was very necessary to secure sufficient accuracy to distinguish between the relatively close values of the partial vapour pressure of some of these compounds, the 'S' bubbler gave results in harmony with those obtained with the modified or 'bulb' bubbler. So in the work apart from the alcohols, both bubblers were used indiscriminately.

The 'S' Bubbler consisted of three glass tubes of fairly wide bore, fused together end to end, at a small angle of inclination to each other, through internal seals with relatively fine jets to break up the nitrogen stream into small bubbles, yet large enough to avoid the danger of choking from dust. The size of the bubble did not change appreciably with the size of the jet used, so wider jets were used and found more convenient than the finer ones previously employed. The nitrogen stream was so regulated that a bubble took approximately 15 seconds to pass through the solution.

From the consistency of experimental results this rate of flow was found quite adequate to ensure complete saturation at the concentrations employed. On leaving the upper limb of the bubbler the vapours passed through a liquid trap <u>cde</u>, which eliminated the danger of entrainment. To avoid premature condensation of the vapours, the exit tube was electrically heated by (1) heating mats on the horizantal portion and (2) on the vertical portion by nick.-chrom. windings carried beneath the level of the thermostat water, from which they were protected by a short glass cyclinder fitted with a one-holed rubber stopper. The heating elements were connected in series and the current adjusted so that the temperature was not very much higher than that of the thermostat itself, as excessive heating was found to decompose some of the liquids employed. As the capacity was about 200 c.cs., the small amount of vapour removed as condensate, generally about ·5 c.cs., made no appreciable difference to the bulk of the liquid.

<u>The 'Bulb' Bubbler</u>. In this bubbler the main departure from that already described, was the provision of a large vapour space relative to that occupied by the standard solution. A greater surface of the solution was thus continually exposed to the nitrogen stream, allowing complete

saturation to be rapidly attained.

It consisted of three bulbs, 250 c.cs. capacity each, joined together in one piece, with limbs suitably placed for introducing or withdrawing solution, the whole being mounted on a stout wooden frame, which was weighted with lead. On entering the bulbs the nitrogen stream was broken up into small bubbles by constrictions in the entrance tubes. It was unnecessary to provide a liquid trap, as from the nature of the bubbler sufficient space was already there to eliminate entrainment. The heating arrangements at the exit of the bubbler were the same as before. Solution was introduced into each bulb by the appropriate limb, but to empty completely the solution in the middle bulb had to be syphoned over into the last bulb, from which it had free exit. The long limb, complete with stop-cock and bulb, connected to the last bulb, served a double purpose (1) to introduce the liquid and (2) to enable samples to be withdrawn for analysis at any time when it was thought necessary. It was found very convenient to make all limbs with ground glass joints and introduce the solution through a filter funnel having the complimentary part of the joints. While an experiment was running, the middle limb was stoppered by a ground glass joint, and the last limb effectively closed by the stop-cock.

<u>The Condenser</u>. Complete condensation of the vapours carried over by the nitrogen stream was obtained in the condenser, which was immersed in a sludge of carbon dioxide snow and ether, contained in a Thermos flask; connection to the bubbler was made through a ground glass joint. The width of the main limb, where condensation occured, prevented the formation of a solid plug with the subsequent stoppage of the nitrogen stream. A calcium chloride tube attached to the condenser prevented the entry of moisture.

<u>The Thermostat</u> had plate-glass sides and was controlled electrically, the temperature remaining constant to ± 0·01°.

<u>Analysis of Condensates</u>: The Zeiss Industrial Interferometer in the laboratory was not suited for the analysis of the solutions employed, as the movable fringes on the upper field of vision were bodily displaced from their normal position of coincidence with those fixed on the lower half of the field, when the cell, charged with solution, was placed in position. At first the water bath was thought to be the cause of the trouble, but this was subsequently proved to be incorrect. The high volatility of the solutions induced us to purchase an 'ether-proof' cell for the instrument, but this still suffered from the same defects as

had been encountered with the ordinary cells.

A new Rayleigh Interferometer, which was subsequently purchased for the department, proved itself singularly free from the difficulties already spoken of, probably because of the superior quality of the cell, as the deformation of the fringes was finally thought to be due to small irregularities in the thickness of the cell wall of the Zeiss instrument, which had no appreciable effect when the refractive index of the liquids used was small. The refractive indices of benzene, carbon tetrachloride and cyclo hexane are all greater than that of water, so this difference was perhaps the origin of the trouble. As no ether proof cell was purchasable for this instrument, a cover glass was used for the cell to cut down as much as possible the evaporation, which at times proved troublesome. Only a 1 cm. cell was purchased. It consisted of two compartments, one for the solution under analysis, the other for the liquid with which it was compared, either pure solvent or a solution of approximately the same concentration, depending on a difference of refractive index of solute and solvent, and consequently the magnitude of the drum reading on the interferometer. The compartments of the cell had to be filled carefully to about one third of their depth, as it was found that larger volumes facilitated the formation of a thin liquid film between the cover glass and the top of the cell, with the consequent acceleration of evaporation. As the time the fringes took to settle, about 15 to 20 minutes, was considerably longer than in the Zeiss instrument, which had a water bath, it was imperative to avoid this creeping film.

It was decided to try a viscometric method of analysis on three occasions, when the approximate coincidence of solute and solvent refractive index made interferometric methods impracticable. These were propyl and butyl bromide in cyclo hexane, and propyl and butyl iodide in benzene, but because of some minute impurity in the solvent, which persisted even after purification, and seemed to concentrate itself in the condensate during the experiment, this method of analysis proved unsuitable. No suitable method of analysis was devised for these systems.

III. PROCEDURE.

Solutions of known concentration were prepared in a long necked 500 c.c. standard flask, with a well ground stopper. Owing to the volatility of the solvents, and in most cases of the solute, which was only required in small quantities, several methods were tried in the preparation of these solutions. The most satisfactory procedure was to weigh a weighing bottle half filled with the solvent, with and without the solute, the weight of which was found by difference. The contents were then quickly washed into the standard flask, already more than half filled with solvent, with solvent from a wash bottle protected from contamination by a calcium chloride tube. Once completed, the standard solution was quickly run into the clean bubbler, which was now fixed up in position in the thermostat, and connected through calcium chloride towers to a nitrogen cyclinder. Dry air was sucked into the condenser tube through a calcium chloride tube attached to the outlet. This was stoppered, immersed in the cooling mixture and after sufficient time had elapsed to allow complete contraction of the air, it was unstoppered and connected to the bubbler. The heating elements were then engaged and the nitrogen stream adjusted to a suitable flow. A run of 10 to 12 hours was sufficient to collect about ·5 c.cs. of condensate. In the analysis of the condensate, in no case was it found necessary to dilute as there was no indication of the formation of a double phase. The condensate was run into the left hand compartment of the interferometer cell and compared with either the pure solvent or a solution of approximately the same concentration as the condensate, depending on its probable concentration. Calibration solutions were now made up roughly by measuring different quantities of solute from a micro-pipette into a fixed volume of solvent, to give readings slightly above and below that obtained for the condensate when compared with the same standard. When suitable readings were obtained, the calibration solutions were made up accurately by weight. By interpolation of the graph, concentration against interferometer reading (I.R.), the value for the condensate could be estimated.

At least two approximately concordant results were obtained in each case, the overall error amounting to about 5%. An uncertainty of this order in the partial vapour pressure corresponds to about ± 100 cals. in RT log $p/_N$.

RESULTS.

I. BLANK EXPERIMENTS.

With the apparatus under the usual conditions experiments were carried out on each of the three solvents in the purified and unpurified state, the results of which are given in Table I. No appreciable difference is noticed by purification, and in the case of benzene and carbon tetrachloride the correction from zero for the condensate is small and can be neglected. With cyclo hexane the correction is larger (+ 9) and has been universally applied in the calculation of the vapour pressure of solutes in this solvent, producing a slight increase or decrease depending on the relative refractive indices of solute and solvent. The magnitude of this correction depends on the slope of the calibration curve, I.R. against concentration, and on the concentration of the condensate; in the majority of cases it is about 2%. However, with carbon tetrachloride as solute, in which the slope of the curve is very small and the concentration of the condensate also small, the negative correction amounts to about 10%, while with methylene chloride, again a small slope, a positive correction of about 7% is involved.

TABLE I./

TABLE I.

Solvent	Pure solvent in cell. I.R. (zero)	Condensate I.R.	Difference in drum divisions.
Benzene purified.	963	965	+ 2
Benzene unpurified.	963	966	+ 3
Carbon tetrachlor. purified.	967	967	0
Carbon tetrachlor. unpurified.	967	968	+ 1
Cyclo hex. purified.	963	956	- 7
Cyclo hex. unpurified.	963	954	- 9

The vapour pressures of benzene and carbon tetrachloride at 25° were obtained from the I.C.T. An interpolated value for cyclo hexane from data in the I.C.T. agreed with a similar interpolated value from figures given in Landolt-Börnstein Tabellen. The vapour pressures at 25° are given below:-

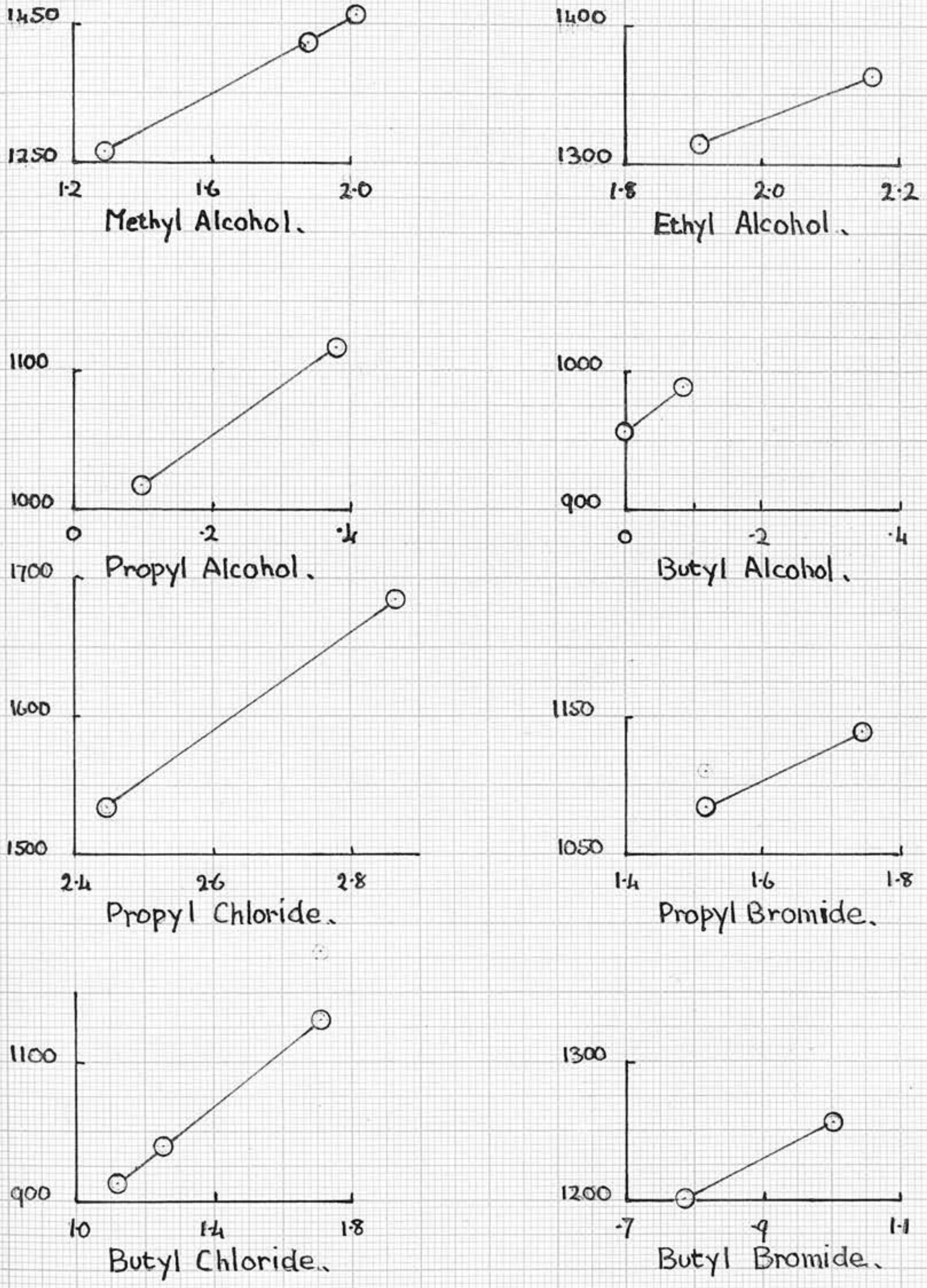
Benzene.................. 94.4 mm.
Carbon tetrachloride.....114.5 mm.
Cyclo hexane............. 96.2 mm.

II. COMPLETED RESULTS for BENZENE as SOLVENT.

These results are collected in Table II. The figures for calibration solutions are given in the second and third columns. N is the mol fraction of solute in the solution, and p its partial vapour pressure. The calibration curves, Figs. 2, 3, and 4, for all three solvents have been drawn to the same relative scale to facilitate comparison of slopes. The originals were drawn on a much wider scale and could be read with ease to .005 mols %. The curves were assumed to be linear over the short range involved.

TABLE II. /

Fig. 2 BENZENE Calibration Curves.

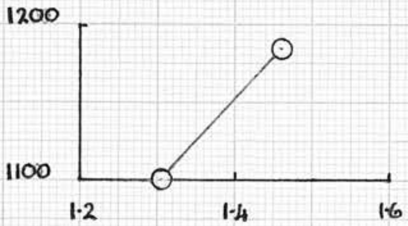


Methyl Alcohol. Ethyl Alcohol. Propyl Alcohol. Butyl Alcohol. Propyl Chloride. Propyl Bromide. Butyl Chloride. Butyl Bromide.

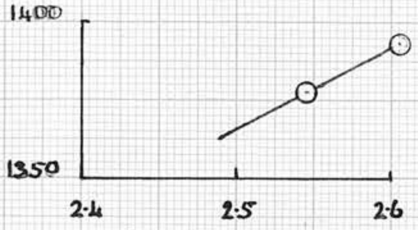
Vertical Axes = Interferometer Reading.

Horizontal Axes = Mols % of Solute.

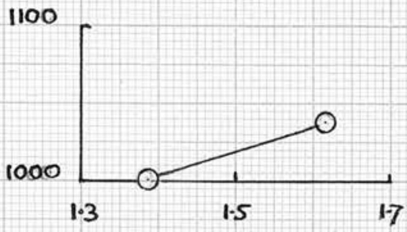
Fig. 2 (continued)



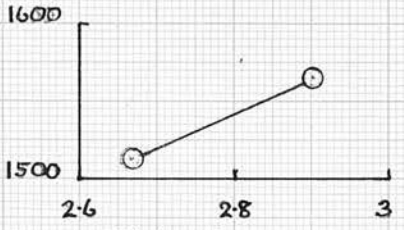
Butyl Nitrite.



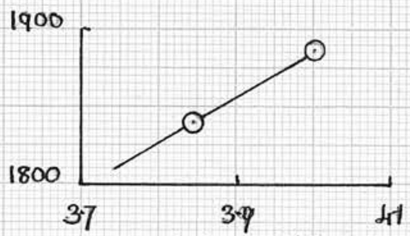
Cyclo Hexane.



Carbon Tetrachloride.



Chloroform.



Methylene Chloride.

Vertical Axes = Interferometer Reading.

Horizontal Axes = Mols % of Solute.

TABLE II.

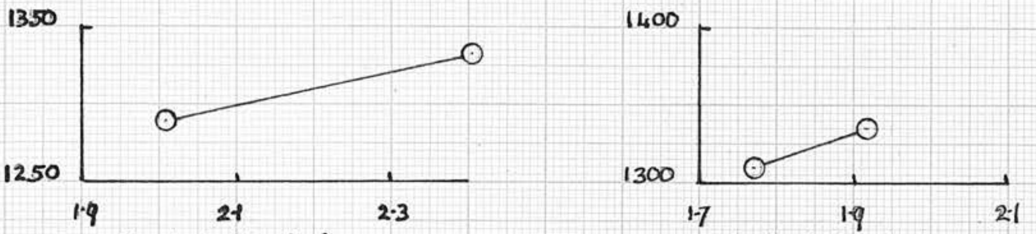
Solute	Calibrn. soln.		$N \times 10^2$	Condensate		p	p/N	mean p/N
	mols%	I.R.mean		I.R.	mols%			
MeOH	1.293	1266	0.053	1310	1.455	1.390	2623	2617
	1.874	1422		1307	1.445	1.384	2610	
	2.015	1462						
EtOH	1.910	1315	0.203	1347	2.070	1.992	981	968
	2.161	1364		1345	2.060	1.936	954	
PrOH	0.094	1016	0.094	1088	0.296	0.280	297.3	304
	0.379	1118		1093	0.310	0.293	311.4	
BuOH	0.085	989	0.085	987	0.083	0.078	92.7	96.6
	0.0	955		990	0.090	0.082	100.5	
PrCl	2.446	1535	0.746	1615	2.668	2.568	344.2	345
	2.863	1685		1620	2.680	2.580	345.7	
PrBr	1.518	1085	1.072	1089	1.538	1.458	136.0	136
	1.745	1139		1088	1.535	1.455	135.8	
BuCl	1.119	925	1.251	1037	1.398	1.322	105.7	106
	1.711	1161		1045	1.410	1.333	106.6	
BuBr	1.010	1256	1.697	1232	0.908	0.843	49.6	49.3
	0.783	1200		1228	0.894	0.830	48.9	
$BuNO_2$	1.304	1100	1.094	1103	1.310	1.240	113.2	115
	1.457	1185		1126	1.350	1.277	116.8	
Cyclo hexane	2.605	1393	1.474	1375	2.530	2.414	163.8	163
	2.545	1378		1365	2.490	2.375	161.2	
CCl_4	1.617	1038	1.246	1043	1.648	1.562	125.3	125
	1.385	1002		1043	1.648	1.562	125.3	
$CHCl_3$	2.902	1566	1.842	1543	2.800	2.670	145.0	144
	2.667	1513		1534	2.760	2.630	142.9	
CH_2Cl_2	3.845	1840	1.201	1820	3.770	3.655	304.2	309
	4.033	1886		1848	3.875	3.761	313.0	

III. COMPLETED RESULTS for CARBON TETRACHLORIDE as SOLVENT.

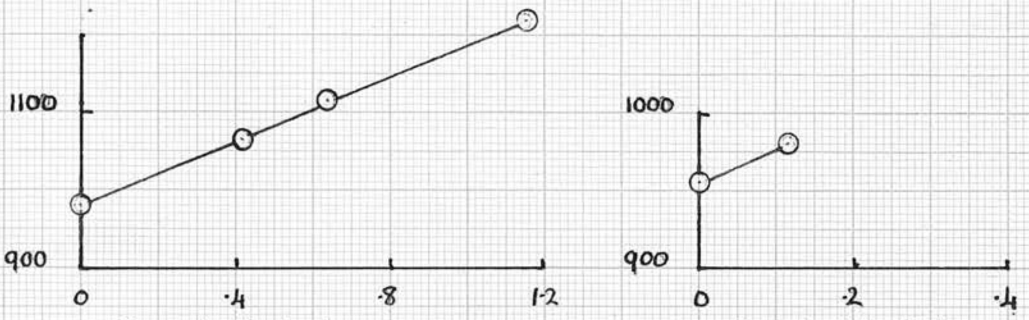
These results are collected in Table III.

TABLE III. /

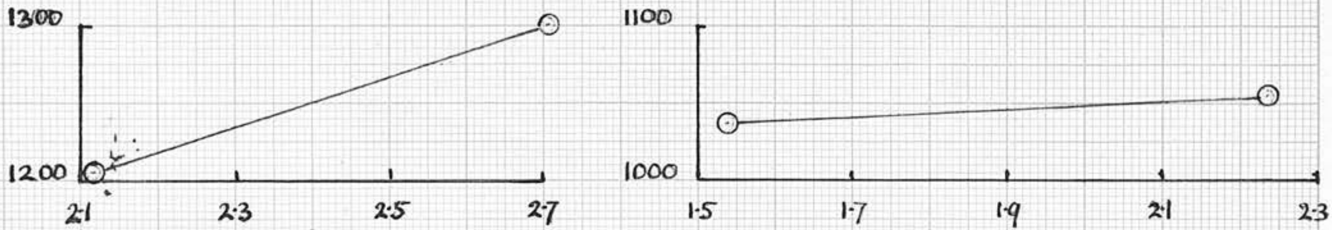
Fig. 3. CARBON TETRACHLORIDE - Calibration Curves.



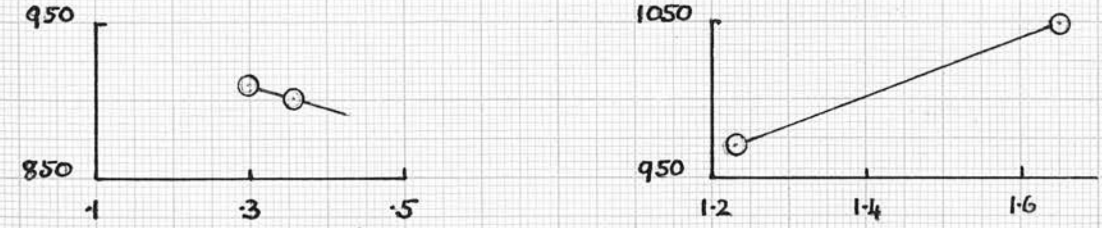
Methyl Alcohol. Ethyl Alcohol.



Propyl Alcohol. Butyl Alcohol.



Propyl Chloride. Propyl Bromide.

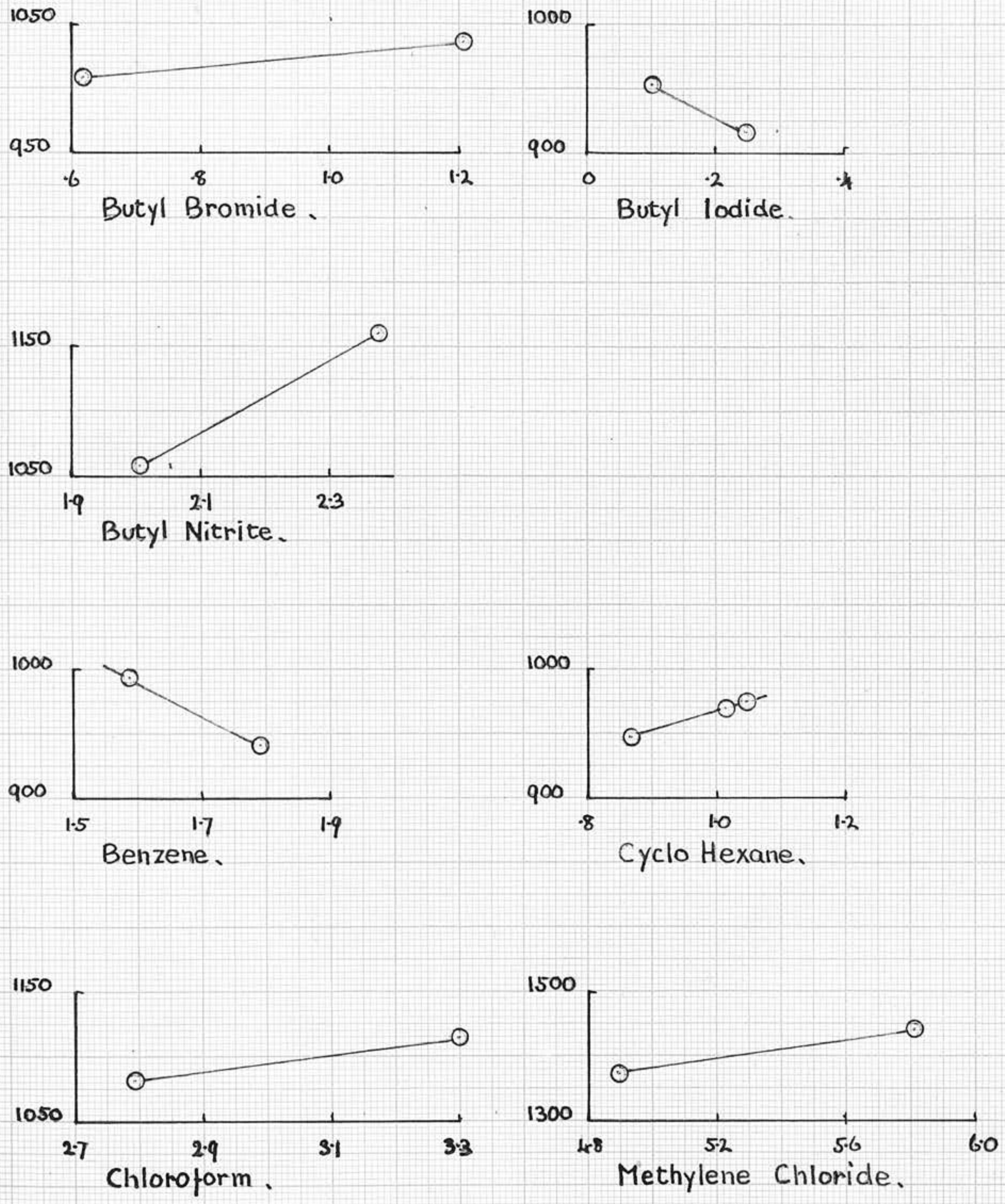


Propyl Iodide. Butyl Chloride.

Vertical Axes = Interferometer Reading.

Horizontal Axes = Mols % of Solute.

Fig 3 (continued)



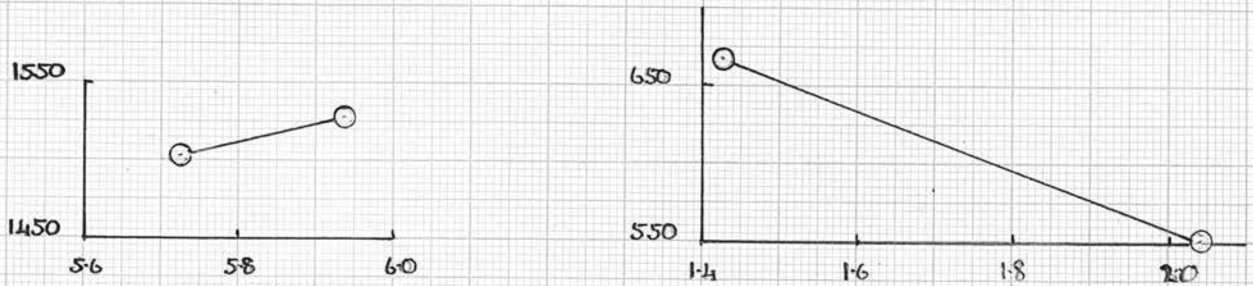
Vertical Axes = Interferometer Reading.

Horizontal Axes = Mols % of Solute.

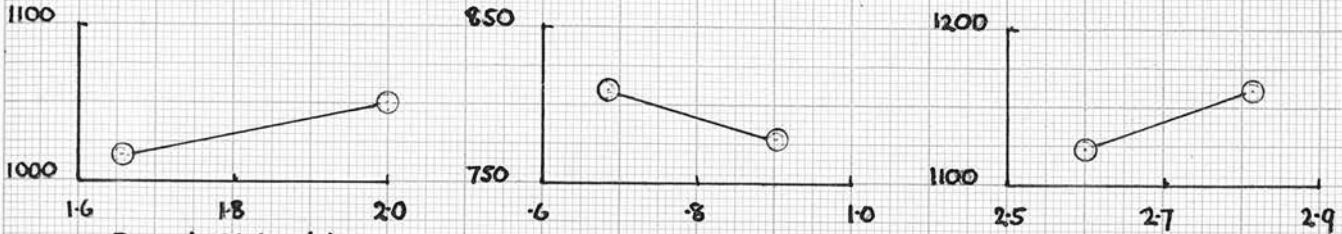
TABLE III.

Solute	Calibrn. soln.		$N \times 10^2$	Condensate		p	p/N	mean p/N
	mols%	I.R.mean		I.R.	mols%			
MeOH	2.402	1333	0.072	1281	1.940	2.263	3145	3131
	2.009	1289		1279	1.923	2.244	3116	
EtOH	1.770	1310	0.186	1323	1.850	2.154	1159	1175
	1.918	1335		1332	1.900	2.213	1191	
PrOH	1.152	1219	0.100	1050	0.340	0.390	390.2	385
	0.421	1067		1048	0.330	0.378	378.7	
	0.0	980						
BuOH	0.115	980	0.115	984	0.134	0.154	133.6	129
	0.0	955		982	0.125	0.143	124.6	
PrCl	2.707	1302	0.692	1287	2.612	3.049	440.7	443
	2.105	1205		1292	2.640	3.082	445.5	
PrBr	2.232	1056	1.237	1045	1.830	2.108	170.5	167
	1.537	1037		1043	1.760	2.026	163.9	
PrI	0.354	902	0.896	901	0.360	0.410	45.8	44.5
	0.300	910		904	0.340	0.387	43.2	
BuCl	1.639	1049	1.231	1002	1.444	1.657	134.6	134
	1.231	970		1001	1.438	1.650	134.1	
BuBr	0.615	1008	1.238	1015	0.686	0.781	63.1	63.0
	1.203	1036		1016	0.683	0.778	62.8	
BuI	0.247	918	1.401	932	0.190	0.215	15.4	16.2
	0.101	953		927	0.210	0.238	17.0	
$BuNO_2$	2.030	1058	1.730	1105	2.178	2.505	144.8	145
	2.372	1159		1109	2.192	2.522	145.7	
Benz.	1.790	942	1.638	999	1.570	1.797	109.7	110
	1.588	994		997	1.578	1.806	110.3	
Cyclo hexane	1.113	969	1.148	975	1.158	1.326	115.4	115
	0.965	949		975	1.158	1.326	115.4	
$CHCl_3$	3.296	1114	1.606	1094	2.990	3.473	216.2	217
	2.792	1081		1095	3.005	3.489	217.3	
CH_2Cl_2	5.806	1443	1.163	1375	4.195	5.849	502.8	508
	4.889	1373		1382	5.000	5.958	512.2	

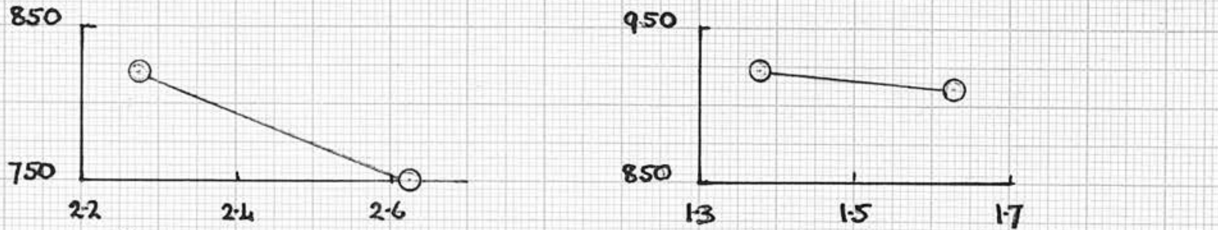
Fig. 4 CYCLO HEXANE Calibration Curves.



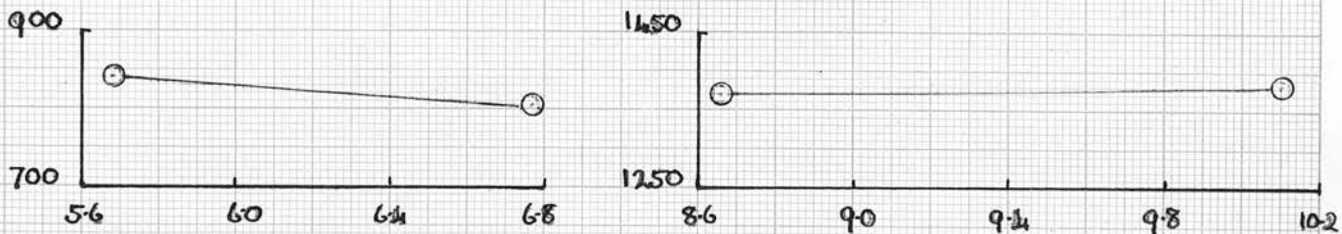
Propyl Chloride. Propyl Iodide.



Butyl Chloride. Butyl Iodide. Butyl Nitrite.



Benzene. Carbon Tetrachloride.



Chloroform. Methylene Chloride.

Vertical Axes = Interferometer Reading.

Horizontal Axes = Mols % of Solute.

IV. COMPLETED RESULTS for CYCLO HEXANE as SOLVENT.

These are given in Table IV.

TABLE IV.

Solute	Calibrn. soln.		$N \times 10^2$	Condensate		p	$p/_N$	mean $p/_N$
	mols%	I.R.mean		I.R.	mols%			
PrCl	5.729	1502	1.193	1523	5.960	6.024	505.0	508
	5.936	1529		1530	6.010	6.078	510.0	
PrI	2.039	550	2.347	670	1.373	1.308	55.7	56.8
	1.425	668		660	1.425	1.358	57.9	
BuCl	1.657	1017	1.221	1033	1.920	1.860	152.4	152
	2.001	1050		1032	1.910	1.850	151.6	
BuI	0.902	778	2.720	801	0.685	0.646	23.7	24.2
	0.684	810		796	0.715	0.674	24.7	
$BuNO_2$	2.601	1123	1.431	1158	2.840	2.771	193.6	192
	2.814	1162		1150	2.797	2.729	190.7	
Benz.	2.275	820	1.393	796	2.354	2.288	164.2	164
	2.623	750		798	2.344	2.277	163.4	
CCl_4	1.375	922	1.002	908	1.510	1.460	145.7	148
	1.625	911		906	1.552	1.502	149.9	
$CHCl_3$	6.769	805	2.007	821	6.000	6.019	299.8	297
	5.685	840		824	5.910	5.923	295.0	
CH_2Cl_2	8.660	1318	1.370	1310	9.000	9.385	685.2	738
	10.100	1333		1325	10.250	10.830	791.2	

V. CALCULATIONS from EXPERIMENTAL DATA.

The distribution ratios $(p/_N)$ of the solutes between the vapour and dilute solution at 25°, the activity coefficient $(p/_{p^oN})$ and related quantities are given in Tables V and VI for the three solvents. The values of p^o at 25° for the solutes were obtained from the I.C.T. or data to which reference was made. In some cases, marked by a dash, an interpolation to 25° was required.

TABLE V.

		BENZENE		CARBON TETRACHLOR.		CYCLO HEXANE	
Solute	p^o	p/N	p/p^oN	p/N	p/p^oN	p/N	p/p^oN
MeOH	122.2	2617	21.40	3131	25.60	-	-
EtOH	59.0	968	16.40	1175	19.90	-	-
PrOH	20.1	304	15.10	385	19.10	-	-
BuOH	6.78	96.6	14.20	129	18.80	-	-
PrCl '	342.8	345	1.01	443	1.29	508	1.48
PrBr '	137.4	136	0.99	167	1.22	-	-
PrI '	43.4	-	-	44.5	1.03	56.8	1.31
BuCl '	104.0	106	1.02	134	1.29	152	1.46
BuBr '	40.1	49.3	1.23	63.0	1.57	-	-
BuI	-	-	-	16.2	-	24.2	-
$BuNO_2$	-	115	-	145	-	192	-
Benz.	94.4	-	-	110	1.17	164	1.73
Cyclo Hexane '	96.2	163	1.69	115	1.20	-	-
CCl_4	114.5	125	1.09	-	-	148	1.29
$CHCl_3$	199.1	144	0.72	217	1.09	297	1.49
CH_2Cl_2 '	419.8	309	0.74	508	1.21	738	1.76

TABLE VI./

TABLE VI.

		BENZENE		CARBON TETRACHLOR.		CYCLO HEXANE	
Solute	RT log p^o	RT log $\frac{p}{N}$	RT log $\frac{p}{p^o_N}$	RT log $\frac{p}{N}$	RT log $\frac{p}{p^o_N}$	RT log $\frac{p}{N}$	RT log $\frac{p}{p^o_N}$
MeOH	2850	4665	1815	4770	1920	-	-
EtOH	2415	4075	1660	4190	1775	-	-
PrOH	1780	3390	1610	3530	1750	-	-
BuOH	1135	2710	1575	2880	1740	-	-
PrCl	3460	3465	5	3610	150	3690	230
PrBr	2920	2910	-5	3030	115	-	-
PrI	2235	-	-	2250	15	2395	160
BuCl	2750	2765	10	2905	150	2975	225
BuBr	2190	2310	120	2455	265	-	-
BuI	-	-	-	1650	-	1890	-
$BuNO_2$	-	2810	-	2950	-	3115	-
Benz.	2695	-	-	2785	90	3020	325
Cyclo Hexane	2705	3020	310	2815	110	-	-
CCl_4	2810	2865	50	-	-	2960	150
$CHCl_3$	3135	2945	-190	3190	50	3375	235
CH_2Cl_2	3580	3395	-185	3690	110	3915	335

Fig. 5.

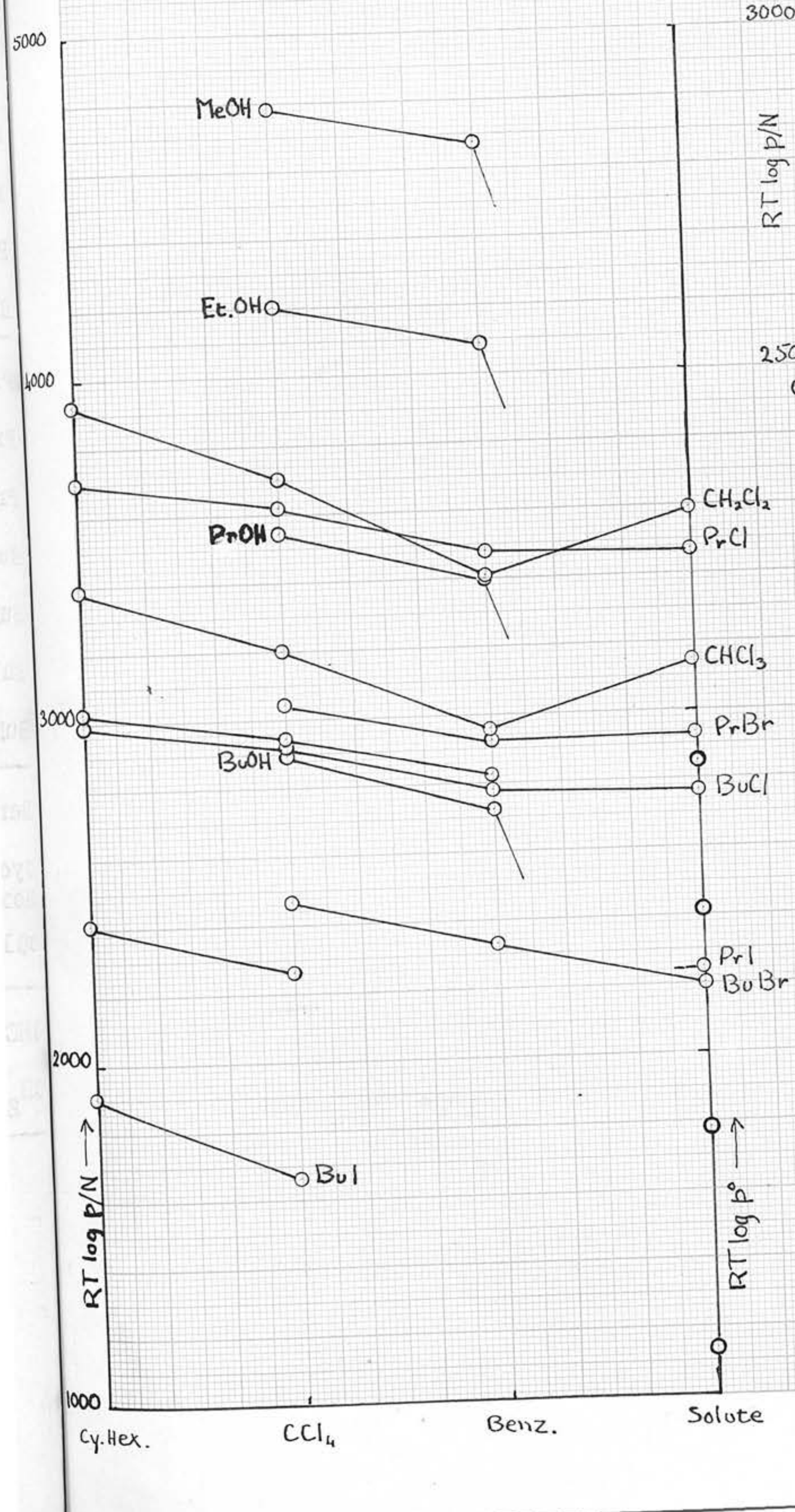


Fig. 7.

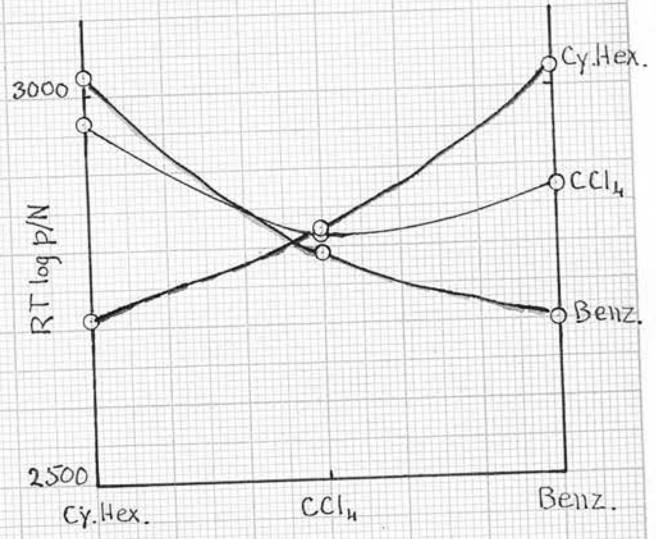
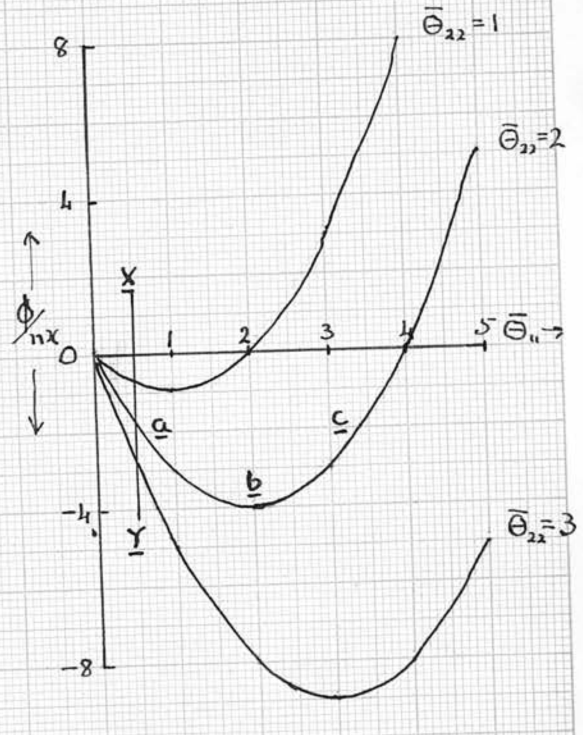


Fig. 6.



DISCUSSION.

The outstanding feature of the results is the regularity exhibited in the values of $RT \log p/N$, which is particularly noticeable in the case of the alcohols. When the pure liquid is taken as the standard of reference (i.e. considering values of $RT \log p/p^oN$) this regularity in general disappears. By using the vapour phase as the standard of reference, it becomes clear at once that there is no abnormality about the alcohols in dilute solution, the large values of $RT \log p/p^oN$ arising from the relatively small values of p^o, due to their association in the pure liquid. The energies of solvation ($RT \log p/N$) decrease as we ascend the series of aliphatic alcohols: this is equivalent to saying that the ease of solubility in benzene, carbon tetrachloride or cyclo hexane increases steadily with each additional methylene group. The reverse is the case when water is used as solvent.

Fig. 5, in which the values of $RT \log p/N$ for each solute are plotted against each solvent, shows that the order of these values is cyclo hexane) carbon tetrachloride) benzene. In addition it is seen that for a given alkyl radical, the solutes form a definite series and fall in the order NO_2) Cl) OH) Br) I.

The halogen derivatives of the alcohols are all nearly ideal solutes in benzene, i.e. the value of p/N is nearly equal to the value of p^o, and the activity coefficient p/p^oN is thus nearly unity. It follows from above that these solutes are not quite so ideal in carbon tetrachloride and cyclo hexane.

In the case of the group carbon tetrachloride, chloroform, methylene chloride, the energy of solvation (RT log p/N) increases as the chlorine atoms are progressively replaced by hydrogen atoms. The value of RT log p/N for methyl chloride in carbon tetrachloride at 20° (about 5000 cals.) and methane in benzene at 25° (7700 cals.) have been calculated from data in the I.C.T. and Hildebrand's 'Solubility'. By comparison of the values in benzene and carbon tetrachloride 5000 cals. can be taken as an approximate value for methylene chloride in benzene at 25°. Collecting the values of the energy of solvation for this group in benzene we have:-

	RT log p/N	Difference
CCl_4..........	2860 cals.	
		100 cals.
$CHCl_3$.........	2950 cals.	
		400 cals.
CH_2Cl_2........	3400 cals.	
		1600 cals.
CH_3Cl.........	5000 cals.	
		3000 cals.
CH_4...........	7700 cals.	

This shows that the progressive replacement of the chlorine atoms by hydrogen atoms is accompanied by a steadily increasing increment in the energy of solvation.

The value for methyl chloride in benzene fits in favourably with the observed order of the solvation energies for the alcohols and their derivatives, as RT log p/N for methyl alcohol is 4660 cals.

Both chloroform and methylene chloride give negative deviations from Raoult's law in benzene. This abnormality in the case of the system chloroform-benzene has been recorded before, (Schmidt, Z. physik. Chem., 99, 71, 1921). Such negative deviations are comparatively rare, and where no compound formation occurs, difficult to explain.

The interpretation of the results is most readily made in terms of Hildebrand's theory of internal pressure. According to this theory, in non polar solutions, a solute is ideal in a solvent which has the same internal pressure, and the deviation from ideality increases as the internal pressure difference between the solute and solvent increases. The order of the internal pressures of the solvents is cyclo hexane $<$ carbon tetrachloride $<$ benzene, while the internal pressures of the solutes are all either equal to or greater than that of benzene. It follows that the deviations from ideality should increase in the order benzene $<$ carbon tetrachloride $<$ cyclo hexane, which is observed to be the case.

It should be observed that Hildebrand's theory applies strictly only to non polar solutes.

The solutes used are all polar (with the exception of solutions of the solvents in each other, which are referred to later), but this does not appear to influence the regularity of the results provided that the pure liquid is not taken as the basis of comparison.

Further progress can only be made by replacing Hildebrand's qualitative theory by a suitable quantitative relation. Some progress in this direction has been made. Butler and Maclennan (loc. cit.) showed that under certain conditions Langmuir's 'principle of independent surface action' leads to conclusions similar to Hildebrand's theory. In the case of a homogeneous solute and solvent it has been shown that, expressed in terms of Langmuir's theory, the energy difference of a molecule (b) in a dilute vapour, and in a very dilute solution is:-

$$\phi = S_a(\gamma_{aa}/2 - \gamma_{ab}) \qquad (1)$$

where S_a = area of molecule,

γ_{aa} = cohesive energy of two unit surfaces of the solvent,

γ_{ab} = adhesive energy of unit surface of the solvent with unit surface of the solute.

The first term represents the energy required to produce a cavity in the solvent, large enough to hold the dissolved molecule, the second, the energy of introducing the solute molecule into the cavity.

Before further progress can be made with this expression, γ_{ab} must be evaluated in terms of γ_{aa}

and γ_{ll}. A result has been obtained by Butler (private communication), which is of use in interpretating the experimental results.

The calculation involves the expression of the above terms as functions of London's equation for the mutual potential, or van der Waals, energy of interaction of two atoms. For two like atoms at a distance r_{11}, the mutual potential is:-

$$\phi_{11} = 3/2 \cdot \varepsilon_1\varepsilon_1/2\varepsilon_1 \cdot \alpha_1^2/r_{11}^6 .$$

or for two different atoms at a distance r_{12}

$$\phi_{12} = 3/2 \cdot \varepsilon_1\varepsilon_2/\varepsilon_1+\varepsilon_2 \cdot \alpha_1\alpha_2/r_{12}^6$$

where $\varepsilon_1, \varepsilon_2$ = the excitation energies of the atoms,

α_1, α_2 = their polarisabilities.

The potential of two like adjacent atoms at their average distance r_{11} may be expressed as:-

$$\phi_{11} = \Theta_{11}^2 \quad \text{where} \quad \Theta_{11} = \sqrt{3/2 \cdot \varepsilon_1\varepsilon_1/2\varepsilon_1 \cdot \alpha_1/r_{11}^3}$$

and similarly, if the average distance of two unlike adjacent atoms is taken as the geometrical mean of the distances of the like atoms, i.e. $r_{12}^2 = r_{11} \cdot r_{22}$ the potential of two adjacent unlike atoms can be expressed as $\phi_{12} = \Theta_{11} \cdot \Theta_{22}$.

The adhesion energy between a solute molecule and surrounding solvent molecules is then given by $\sum_{\text{surface}} \Theta_{11}\Theta_{22}$, where the summation is made for each atom in the molecule with adjacent atoms of the solvent molecules. Similarly the cohesion energy of any surface drawn between the molecules of the solvent is $\sum_{surface}\Theta_{11}\Theta_{11}$, and the energy required to create a cavity, having the same surface area, is half of this, so that the energy required to introduce the molecule into the solvent is:-

$$\phi = \frac{1}{2}\sum_{surface}\Theta_{11}^2 - \sum_{surface}\Theta_{11}\Theta_{22} \qquad (2)$$

By an approximate averaging process Butler has put this equation in a more convenient form as:-

$$\phi = \frac{1}{2} n'x'\bar{\Theta}_{11}^2 - nx\bar{\Theta}_{11}\bar{\Theta}_{22} \qquad (3)$$

where n' is the number of inside atoms adjacent to x' outside atoms in a volume of the solvent equal to that of the solute molecule, and n is the number of atoms on the surface of the solute molecule, adjacent to x atoms of the surrounding solvent molecules.

$\bar{\Theta}_{11}$ and $\bar{\Theta}_{22}$ are average values of Θ_{11} and Θ_{22}.

If $n'x' = nx$, i.e. if the contacts between a solute molecule and surrounding solvent molecules replace an equal number of solvent-solvent contacts, equation (3) becomes:-

$$\phi = \frac{1}{2} nx\bar{\Theta}_{11}^2 - nx\bar{\Theta}_{11}\bar{\Theta}_{22} \qquad (3a)$$

This holds when solute and solvent molecules are approximately the same size.

The general shape of the curve obtained from (3a), when ϕ and $\bar{\Theta}_{11}$ are taken as variables, is shown in fig. 6.

Differentiating (3a) with respect to $\bar{\Theta}_{11}$ we have

$$\frac{d\phi}{d\bar{\Theta}_{11}} = n\chi\left(\bar{\Theta}_{11} - \bar{\Theta}_{22}\right)$$

The following conclusions can be drawn from this differentiation:-

(1) ϕ is a minimum when $\bar{\Theta}_{11} = \bar{\Theta}_{22}$ and is then equal to $-\frac{1}{2} n\chi \bar{\Theta}_{11}^2$

(2) For a given value of $\bar{\Theta}_{22}$, ϕ decreases with increasing values of $\bar{\Theta}_{11}$, when $\bar{\Theta}_{11} < \bar{\Theta}_{22}$

(3) For a given value of $\bar{\Theta}_{22}$, ϕ increases with increasing values of $\bar{\Theta}_{11}$, when $\bar{\Theta}_{11} > \bar{\Theta}_{22}$

Differentiating (3a) with respect to $\bar{\Theta}_{22}$ we have

$$\frac{d\phi}{d\bar{\Theta}_{22}} = -n\chi\bar{\Theta}_{11}$$

This indicates that for a given value of $\bar{\Theta}_{11}$, ϕ decreases with increasing values of $\bar{\Theta}_{22}$. This in particular is only true when solute and solvent molecules are approximately the same size.

It is difficult to make precise calculations with these equations owing to the uncertainty in the value of $n\chi$.

The values of $\bar{\Theta}_{11}$ and $\bar{\Theta}_{22}$ are closely related to the internal pressures of the pure liquids. The internal pressure of a liquid is the cohesive energy of a unit surface drawn between the molecules, and is equal to $\Pi = n\bar{\Theta}_{11}^2$, where n is the number of atomic contacts for such a unit surface. For liquids which have on the average the same number of atoms per unit surface, the order of internal pressures will be the same as the order of the $\bar{\Theta}_{11}$'s. In such cases the above equations are a quantative expression of the internal pressure theory. When the average number of atoms in unit surface differs considerably, these expressions may be expected to be a more accurate representation of the interactions.

ϕ represents the total energy of interaction of solute with solvent, whereas the experiments give RT log p/N, which is the free energy of interaction. The two differ by a quantity which is proportional to the entropy of solution of the solute, but it is probable (by analogy with Trouton's rule) that this does not vary very much among similar compounds.

The conclusions drawn from the equations seem to be borne out reasonably well by the experimental results.

The general shape of the curves in fig. 5, in which the values of RT log p/N (or RT log p^0 in the case of the solute itself) are plotted against the solvents arranged in the order of increasing internal pressure, is similar to that of the theoretical curves in fig. 6. As the internal pressures of the solutes are all greater than, or equal to that of benzene, we would expect these curves to have the same kind of slope as <u>ab</u> in fig. 6.

With different solutes in the same solvent, values of ϕ would lie on <u>XY</u> in fig. 6. Fig. 5 bears this out. It would seem, therefore, that the internal pressures of the halogen derivatives of the alcohols, which are probably all of the same mol-

I > OH. The order of the electrostatic energy of transfer for a solute from a vacuum to a given solvent may be modified considerably by small differences in the molecular radius. For a given group, such as an alcohol and its derivatives, the radius can be taken as approximately constant, so that the electrostatic energies of transfer and, therefore, values of RT log p/N should be in the order of the dipole moments. The order of RT log p/N values is $NO_2 > Cl > OH > Br > I$. With the exception of the alcohol itself, fair agreement is shown.

For a given solute the increments Δ RT log p/N, as the solvent is changed, should be equal to $\mu^2/3a^3\left(1/D_1 - 1/D_2\right)$ according to Martin's equation, (loc. cit.)

Reasonable values for a solute are

$$\mu = 2 \times 10^{-18} \text{ c.g.s. units.} \quad a = 2 \times 10^{-8} \text{ cms.}$$

hence $\mu^2/3a^3 = \cdot 2 \times 10^{-12}$ ergs per molecule,

$= 3000$ cals per mol.

The following table gives the approximate values for the free energy difference of a given solute in cyclo hexane, carbon tetrachloride and benzene, as calculated and observed.

	Cyclo hexane.	Carbon tetrachlor.	Benzene.
D at 20°	2.05	2.24	2.28
1/D	.488	.448	.440
$\mu^2/3a^3\left(1/D_1 - 1/D_2\right)$		120 cals	24 cals
Δ RT log p/N		90 cals (approx.)	130 cals (approx.)

Although the calculated values are of the right magnitude, the order of the increments for change of solvent is the reverse from what is observed.

The results are more fully interpretated in terms of the internal pressure theory. The chief factor determining the solubility of even polar substances in non polar solvents seems, therefore, to be the van der Waals or dispersion forces.

SUMMARY.

(1) A rapid and reliable method has been devised for the determination of the energy transfer of a solute from the dilute vapour (RT log p/N) or pure liquid (RT log $p/p^{o}N$) to a dilute solution.

(2) The partial vapour pressures at low concentrations of four lower aliphatic alcohols, some derivatives, and a few other organic compounds have been determined in benzene at 25^{o}.

(3) Similar determinations have been made in carbon tetrachloride.

(4) With the exception of the alcohols, similar determinations have been made in cyclo hexane.

(5) The energies of solvation (RT log p/N) and dilution (RT log $p/p^{o}N$) have been calculated for the solutes in benzene, carbon tetrachloride and cyclo hexane.

(6) The advantage of using values of RT log p/N as against RT log $p/p^{o}N$, for theoretical considerations, is demonstrated by the regularity of these values, shown in the Tables, compared with the erratic figures for RT log $p/p^{o}N$.

(7) The results are interpretated in terms of Hildebrand's internal pressure theory, and show agreement with a semi-quantitative equation, based

on London's equation for the mutual potential of two atoms, and Langmuir's theory of independent surface action, derived by Butler (unpublished).

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