This is to certify that Mr IAN M. BARCLAY has successfully sustained an oral examination on the subject matter of his thesis by a committee of the Department of Chemistry.

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Members
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Committee.

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TABLE OF CONTENTS

Page

INTRODUCTION.

The phenomenon of solubility has been studied by chemists for many years, yet because of its wide and complex nature, it has been found to present some of the most perplexing problems tackled and for this reason no single theory has been advanced to account adequately for the behaviour of all solutions. The aim of all investigators has been to find some unifying principle, by means of which the experimental results obtained could be made to fit into some simple systematic form and although the problem is far from being solved completely, the researches of Dolezalek, van Laar and Rothmund, followed in recent times by those of Hildebrand and his co-workers have opened up viewpoints which are not only of theoretical interest but also of considerable practical importance.

During last century empirical laws were formulated by Henry, van't Hoff and Raoult, Raoult's being subsequently used as the basis for further expansion in theories of solubility.

Henry (Phil. Trans., 29, 1803; Gilb. Ann., 20, 147, 1805) in his study of the solubility of gases in liquids, discovered that the amount of gas which will dissolve in a given volume of the solvent, was proportional to the partial pressure of that gas above the solution. Expressing the solubility of the gas in terms of mol fraction, we obtain the relation,

$$p_2 / N_2 = K_2 \qquad (1)$$

where p_2 = partial pressure of the gas,

N_2 = molar fraction of the gas in the liquid,

and K_2 = Henry's Law constant.

The analogy between gases and substances in dilute solution was first stated by van't Hoff (Phil. Mag., 3, 157, 1888) who showed from a study of the experimental data of Pfeffer and others that the osmotic pressure of a solution, measured against the pure solvent, is numerically equal to the pressure which the solute would exert as an ideal gas under similar conditions; so that

$$\pi V = n_2RT \qquad (2)$$

where π = Osmotic Pressure of the solution,

V = Volume of Solution containing 1 gram-molecule of the solute, where n_2 = number of mols of solute,

T = Absolute Temperature

and R = Ideal Gas Constant.

On a much firmer theoretical basis is Raoult's Law (Compt. rend., 104, 1430, 1887; Z. physik. Chem., 2, 353, 1888) which states that the partial vapour pressure of a substance in solution is proportional to its molar fraction. In the pure substance the molar fraction is unity, so that Raoult's Law can be expressed mathematically as follows. Let p_1 be the partial vapour pressure of a component A over the solution, in which its molar fraction is N_1, $p_1°$ the vapour pressure of the same substance as a pure liquid at the same temperature; then

$$p_1 = p_1°N_1. \qquad (3)$$

Similarly the partial vapour pressure of another component B is given by

$$p_2 = p_2°N_2 \qquad (4)$$

where N_2 is its molar fraction and

$p_2°$, the vapour pressure of the pure liquid.

Zawidski (Z. physik. Chem., 35, 129, 1900) later found, that for certain binary systems such as ethylene chloride and benzene, the relation held for both components over the whole range of concentrations.

The great theoretical importance of Raoult's Law was demonstrated by van't Hoff, who showed that the lowering of the vapour pressure of a solution was related directly to its osmotic pressure. The assumptions involved in the deduction of Raoult's Law from van't Hoff's theory of osmotic pressure are only true for very dilute solutions and thus, although the two laws become identical at infinite dilution, at appreciable concentrations the results obtained diverge very markedly and as a basis of subsequent treatment it was necessary to choose only one of these equations. A number of mixtures of two components to which the Raoult equation is applicable over the whole range of concentrations are known and for this and other reasons, modern theories of solubility have been founded on this fundamental equation to represent the behaviour of an ideal solution.

Provided the mol fractions are evaluated properly, it can be shown that Raoult's law is universally true for the solvent for very small concentrations of the solute, and, from thermodynamic principles, it follows that, if Raoult's law holds under these conditions, Henry's law is valid too. (Butler's Fundamentals of Chemical Thermodynamics, vol. II, p. 83).

And so, by comparison of equations (1) and (4), it follows that the constant of Henry's law is $K_2 = p_2°$. In general, however, this is not true. Most systems show deviations from Raoult's law, so that the Henry's law constant (i.e. the ratio of partial vapour 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 $p_2°$, as is required by the extended applications of Raoult's law, is a special case, which is only valid for ideal solutions.

Generally it may be stated that Raoult's law is valid in cases where the two liquids are chosen such that the attractive forces between the molecules of each are the same so that on mixing these liquids the forces acting on a given molecule will vary little from those operating in the pure liquid. In particular, Hildebrand (Solubility, 2nd Edition, pages 57-59) has pointed out that, if, when the pure liquids are mixed, there is (1) no heat effect and (2) no volume change, Raoult's law is probably valid. In themselves, however, these conditions are not alone sufficient to ensure that Raoult's equation is obeyed. Large heat effects and thus large deviations can be expected when solute and solvent differ considerably in polar character and other factors also causing deviations are molecular association and compound formation.

The influence of association and compound formation in causing deviations from Raoult's law was first discussed by Dolezalek (Z. physik. Chem., <u>64</u>, 727, 1908 etc.) but there is little doubt that he overstressed the effect of association. His work, which extended over a long period of 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. On the other hand it is worth noting that the comprehensive studies on compound formation and its effect on solubility, carried out by Kendall and co-workers (Kendall, Davidson and Adler, J.A.C.S., <u>43</u>, 1481, 1921) in systems containing both polar and non-polar constituents, have shown that the tendency to compound formation between the components of a mixture and mutual solubility are definitely parallel.

Proceeding now to a study of the physical aspects of the subject, we find that deviations from ideality were attributed by van der Waals (Z. physik. Chem., <u>5</u>, 133, 1890) to the cohesive forces between the molecules, similar to those he had postulated in deducing his pressure-volume isotherms. A modification was later given by van Laar (ibid., <u>72</u>, 723, 1910; <u>83</u>, 599, 1913). The principal conclusion reached from the works of these authors and others is that the total vapour pressure of a solution should vary linearly with the molar fraction, only when the components of the mixture have equal critical pressures. Since the critical pressure, in terms of the van der Waals' theory, is given by the equation, $P_c = \frac{8a}{27b^2}$ 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.

The internal pressure theory is chiefly associated with the name of Hildebrand and arose from the work of Rothmund and Walden. After Rothmund (Z. physik. Chem., 26, 489, 1898) had indicated a relation between the dielectric constant and the solubility in some aqueous solutions, Walden (ibid., 66, 409, 1909) pointed out the approximate parallelism between the dielectric constants and the internal pressures, forming the qualitative rule for the relative solubilities of various liquids in water, that the smaller the difference in the 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 the more correct. Walden's statement is probably the first of the internal pressure theory of solubility, more commonly associated with Hildebrand (J.A.C.S., 38, 1452, 1916). Hildebrand's conclusion is that, if the internal pressures of the two components are the same, then in a solution each molecule will be under the same forces as it experiences in the pure liquid. The partial vapour pressures are then determined merely by the proportions of the two types of molecule present. After studying the solubilities of a large number of solids, it became apparent to Hildebrand that where both components are non-polar, normal substances, the curves for any one solute in a number of different solvents form a family of curves, indicating a regularity not shown where there is association or solvation of one or both components. In the development of an equation to cover such relationships, Hildebrand (J.A.C.S., 51, 66, 1929) made the assumption that for a regular solution, the entropy of solution is that of an ideal solution or in other words, the entropy change in the transfer of a small amount of a component of a regular solution to an ideal solution, of the same composition, the total volume remaining unchanged, is zero. For an ideal solution, the change in free energy corresponding to the transfer of a mol of the component X_2 from the pure liquid to a solution in which the mol fraction is N_2, is

$$\bar{F}_2 - F_2^\circ = RT \log N_2 \qquad (5)$$

The corresponding entropy change is

$$\Delta S_2 = \frac{d(\overline{F}_2 - F_2^\circ)}{dT} = -R \log N_2 \qquad (6)$$

Again, the partial molal heat of mixing is given by $\Delta H = \beta N_1^2$, so that, since $\Delta F = \Delta H - T\Delta S$, we obtain for a regular solution,

$$\Delta F = \overline{F}_2 - F_2^\circ = RT \log N_2 + \beta N_1^2. \qquad (7)$$

Hildebrand suggested a proportionality between the constant β and the difference in internal pressures of the two components and the equation was applied with great success to various families of solubility curves, the solutions found to satisfy the equation being termed 'regular solutions', characterised by the absence of orienting and chemical effects.

The relationship between the departure of the solubility from the ideal and the difference in internal pressure of solvent and solute given above was of a very qualitative nature, but by the application to the concept of regular solutions, of Menke's suggestion obtained as a result of X-ray studies, namely, that the molecules are assumed to be arranged in a completely random manner, Hildebrand and Wood (J. Chem. Physics, 1, 817, 1933) were able to deduce a modified expression which has a definite quantitative connection. The equation developed by these authors may be written in the form:-

$$\overline{F}_2 - \overline{F}_2^\circ = RT \log N_2 - A_{12} v_1^2, \qquad (8)$$

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

v_1 = volume fraction of component I,

E_1 and E_2 = the cohesive energies of the two constituents of the solution,

and V_1 and V_2 = the molecular volumes.

When solvent and solute have the same internal pressure the right-hand side of the equation is zero and so the actual solubility is then equal to the ideal value. If the molecular volumes are equal, the two equations (7) and (8) become identical. The constants β and A_{12} give a measure of the departure of the system from ideality. Experimental tests on equation (8) have been made and in many cases, in which the molecular structure of the components was known, the agreement between the solubility as calculated by means of the equation and that obtained by experiment, was quite satisfactory.

The close parallelism between the mutual solubility of liquids and their interfacial energy is the foundation of the "principle of independent surface action", due to Langmuir (Coll. Symp. Mono., 3, 48, 1925). According to this principle the potential energy of a given molecule in a liquid is composed additively of the various 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. With non-polar solutions, they found a qualitative agreement, but in other cases, considerable discrepances occurred, which were attributed to the presence of dipoles in the molecules. The work of Butler (Butler, Thomson and MacLennan, J.C.S., 674, 1933) on the partial vapour pressures of the lower n-aliphatic alcohols in water, shows a general qualitative agreement with the theory.

In the general treatment of solubility, substances have been grouped into two classes, namely electrolytes and non-electrolytes, the former giving charged ions in aqueous solution. In aqueous solutions, the 'long range' forces between these ions are very important and considerable progress has been made in the treatment of such electrolytic solutions by a consideration of them.
Born (Z. physik. Chem., 1, 45, 1920) showed that the electrical energy involved in changing the surroundings of a charged ion was given by the expression,

$$F_e = \frac{\varepsilon^2}{2r}\left(\frac{1}{D_1} - \frac{1}{D_2}\right) \qquad (9)$$

where ε and r = charge and radius of the ion respectively,

and D_1 and D_2 = dielectric constants of the two media.

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

While such forces are no doubt of major importance in aqueous solutions, in solvents of low dielectric constant, where free ions cannot exist, other forces of similar origin may be of importance. When the individual charges of the component parts of a molecule are unsymmetrically arranged, the resultant effect is the production of an electric field round the molecule and attempts have been made on similar lines to those of Born to calculate the energy of transfer of such molecules, known as dipoles etc., to non-polar media. 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 dielectric constant D, is given by

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

Where μ = dipole moment of molecule,

and a = radius of molecule.

Using as a model, 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, Bell (Trans. Far. Soc., 27, 797, 1931) derived a similar expression,

$$F_e = \frac{\mu^2}{3a^3}\left(\frac{D - 1}{2D + 1}\right) \qquad (11)$$

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

The most important advance in recent years has been the theoretical calculation of the value of the 'short range' van der Waals' forces between two atoms by London (Z. physik. Chem., 63, 245, 1930), who has shown that these are due mainly to an interaction between short period electronic vibrations. The 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 chief types of interaction of molecules in solutions, governing solubility, may now be summarised as
(1) that due to the van der Waals' or dispersion forces, the approximate value of which for any two atoms is given by London's expression;
(2) the interaction of electric dipoles with other dipoles on the one hand and with polarisable molecules (induced dipoles) on the other;
(3) the interaction of electrically charged ions with each other, with dipoles, and with polarisable molecules; and (4) the interaction of two molecules involving compound formation by the mutual sharing of electrons.

The relative importance of each of these factors depends upon the system under consideration.

THERMODYNAMICAL THEORY:

The Free Energy of Solution

The partial molar free energy of a solute in a binary solution at a given temperature may be expressed as

$$\overline{F}_2 = F^\circ_2 + RT \log p_2/p_2^\circ , \qquad (12)$$

where F°_2 = molar free energy of the pure liquid solute;

p_2 = partial vapour pressure of solute,

and p_2° = vapour pressure of the pure solute.

In a solution which obeys Raoult's Law,

$$p_2/p_2^\circ = \frac{n_2}{n_1 + n_2} = N_2 \qquad (13)$$

When Raoult's Law is not obeyed, we may write

$$p_2/p_2^\circ = N_2 f_2 , \qquad (14)$$

where f_2 is an activity coefficient which measures the divergence from Raoult's Law. As defined, $f_2 = 1$ in the pure liquid.

Substituting for p_2/p_2° in equation (12) the value

N_2f_2, we have

$$F_2 = F^\circ_2 + RT \log N_2f_2, \qquad (15)$$

Again, in an infinitely dilute solution, where the solute molecules are not associated, the partial molar free energy may be written as

$$\overline{F}_2 = \overline{F}^\circ_2 + RT \log N_2, \qquad (16)$$

where $\overline{F}^\circ_2$ = standard molar free energy for the dilute solution.

If, in this dilute solution, f_2° is the activity coefficient, then, by combining equations (15) and (16), we obtain

$$\overline{F}^\circ_2 - F^\circ_2 = RT \log f_2^\circ \qquad (17)$$

Thus defined, the quantity RT log f_2° is equal to the difference between the standard free energy for dilute solutions of the component in a given solvent and its free energy in the pure liquid.

The quantity RT log f_2°, however, is not very susceptible to theoretical interpretation, and it is preferable to take as the standard the gaseous state, since the above method involves a consideration of the substance as a pure liquid, which itself is a complex state.

Thus, if $(F^\circ{}_g)_2$ is the molar free energy of the solute in the vapour at unit pressure (1 mm. Hg), its free energy at a pressure p_2 is

$$\overline{F}_2 = (F^\circ{}_g)_2 + RT \log p_2, \qquad (18)$$

so that, if p_2 is the partial vapour pressure of the solute over a very dilute solution, of molar fraction N_2, combining equations (16) and (18), we have

$\overline{F}^\circ_2 + RT \log N_2 = \overline{F}_2 = (F^\circ_g)_2 + RT \log p_2$, so that

$$\overline{F}^\circ_2 - (F^\circ_g)_2 = RT \log \frac{p_2}{N_2} , \qquad (19)$$

and this quantity may be called the free energy of solution.

The ratio p_2/N_2, which is the limiting value, at small concentrations, of the distribution ratio of the solute between the vapour and the solution can be measured in two ways:-

(a) by direct measurement of the partial vapour pressure, p_2, in a solution sufficiently dilute to prevent interactions between solute molecules, or

(b) when the miscibility is low, by the ratio p_2°/N_s, where p_2° is the vapour pressure of the pure solute and N_s its molar fraction in the (dilute) saturated solution.

In case (a), assuming that Raoult's Law holds for the solvent, $p_1 = p_1^\circ N_1$, and if we measure the relative molar concentrations, n_1 and n_2, of the solvent and solute in the vapour, then

$$\frac{n_2}{n_1} = \frac{p_2}{p_1^\circ N_1} \text{ , from which } p_2 \text{ can be found.}$$

By these methods Butler (Butler, Ramchandani and

Thomson, J.C.S., 280, 1935) determined the free energy of solution for the aliphatic alcohols (C_3 to C_8) in water, and of the lower n-aliphatic alcohols (C_1 to C_4), and other substances, in non-polar solvents (Butler and Harrower, Trans. Far. Soc., 33, 171, 1937).

Although p/N is convenient in practice, a more natural expression of the distribution coefficient is in terms of the Ostwald coefficient $\lambda = \frac{c_l}{c_g}$, where c_l, c_g are the concentrations of the solute in the liquid and the vapour in mols./c.c. When the standard states are defined in terms of these units the free energy change is

$$\Delta F_C = RT \log c_g/c_l \qquad (20)$$

The relation between these expressions is

$$\frac{p}{N} = 1{\cdot}7032 \times 10^4 Td/273{\cdot}1\, M_1 \lambda\,, \qquad (21)$$

where M_1 is the molecular weight of the solvent and d its density.

The Heat of Solution.

This thermodynamic function represents the heat absorbed in bringing the solute molecule from the vapour into the dilute solution, i.e. it is the heat of solution of the solute vapour. The heat of solution of the solute vapour at infinite dilution can be obtained from

$$\Delta H = \theta - Q, \tag{22}$$

where Q is the heat of vaporisation of the liquid solute and θ its heat of solution at infinite dilution. Determinations of θ for a number of compounds have been made by Butler (Butler, Ramchandani and Thomson, loc. cit.) and by Wolf (Wolf, Pahlke and Wehage, Z. physik. Chem., B <u>28</u>, 1, 1935) and Q can often be calculated from the vapour pressures. ΔH may also be determined by measurements of ΔF and its temperature coefficient.

The Entropy of Solution.

The free energy of solution is determined by the heat and entropy of solution, according to

$$\Delta F = \Delta H - T\Delta S, \tag{23}$$

where ΔH is the heat of solution and ΔS the corresponding entropy change.

ΔS can be obtained in two ways:-

(a) from the temperature coefficient of ΔF, by

$\frac{d(\Delta F)}{dT} = -\Delta S$. In practice the approximation,

$$\frac{\Delta F_{T_2} - \Delta F_{T_1}}{T_2 - T_1} = -\Delta S_{T_0} \quad \text{is convenient.}$$

ΔF_{T_2} and ΔF_{T_1} are the free energies of solution at the absolute temperatures T_2 and T_1, and $-\Delta S_{T_0}$ the entropy of solution at the temperature T_0, where $\frac{T_2 + T_1}{2} = T_0$; or

(b) from ΔF and the thermochemical value of ΔH using relation (23). Equation (23) namely $\Delta F = \Delta H - T\Delta S$ gives the relationship which exists between changes in the three molal quantities, heat content, free energy and entropy and from a thermodynamic point of view the transfer of a molecule from the vapour phase to a solution is completely characterised by the change in any two of these quantities. If a further relation could be derived between ΔF, ΔH and ΔS, which would be valid for a series of systems, then it would be possible from a knowledge of any one of these three quantities, to determine the other two. Such relations might be of two kinds, namely

(a) A relation valid for a given solute in a series of different solvents;

or (b) a relation valid for a series of different solutes in the same solvent.

Several authors have recently suggested that such relationships might exist and in the following paragraphs, their conclusions are summarised. The available data for the solubility of solids in liquids have been examined by Evans and Polanyi (Trans. Far. Soc., 32, 1333, 1936; 33, 166, 1937) and they have come to the conclusion that a relation of type (a) is valid. The relation is of the simple form

$$T\Delta S = \alpha\Delta H + \beta , \qquad (24)$$

where ΔS and ΔH refer to the solution of the same solute in a series of different solvents and α and β are independent of the solvent.

The case of gaseous solutes has been examined by Bell (Trans. Far. Soc., 33, 496, 1937), who finds that for them a relationship of type (b) is valid. Linear relations between ΔH and ΔS have been found by Butler (Trans. Far. Soc., 33, 171, 129, 1937) to exist for the solubility of ten alcohols in water, four alcohols in benzene and a number of non-polar solutes in water, and it is noticeable that the values of ΔS in the case of water as solvent are distinctly higher cf. the values for the same solutes in a normal liquid.

The experimental work to be described was undertaken with a view to covering the gap between the gaseous solutes on the one hand and the solid solutes on the other. Experiments were therefore carried out to determine the free energy and entropy of solution of a number of liquid solutes in the solvents acetone and ethyl alcohol, the latter being chosen since it is intermediate in character as regards association between water, a strongly associated liquid, and normal (non-associated) liquids.

EXPERIMENTAL.

I. Purification of Materials.

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

(a) Solutes.

(1) Benzene (B.D.H.)

Extra pure benzene for molecular weight determinations, free from thiophene, was used. It was dried over freshly burned lime, fractionally distilled and then fractionally frozen three times.

B.P. 79·72° - 79·77°/ 750·9 mms.; 79·91°/ 760 mms.

(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. 75·89° - 75·96°/ 758·2 mms.; 75·97°/ 760 mms.

(3) Chloroform

The MacFarlane and Co., (B.P.) product was used. This was shaken with concentrated sulphuric acid for 15 minutes to remove alcohol, washed with caustic soda solution and then with water. After drying over anhydrous potassium carbonate it was fractionated.

B.P. 61·03° - 61·10°/ 750·5 mms.; 61·20°/ 760 mms.

(4) Carbon Disulphide (B.D.H.)

This product was free from objectionable impurities and was twice fractionated before use.

B.P. 46·41° - 46·50/ 774 mms.; 46·33°/ 760 mms.

(5) Chlorobenzene (B.D.H.)

This was dried by allowing it to stand over anhydrous calcium chloride for a few days. It was then fractionated, the middle fractiom with a boiling range of 0·15° being collected for use in the experiments.

B.P. 131·80° - 131·95°/ 755 mms.; 132·0°/ 760 mms.

(b) Solvents.

(1) 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 contamination 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. 78·31° - 78·42°/ 755 mms.; 78·47°/ 760 mms.

(2) Acetone.

Hopkin and William's A.R. Acetone was dried over anhydrous calcium chloride and then fractionally distilled, the middle fraction boiling within a suitable range being collected for use in the experiments.

B.P. 56·60° - 56·68°/ 770 mms.; 56·52°/ 760 mms.

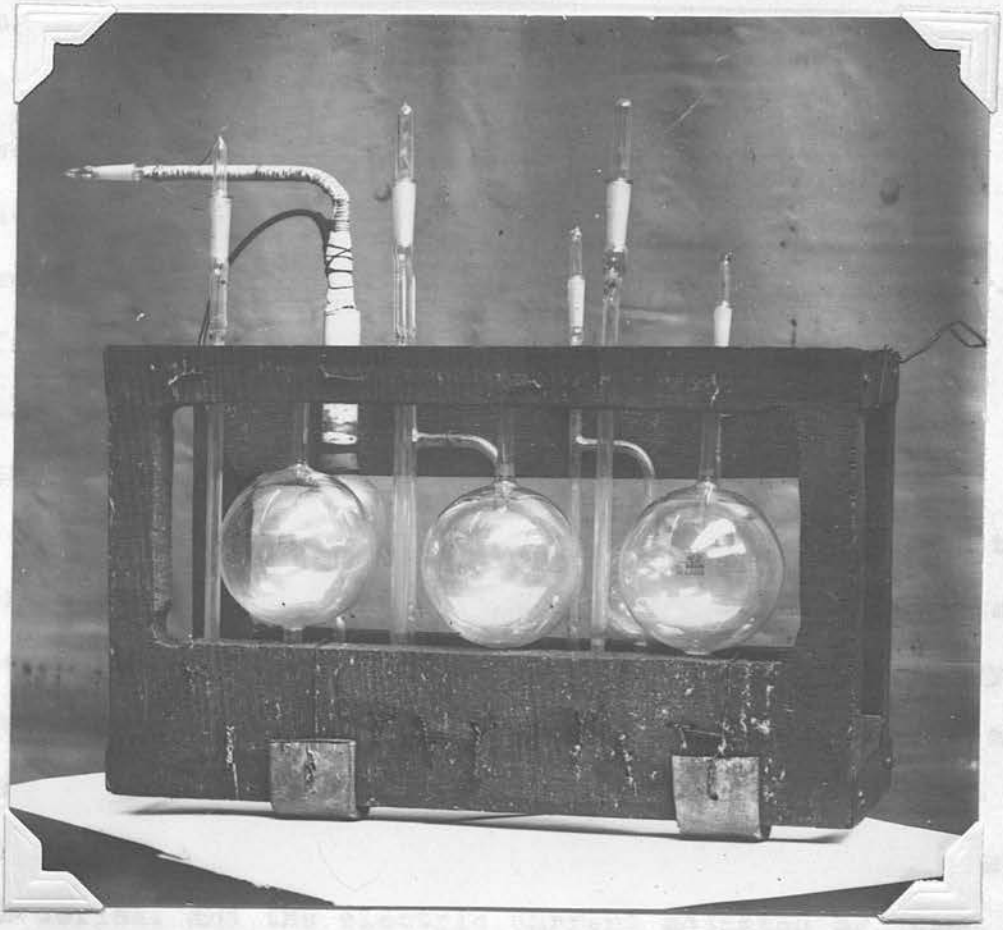
II. Apparatus.

The partial vapour pressures were determined by bubbling a slow stream of nitrogen over the standard solution, which was contained in a series of bulbs, the vapour carried over being collected in a condenser, immersed in a slush of carbon dioxide snow and ether, contained in a thermos flask.

To ensure complete saturation of the nitrogen stream at the low concentrations used, a Six-Bulb Bubbler was employed. It provided a vapour space large compared with that occupied by the standard solution so that a large surface was continually exposed to the nitrogen stream, allowing of complete saturation to be rapidly attained.

It consisted of two sets of three bulbs, the larger set being composed of bulbs of 250 ccs. capacity, the smaller of 50 ccs. The nitrogen passed through the larger bulbs first where saturation was almost completed and the smaller set ensured perfect saturation.

The six bulbs were joined together in one piece, with limbs suitably placed for introducing solution, the complete arrangement of bulbs being mounted on a stout wooden frame, weighted with lead. It was found convenient to fit all limbs with ground glass joints, which enabled the standard solution to be introduced through filter funnels having the complimentary part



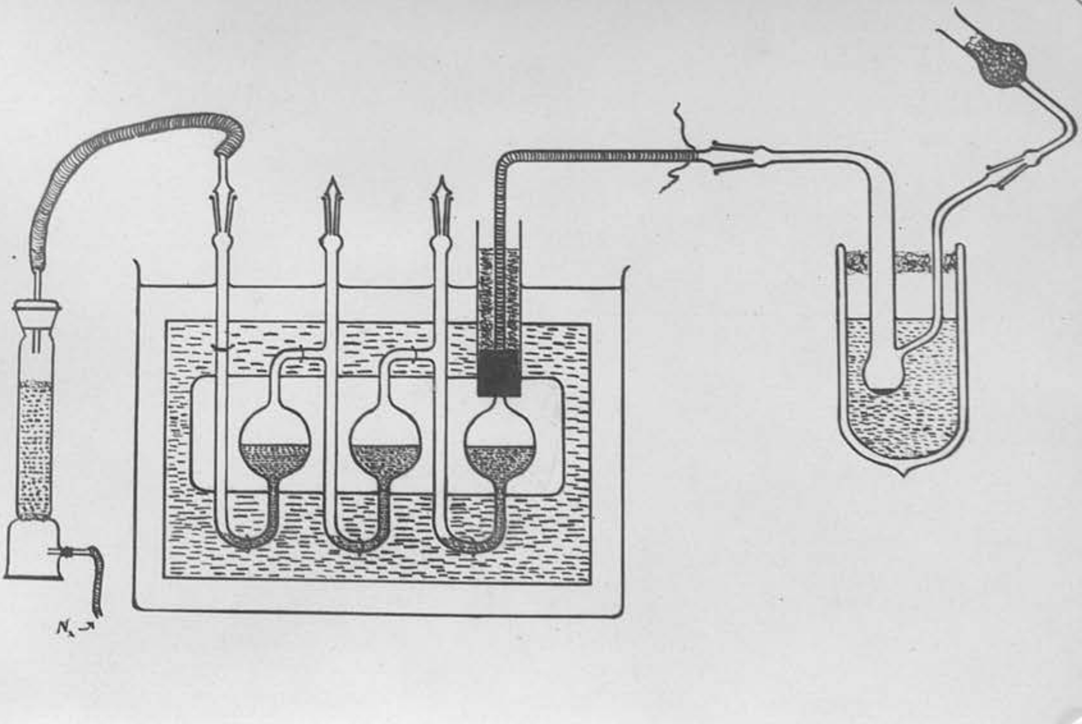


Figure 1 .

of the joints. The constrictions on the entrance tubes broke up the nitrogen stream into bubbles, which were allowed to pass at the rate of one bubble per second. A liquid trap was found to be unnecessary, as from the nature of the bubbler there was space sufficient to eliminate entrainment. The Bubbler is illustrated diagrammatically in Figure I and a photograph is also given.

To avoid premature condensation of the vapours, the exit tube was fitted with heating elements, carried below the level of the thermostat water, from which they were protected by a short glass cylinder fitted with a one-holed rubber stopper. Heating mats on the horizontal portion of the exit tube were connected to these in series, and the electric current adjusted by means of a rheostat, to give a temperature slightly higher than that of the thermostat.

Of the two thermostats used, that at 25°C was electrically heated while the other, at 35°C was gas heated. The temperatures were steady in both cases to ±0·01°C.

The Condensers:

(a) for liquid solutes: The vapours carried over in the nitrogen stream were liquefied by means of the condenser shown in Fig. II. Connection to the bubbler was made through a ground glass joint and during an experi-

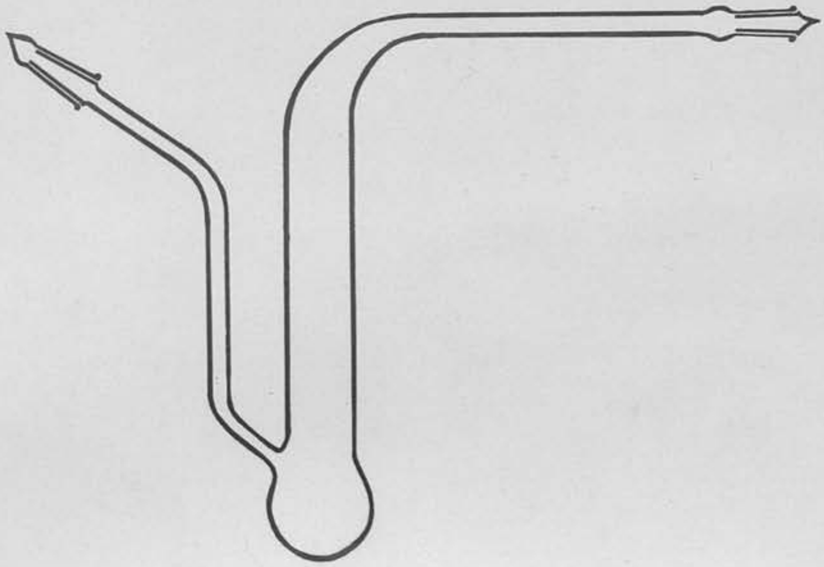
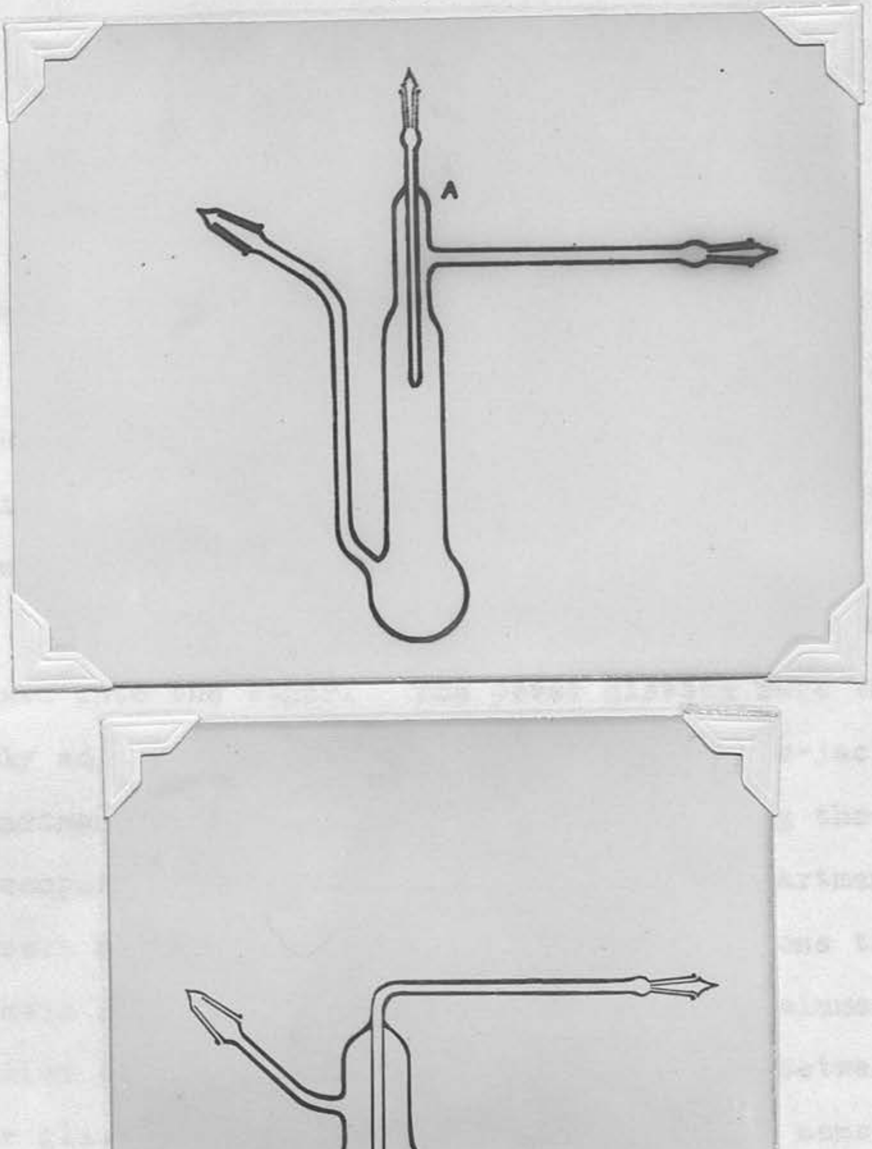


Figure II .



Figures III (a) and
(b).

III. Analysis of Condensates.

(a) Liquid Solutes:

To determine the weight concentration of the solute in the condensate, a Rayleigh Interferometer was employed. This gave two series of vertical fringes in the eyepiece, the upper series being movable. In order to take a reading, a one centimetre cell, composed of two compartments, was used. The reference solution, usually the pure solvent was run into one cell compartment, the condensate into the other. The cover glasses were then firmly adjusted and the cell placed in a water-jacketed compartment, kept at 15°C by water circulating through the compartment from a thermostat. 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.

By exercising care in the filling of the cell compartments, the adjustment of the cover glasses and the placing of the cell in the instrument, it was found possible to obtain steady interferometer readings from five to ten minutes after insertion of the cell. The cell was so placed as to give a positive reading on matching the fringes and the position of the condensate denoted R or L according as the latter had to be run into the right or left-handed compartment. The solution of higher refractive index appeared on the right. The zero reading was taken in each case by having the solvent in both compartments and was always about 1 drum division above the zero mark on the scale, so that 1 drum division was subtracted from each reading taken.

In the case of the experiments on carbon disulphide in ethyl alcohol, the concentrations of carbon disulphide in the condensates at the concentrations used, were always too large to give readings on the scale of the instrument; thus the collecting tube was weighed before and after the experiment, the difference giving the weight of condensate collected, w. Pure solvent was then run into the receiver to give a solution sufficiently dilute to be analysed in the Interferometer. If the weight of diluted condensate be denoted by s, its weight concentration being c gms.%, then the weight percentage of solute in the original solution was obtained by evaluating $\frac{s \times c}{w}$.

For all the liquid solutes, c was determined by preparing two accurate calibration solutions with readings on either side of the condensate reading. About 50 drum divisions separated the calibration solution readings. The readings for condensate and calibration solutions were taken one after the other to ensure that in each case the same fringes had been matched. The approximate concentration of solute in the condensate was first found by running known volumes from a 0·5 c.c. pipette into 10 ccs. solvent and so calibrating over a wide range. The accurate calibrations could then be adjusted by volume, accurate weighings also being carried out during the various operations.

Over the short range (50 - 100 drum divisions) involved, the relation between refractive index and concentration may be assumed linear, so that the required concentration, c, of the condensate could be read off from a large scale graph to 0·001%.

Or, if I_1 and I_2 are the interferometer readings of the two calibration solutions corresponding to concentrations of c_1 and c_2 respectively, where $I_2 > I_1$ and $c_2 > c_1$, then a condensate of reading I, has a concentration $c = c_1 + \frac{I - I_1}{I_2 - I_1}(c_2 - c_1)$, where $I_2 > I > I_1$.

(b) Gaseous Solutes:

The gaseous solutes employed were sulphur dioxide and ammonia and analyses of their condensates were carried out by titrimetric methods. In the case of sulphur dioxide, the analysis was performed by adding an excess of standard iodine to react with the sulphur dioxide, the excess being determined by back titration against standard sodium thiosulphate solution. For ammonia, standard hydrochloric acid solution was added, the excess in this case being determined by titration with standard sodium hydroxide solution. The first condensate receiver was weighed in each case before and after the experiment in order to obtain the weight of condensate collected. Excess of the required reagent was then added to the receiver through the tube marked A in the diagram of the condenser. The contents of the receiver were then washed out into a conical flask for determination of the excess of reagent added by means of the requisite standard solution. The weight of gas carried over into the second receiver was determined by similar methods and thus the corrĕction to be applied was readily obtained. By such methods it was possible to calculate the true weight percentage of gas in their respective condensates.

IV. Experimental Method.

Solutions of known concentration were prepared in a long-necked 1000 c.cs. standard flask, fitted 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, previously weighed empty, with solvent from a wash-bottle protected from contamination by a calcium chloride tube.

Standard solutions of the gaseous solutes were prepared by dilution of concentrated solutions and analysis of the latter by the methods described above.

Once completed, the standard solution was quickly run into the clean and dry bubblers, which were now fixed up in position in the thermostats, and connected through calcium chloride towers to a nitrogen cylinder. The bubblers were left for a period of fifteen minutes to attain the thermostat temperatures.

Meanwhile the collecting tubes were thoroughly cleaned and dried and the calcium chloride guard tubes attached. When the thermostats had regained their temperatures, nitrogen, dried by passing through calcium chloride towers, was passed through both bubblers simultaneously for ten minutes, in order to saturate the solution with the gas. This ensured that the same conditions held at the beginning and the end of each experiment. The nitrogen flow was regulated by means of screw clips to one bubble per second.

Dry air was then sucked into the condensers through the calcium chloride guard tubes and the condensers immersed in freezing mixtures of carbon dioxide snow and ether. After connecting the condensers to the bubblers, the various heating elements were engaged and the electric current switched on. Any errors due to differences in the construction of the bubblers were eliminated by interchanging them on the second running.

A run of from eight to ten hours was sufficient to collect 0·5 c.c. condensate. On removal from the freezing mixtures, the condensates were allowed to regain atmospheric pressure and temperature by leaving the calcium chloride tubes attached for a few minutes before finally stoppering them up. This ensured that no atmospheric moisture would subsequently be sucked into the condensers. The condensates were then analysed by the methods described in the previous section.

At least two concordant results were obtained in each case, the overall error in p/N amounting to about 2%. An uncertainty of this order in the partial vapour pressure corresponds to about ± 15 cals. in RT log p/N.

RESULTS.

(a) Blank Experiments.

Experiments were carried out with the pure solvents in the bubblers. The condensate readings were then taken against the pure solvents, and the error involved as a result of distillation of the solvent during an actual experiment thus found. The results are given in Table I.

The letters R and L indicate that the condensate had to be placed in the right or left-handed compartment of the interferometer cell in order to obtain a positive reading.

When an actual experiment was run, the position of the condensate was noted. Obviously these distillation differences were subtracted from the condensate readings when the condensate collected from a mixture appeared in the same cell compartment, and added under the reverse conditions.

The solvents were distilled before use in each experiment in order that the corrections should apply universally.

Table I.

Solvent	Condensate (25°C) I.R.	Mean I.R.	Condensate (35°C) I.R.	Mean I.R.
Ethyl Alcohol R	8·0 7·5	8·0	8·0 8·0	8·0
Acetone L	1·0 1·0	1·0	1·5 2·0	2·0

Table II gives the vapour pressures of the pure solvents used. These were obtained from the International Critical Tables (Vol. III, p. 217).

Table II - Vapour Pressures.

Solvent	V.P. mms. (25°C)	V.P. mms. (35°C)
Ethyl Alcohol	59·0	103·4
Acetone	229·2	346·4

(b) The completed results for the various solutes in the solvents in ethyl alcohol and acetone are given in Tables III to XIII. N is the molar fraction of the solute in the solution, c is its concentration (expressed as weight percentage) in the condensate and p its partial vapour pressure over the solution. The original calibration curves were drawn on a very much wider scale so that c could be read off very easily to 0·001 gms.%. The curves were assumed linear over the short range involved.

Table III

Solvent - Acetone   Solute - Carbon Disulphide (R.)

			Calibrations		Condensates
		Condensates	I.R.	c%	c%
Experiment I	25°	1,658	1,682	3·540	3·491
			1,649	3·473	
	35°	1,510	1,510	3·196	3·196
Experiment II	25°	1,466	1,464	3·102	3·106
			1,341	2·850	
	35°	1,323	1,320	2·808	2·814

		$N \times 10^3$	c%	p mms.	p/N	RT log p/N
Experiment I	25°	4·963	3·491	6·290	1,267	4,238
	35°		3·196	8·677	1,748	4,579
Experiment II	25°	4·395	3·106	5·578	1,269	4,240
	35°		2·814	7·615	1,733	4,574

ΔF_{25} = 4,239 cals.

ΔF_{35} = 4,577 cals.

$-\Delta S_{30}$ = 33·8 cals./deg.

$-T\Delta S$ = 10·08 k-cals.

$-\Delta H_{25}$ = 5·84 k-cals.

Table IV

<u>Solvent</u> - Acetone <u>Solute</u> - Benzene (R.)

			Calibrations		Condensates
		Condensates	I.R.	c%	c%
Experiment I	25°	268			0·728
	35°	273	267	0·725	0·741
Experiment II	25°	266	282	0·766	0·722
	35°	269			0·730

		$N \times 10^2$	c%	p mms.	p/N	RT log p/N
Experiment I	25°	1·031	0·728	1·234	119·7	2,838
	35°		0·741	1·899	184·2	3,199
Experiment II	25°	1·015	0·722	1·224	120·6	2,844
	35°		0·730	1·871	184·4	3,201

ΔF_{25} = 2,841 cals.

ΔF_{35} = 3,200 cals.

$-\Delta S_{30}$ = 35·9 cals./deg.

$-T\Delta S$ = 10·70 k-cals.

$-\Delta H_{25}$ = 7·86 k-cals.

Table V

Solvent - Acetone   Solute - Chloroform (R.)

			Calibrations		Condensates
		Condensates	I.R.	c%	c%
Experiment I	25°	91			0·663
	35°	96	103	0·751	0·700
Experiment II	25°	86	64	0·468	0·626
	35°	92			0·670

		$N \times 10^3$	c%	p mms.	p/N	RT log p/N
Experiment I	25°	9·972	0·663	0·7361	73·81	2,551
	35°		0·700	1·176	117·9	2,925
Experiment II	25°	9·448	0·626	0·6955	73·60	2,550
	35°		0·670	1·126	119·1	2,931

ΔF_{25} = 2,551 cals.

ΔF_{35} = 2,928 cals.

$-\Delta S_{30}$ = 37·7 cals./deg.

$-T\Delta S$ = 11·24 k-cals.

$-\Delta H_{25}$ = 8·69 k-cals.

Table VI.

Solvent - Acetone   Solute - Chlorobenzene (R.)

			Calibrations		Condensates
		Condensates	I.R.	c%	c%
Experiment I	25°	50			0·135
	35°	56	51	0·138	0·152
Experiment II	25°	49	36	0·097	0·132
	35°	54			0·147

		$N \times 10^3$	c%	p mms.	p/N	RT log p/N
Experiment I	25°	9·042	0·135	0·1586	17·54	1,698
	35°		0·152	0·2699	29·86	2,083
Experiment II	25°	8·954	0·132	0·1550	17·31	1,691
	35°		0·147	0·2611	29·16	2,069

ΔF_{25} = 1,695 cals.

ΔF_{35} = 2,076 cals.

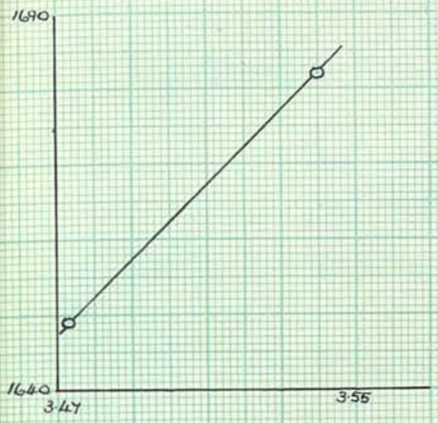
$-\Delta S_{30}$ = 38·1 cals./deg.

$-T\Delta S$ = 11·36 k-cals.

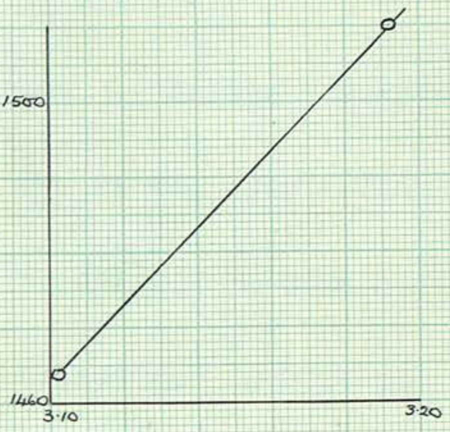
$-\Delta H_{25}$ = 9·66 k-cals.

CALIBRATION CURVES

SOLVENT - ACETONE



SOLUTE - CARBON DISULPHIDE



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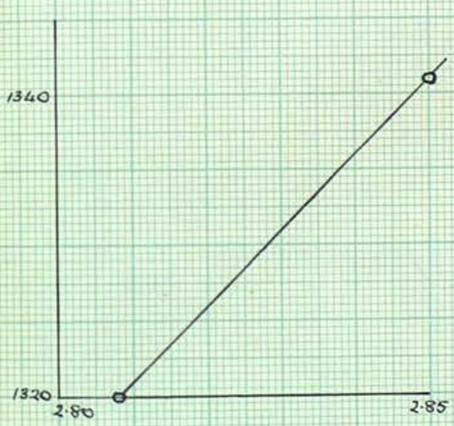

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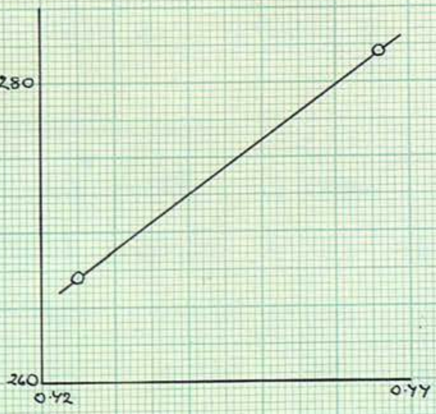
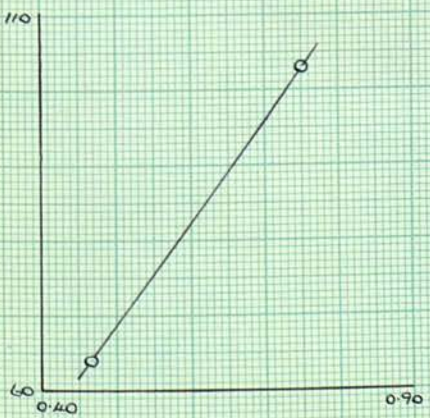
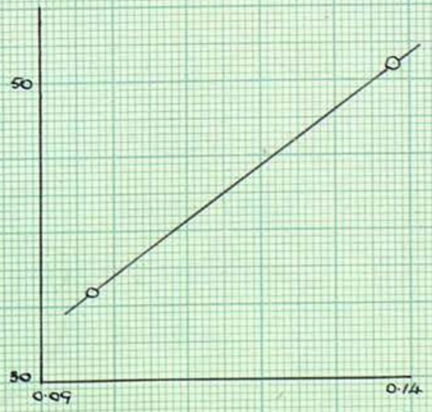


SOLUTE - BENZENE



SOLUTE - CHLOROFORM



SOLUTE - CHLOROBENZENE

HORIZ. CONCENTRATION % SOLUTE

VERT. INTERFEROMETER READING

Table VII.

Solvent - Ethyl Alcohol   Solute - Sulphur Dioxide

		Wt. of condensate	Wt. of SO_2	Correction	True conc. (c%)
25°	Expt. I	0·4737 g.	0·0453 g.	0·0026 g.	$\frac{0\cdot0479 \times 100}{0\cdot4763} = 10\cdot06$
	" II	0·4848 g.	0·0463 g.	0·0024 g.	$\frac{0\cdot0487 \times 100}{0\cdot4872} = 9\cdot992$
35°	" I	0·4703 g.	0·0386 g.	0·0012 g.	$\frac{0\cdot0398 \times 100}{0\cdot4715} = 8\cdot441$
	II	0·4142 g.	0·0334 g.	0·0011 g.	$\frac{0\cdot0345 \times 100}{0\cdot4153} = 8\cdot307$

		$N \times 10^3$	c%	p mms.	p/N	RT log p/N
25°	Experiment I	2·223	10·06	4·731	2,129	4,543
	" II	2·206	9·992	4·699	2,130	4,543
35°	" I	2·259	8·441	6·854	3,035	4,918
	" II	2·224	8·307	6·737	3,029	4,916

ΔF_{25} = 4,543 cals.

ΔF_{35} = 4,917 cals.

$-\Delta S_{30}$ = 37·4 cals./deg.

$-T\Delta S$ = 11·15 k-cals.

$-\Delta H_{25}$ = 6·61 k-cals.

Table VIII.

Solvent - Ethyl Alcohol   Solute - Ammonia

		Wt. of condensate	Wt. of NH_3	Correction	True conc. (c%)
25°	Expt. I	0·4071 g.	0·0171 g.	0·0012 g.	$\frac{0{\cdot}0183 \times 100}{0{\cdot}4083} = 4{\cdot}482$
	" II	0·3104 g.	0·0126 g.	0·0011 g.	$\frac{0{\cdot}0137 \times 100}{0{\cdot}3115} = 4{\cdot}397$
35°	" I	0·5064 g.	0·0174 g.	0·0008 g.	$\frac{0{\cdot}0182 \times 100}{0{\cdot}5072} = 3{\cdot}588$
	" II	0·4675 g.	0·0162 g.	0·0006 g.	$\frac{0{\cdot}0168 \times 100}{0{\cdot}4681} = 3{\cdot}589$

		$N \times 10^3$	c%	p mms.	p/N	RT log p/N
25°	Experiment I	4·053	4·482	7·471	1,844	4,460
	" II	3·983	4·397	7·325	1,839	4,458
35°	" I	3·940	3·588	10·42	2,644	4,833
	" II	3·896	3·589	10·42	2,674	4,840

ΔF_{25} = 4,459 cals.

ΔF_{35} = 4,837 cals.

$-\Delta S_{30}$ = 37·8 cals./deg.

$-T\Delta S$ = 11·27 k-cals.

$-\Delta H_{25}$ = 6·81 k-cals.

Table IX

Solvent - Ethyl Alcohol   Solute - Carbon Disulphide

		Diluted Condensate	w	s	Calibrations I.R.	Calibrations c%	Original Condensate c%
Expt. I	25°	744	0·6388 g.	4·649 g.			$\frac{1{\cdot}543 \times 4{\cdot}649}{0{\cdot}6388} = 11{\cdot}23$
	35°	752	0·5214 g.	3·084 g.	710	1·470	$\frac{1{\cdot}560 \times 3{\cdot}084}{0{\cdot}5214} = 9{\cdot}231$
Expt. II	25°	785	0·3960 g.	2·555 g.	790	1·642	$\frac{1{\cdot}631 \times 2{\cdot}555}{0{\cdot}3960} = 10{\cdot}53$
					768	1·594	
	35°	712	0·6028 g.	3·632 g.			$\frac{1{\cdot}475 \times 3{\cdot}632}{0{\cdot}6028} = 8{\cdot}886$

		$N \times 10^3$	c%	p mms.	p/N	RT log p/N
Experiment I	25°	2·632	11·23	4·505	1,712	4,415
	35°		9·231	6·364	2,419	4,779
Experiment II	25°	2·492	10·53	4·192	1,682	4,405
	35°		8·886	6·104	2,449	4,787

ΔF_{25} = 4,410 cals.

ΔF_{35} = 4,783 cals.

$-\Delta S_{30}$ = 37·3 cals./deg.

$-T\Delta S$ = 11·12 k-cals.

$-\Delta H_{25}$ = 6·71 k-cals.

Table X

<u>Solvent</u> - Ethyl Alcohol   <u>Solute</u> - Carbon Tetrachloride

			Calibrations		Condensates
		Condensates	I.R.	c%	c%
	25°	820			5·654
Experiment I			705	4·875	
	35°	722	760	5·253	4·991
	25°	857	817	5·632	5·905
Experiment II			861	5·936	
	35°	754			5·210

		$N \times 10^3$	c%	p mms.	p/N	RT log p/N
Experiment I	25°	2·105	5·654	1·057	502·2	3,689
	35°		4·991	1·628	773·7	4,080
Experiment II	25°	2·204	5·905	1·107	501·7	3,688
	35°		5·210	1·703	772·1	4,078

ΔF_{25} = 3,689 cals.

ΔF_{35} = 4,079 cals.

$-\Delta S_{30}$ = 39·0 cals./deg.

$-T\Delta S$ = 11·63 k-cals.

$-\Delta H_{25}$ = 7·94 k-cals.

Table XI

Solvent - Ethyl Alcohol   Solute - Benzene

			Calibrations		Condensates
		Condensates	I.R.	c%	c%
Experiment I	25°	1,220			3·217
			1,061	2·802	
	35°	1,095	1,124	2·965	2·890
Experiment II	25°	1,181	1,181	3·114	3·114
			1,216	3·206	
	35°	1,053			2·781

		$N \times 10^3$	c%	p mms.	p/N	RT log p/N
Experiment I	25°	2·777	3·217	1·154	415·5	3,576
	35°		2·890	1·816	653·9	3,976
Experiment II	25°	2·653	3·114	1·113	419·4	3,582
	35°		2·781	1·745	657·7	3,979

ΔF_{25} = 3,579 cals.

ΔF_{35} = 3,978 cals.

$-\Delta S_{30}$ = 39·9 cals./deg.

$-T\Delta S$ = 11·89 k-cals.

$-\Delta H_{25}$ = 8·31 k-cals.

Table XII

Solvent - Ethyl Alcohol Solute - Chloroform

			Calibrations		Condensates
		Condensates	I.R.	c%	c%
Experiment I	25°	542			4·175
	35°	504	463	3·551	3·883
Experiment II	25°	531	503	3·875	4·088
			552	4·251	
	35°	492			3·783

		$N \times 10^3$	c%	p mms.	p/N	RT log p/N
Experiment I	25°	3·573	4·175	0·9880	276·5	3,336
	35°		3·883	1·610	450·5	3,748
Experiment II	25°	3·480	4·088	0·9672	278·0	3,338
	35°		3·783	1·567	450·3	3,748

ΔF_{25} = 3,337 cals.

ΔF_{35} = 3,748 cals.

$-\Delta S_{30}$ = 41·1 cals./deg.

$-T\Delta S$ = 12·25 k-cals.

$-\Delta H_{25}$ = 8·91 k-cals.

Table XIII

<u>Solvent</u> - Ethyl Alcohol <u>Solute</u> - Chlorobenzene

			Calibrations		Condensates
		Condensates	I.R.	c%	c%
Experiment I	25°	965			2·606
	35°	951	965	2·606	2·565
Experiment II	25°	962	926	2·492	2·597
	35°	942			2·539

		$N \times 10^2$	c%	p mms.	p/N	RT log p/N
Experiment I	25°	1·035	2·606	0·6399	61·83	2,446
	35°		2·565	1·106	106·9	2,865
Experiment II	25°	1·034	2·597	0·6376	61·65	2,445
	35°		2·539	1·094	105·9	2,860

ΔF_{25} = 2,446 cals.

ΔF_{35} = 2,863 cals.

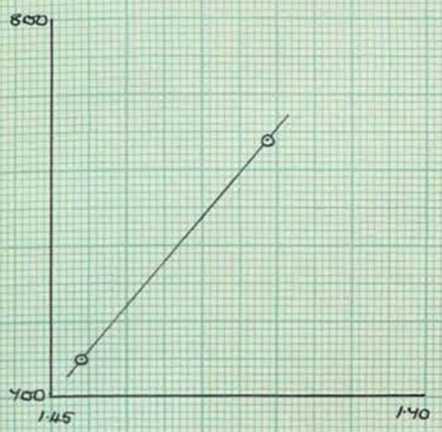
$-\Delta S_{30}$ = 41·7 cals./deg.

$-T\Delta S$ = 12·43 k-cals.

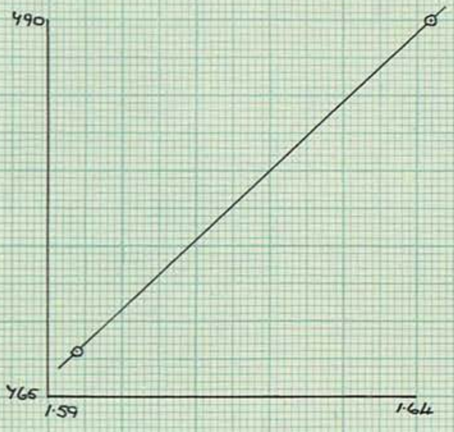
$-\Delta H_{25}$ = 9·98 k-cals.

CALIBRATION CURVES

SOLVENT - ETHYL ALCOHOL



SOLUTE - CARBON DISULPHIDE



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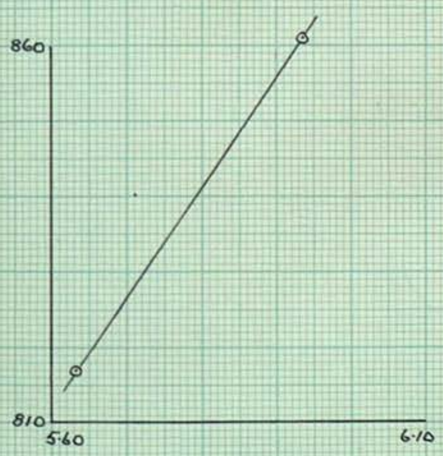
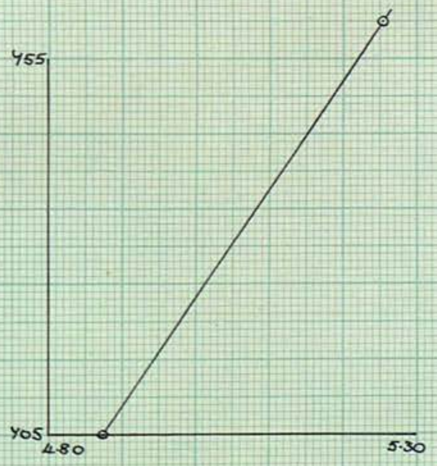


SOLUTE - CARBON TETRACHLORIDE



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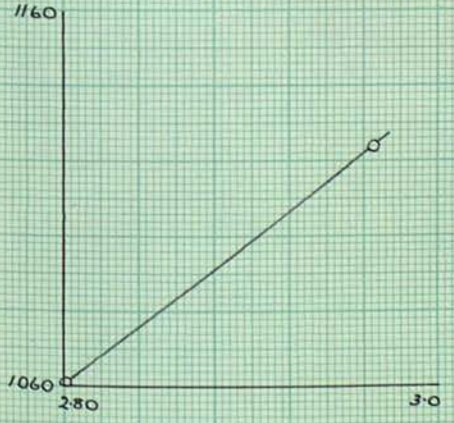
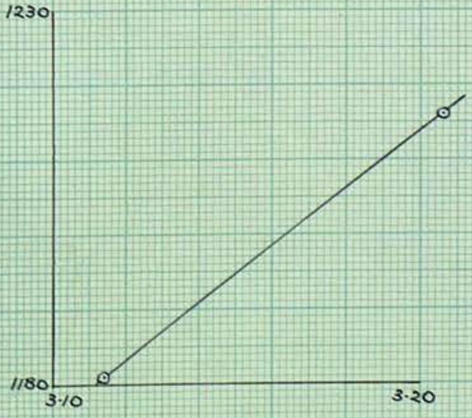


SOLUTE - BENZENE



SOLUTE - BENZENE

HORIZ. CONCENTRATION % SOLUTE

VERT. INTERFEROMETER READING

The experimental results are collected and summarised in Tables XIV and XV.

Table XIV

Solvent - Acetone

	25°C			35°C					
Solute	p/N	Po	p/p_oN	p/N	$\Delta F_{p_{25}}$	$\Delta F_{p_{35}}$	$-\Delta S_{p_{30}}$	$-T\Delta S_p$	$-\Delta H_{p_{25}}$
Carbon Disulphide	1,268	359·0	3·53	1,741	4,239	4,577	33·8	10·08	5·84
Benzene	120·2	94·4	1·27	184·3	2,841	3,200	35·9	10·70	7·86
Chloroform	73·71	199·1	0·37	118·5	2,551	2,928	37·7	11·24	8·69
Chlorobenzene	17·43	11·63	1·50	29·51	1,695	2,076	38·1	11·36	9·66

Table XV

Solvent - Ethyl Alcohol

	25°C			35°C					
Solute	p/N	Po	p/p_oN	p/N	$\Delta F_{p_{25}}$	$\Delta F_{p_{35}}$	$-\Delta S_{p_{30}}$	$-T\Delta S_p$	$-\Delta H_{p_{25}}$
Sulphur dioxide	2,130	-	-	3,032	4,543	4,917	37·4	11·15	6·61
Ammonia	1,832	-	-	2,659	4,459	4,837	37·8	11·27	6·81
Carbon Disulphide	1,697	359·0	4·73	2,434	4,410	4,783	37·3	11·12	6·71
Carbon Tetrachloride	502·0	114·5	4·38	772·9	3,689	4,079	39·0	11·63	7·94
Benzene	417·5	94·4	4·53	655·8	3,579	3,978	39·9	11·89	8·31
Chloroform	277·3	199·1	1·39	450·4	3,337	3,748	41·1	12·25	8·91
Chlorobenzene	61·74	11·63	5·31	106·4	2,446	2,863	41·7	12·43	9·98

ΔF_p in cals./mole $-\Delta S_p$ in cals./deg./mole

$-\Delta H_p$ in k.cals./mole.

The solubility of a gas is usually expressed in terms of the Ostwald coefficient,

$$\lambda = c_{\ell} / c_{g} \ ,$$

where c_{ℓ}, c_{g} are the concentrations of the solute in the liquid and vapour in mols./c.c.

The free energy of solution in terms of these units is then

$$\Delta F_c = RT \log c_{g}/c_{\ell} \ = \ - RT \log \lambda \ .$$

The relation between the two expressions at absolute temperature T is

$$p/N = 1{\cdot}7032 \times 10^{7} \times T \times d_1 \ / \ 273{\cdot}1 \times M_1 \times \lambda \ ,$$

where M_1 is the molecular weight of the solvent and d_1 its density. So that

$$\Delta F_p - \Delta F_c \ = \ RT \log \left(\frac{1{\cdot}7032 \times 10^{7} \times T \times d_1}{273{\cdot}1 \times M_1} \right)$$

By finding this scale difference at 20°C and 30°C, we thus find the corresponding entropy difference at 25°C, from the relation $d(\Delta F)/dT = - \Delta S$.

These scale differences have been calculated for the solvents acetone and ethyl alcohol. The results are given in Tables XVI(a) and XVI(b) and have been used in the calculations of the heat and entropy of solution of the rare gases in ethyl alcohol and for the reduction to the pressure scale of a number of results for gases in acetone, given by Bell (Trans. Far. Soc., 33, 496, 1937). The densities in Table XVI(a) were obtained from the I.C.T. (Vol. III, p. 27).

Table XVI(a)

Solvent	Density (20°C)	Density (25°C)	Density (30°C)
Acetone	0·7902	0·7845	0·7787
Ethyl Alcohol	0·7893	0·7851	0·7808

Table XVI(b)

Solvent	$(\Delta F_p - \Delta F_c)_{20^\circ}$	$(\Delta F_p - \Delta F_c)_{25^\circ}$	$(\Delta F_p - \Delta F_c)_{30^\circ}$	$(\Delta S_c - \Delta S_p)_{25^\circ}$	$T(\Delta S_c - \Delta S_p)_{25^\circ}$
Acetone	7,250	7,376	7,505	25·5	7,600
Ethyl Alcohol	7,383	7,517	7,647	26·4	7,869

Accurate solubility data for gases in the solvent ethyl alcohol is not obtainable, with the exception of the work of Lannung (J. Amer. Chem. Soc., 1930, <u>52</u>, 68) on the solubility of the rare gases in that solvent. From his data, the free energy, heat and entropy of solution have been calculated, the results being contained in Table XVII.

Table XVII

Solvent - Ethyl Alcohol

Solute	T°C	λ	ΔF_c	ΔF_p	$-\Delta S_{p_{25}}$	$-T\Delta S_{p_{25}}$	$-\Delta H_{p_{25}}$
	20	0·0302	2,042	9,425			
Helium	25	0·0321	2,042	9,559	26·3	7·84	-1·72
	30	0·0340	2,041	9,688			
	20	0·0431	1,835	9,218			
Neon	25	0·0455	1,833	9,350	26·0	7·75	-1·60
	30	0·0481	1,831	9,478			
	20	0·258	791	8,174			
Argon	25	0·258	803	8,320	28·6	8·53	+0·21
	30	0·260	813	8,460			

ΔF_p in cals./mole $-\Delta S_p$ in cals./deg./mole

$-\Delta H$ in k.cals./mole.

Table XVIII gives the values on the pressure scale of the heat and entropy of solution of a number of gases in acetone. They are taken from Bell's paper (Trans. Far. Soc., <u>33</u>, 496, 1937) and have been reduced to the pressure scale by adding to his values of $T\Delta S$, the constant $T(\Delta S_c - \Delta S_p)$, which at 25°C is 7·60 k-cals.

Table XVIII

Solvent - Acetone (T = 25°C)

Solute	$-T\Delta S_c$	$-T\Delta S_p$	$-\Delta H_p$
Helium	-1·28	6·32	-3·24
Neon	-0·23	7·37	-1·96
Argon	-0·04	7·56	-0·74
Hydrogen	0·12	7·72	-1·22
Nitrogen	0·37	7·97	-0·62
Oxygen	0·44	8·04	-0·30
Carbon Monoxide	0·47	8·07	-0·31
Nitrous Oxide	1·81	9·41	2·87
Methane	0·70	8·30	0·42
Acetylene	1·93	9·53	3·75
Ethylene	1·12	8·72	1·89
Ethane	1·27	8·87	1·97

DISCUSSION

The experimental results contained in Tables XIV and XV of the previous section are shown in graphical form in Figure 1, where $-T\Delta S_p$ is plotted against $-\Delta H_p$. The values for gases contained in Tables XVII and XVIII are also shown and it can be seen that in acetone the new results extend the linear relation given by gaseous solutes from heats of solution of four to ten k-cals., the solutes being purposely chosen to represent a wide range of behaviour. The values of p/p_0N, the activity coefficients, at 25°C are also given and an examination of them shows that benzene, chlorobenzene and carbon disulphide give positive deviations from Raoult's law, while chloroform has a large positive heat of solution and exhibits a large negative deviation from Raoult's law, owing to compound formation with the acetone. This does not seem to cause any great divergence from the linear relation.

With the exception of Lannung's data for the rare

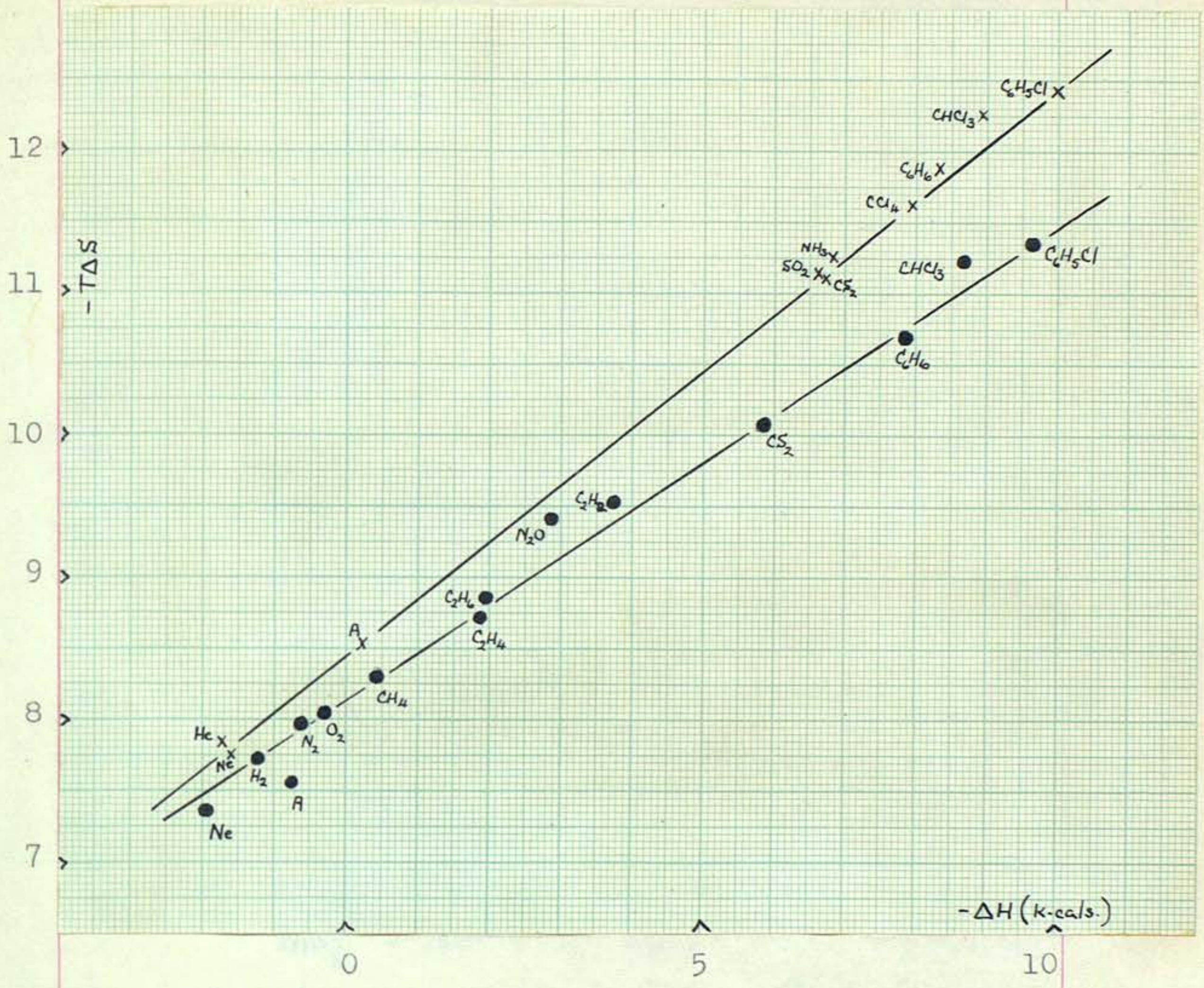


Figure 1. Heats and Entropies of Solution in Acetone (●) and Ethyl Alcohol (X).

gases in alcohol (J. Amer. Chem. Soc., 1930, 52, 68) there are no sufficiently reliable gas solubilities, but the entropies determined are appreciably higher than those in acetone for the same heats of solution, and taking into account the calculated values for the rare gases, appear to be compatible with a linear relation of somewhat greater slope than the acetone line. All the liquid solutes in alcohol exhibit positive deviations from Raoult's law.

It was found that the entropies of vaporisation of acetone and ethyl alcohol lay on their respective solvent lines and this result led to an examination of the entropies of vaporisation of other liquids at 25°C. These are given, on the pressure scale, by

$$T\Delta S_p = \Delta H + RT \log p,$$

where ΔH is the heat of vaporisation and p, the vapour pressure at the temperature T. Some values of these quantities are given in Table I. In all cases (unless otherwise indicated) ΔH is the value determined calorimetrically at or near 25°, as given in Tables Annuelles de Constantes etc., Vol. XI, Chap. 12 (Thermochimie). Some values for associated liquids are added for comparison.

Table I - Entropies of Vaporisation at 25°C.

	ΔH	p (mms)	RT log p	TΔS
CH_3Cl	4·7	4,250*	4·98	9·68
C_2H_5Cl	5·87	1,180*	4·22	10·09
$(C_2H_5)_2O$	6·43	527·0	3·75	10·18
CS_2	6·81 (21°)	359·0	3·51	10·32
$CHCl_3$	7·75	199·1	3·15	10·90
$CH_3·CO·CH_3$	7·80	229·2	3·24	11·04
CCl_4	7·95	114·5	2·82	10·77
C_6H_6	8·05	94·4	2·70	10·75
$CH_3·COOC_2H_5$	8·67	93·0*	2·70	11·37
$C_6H_5·CH_3$	9·42	28·3	2·00	11·42
$C_6H_4(CH_3)_2$ (o-)	10·03 §	-	-	11·12
" (m-)	10·23 §	-	-	11·40
" (p-)	10·49 §	-	-	11·62
$C_6H_3(CH_3)_3$	10·93 §	-	-	11·78
$C(CH_3)_4$	5·44 (10°) †	-	-	9·64

The values in the last five cases were obtained from vapour pressure relations: § Kassel, J.A.C.S., 1936, 58, 670; † Aston and Messerly, 1936, 58, 2354; * by interpolation.

Associated Liquids

	ΔH	p (mms)	RT log p	TΔS
H_2O	10·47	23·76	1·88	12·34
CH_3OH	8·04	122·2	2·85	10·89
C_2H_5OH	10·12	59·0	2·42	12·54
C_3H_7OH (n)	11·05	20·1	1·78	12·83
$C_5H_{11}OH$ (n)	12·45	2·50*	0·54	12·99
$C_6H_{13}OH$	13·05	0·719*	-0·20	12·85

* by interpolation.

The values for non-associated liquids are all reasonably close, considering the possible error of the heats of vaporisation, to the relation shown by dilute solutions.

Fig. 2 shows all the available data on one diagram, comprising entropies of solution of (1) gases in various non-associated solvents; (2) carbon disulphide, benzene, chloroform and chlorobenzene in acetone; (3) the four lower alcohols in benzene (Harrower and Butler, Trans. Far. Soc., 1937, 33, 171) and the entropies of vaporisation of a number of non-associated liquids. The divergence from a unique relation between the entropy and the heat, represented by $\Delta S_p = 0{\cdot}0277 + 0{\cdot}0011\,\Delta H$, is in no case very great, and while it cannot be claimed that if complete accuracy were obtained, all these points would lie on a single straight line, as an approximation it cannot be doubted that up to heats of solution of ca. 12 k-cals. such a general relation exists.

It will be remembered that Trouton showed that the entropy of vaporisation of non-associated liquids, determined at the boiling point, is approximately constant, but it has been recognised for a long time that this quantity shows a tendency to increase with the boiling point (c.f. O. K. Rice, J. Chem. Physics, 1937, 5, 353) and it should therefore increase with the heat of vaporisation. An examination of the best established values (vide Fig. 3) shows that the increase is most marked with

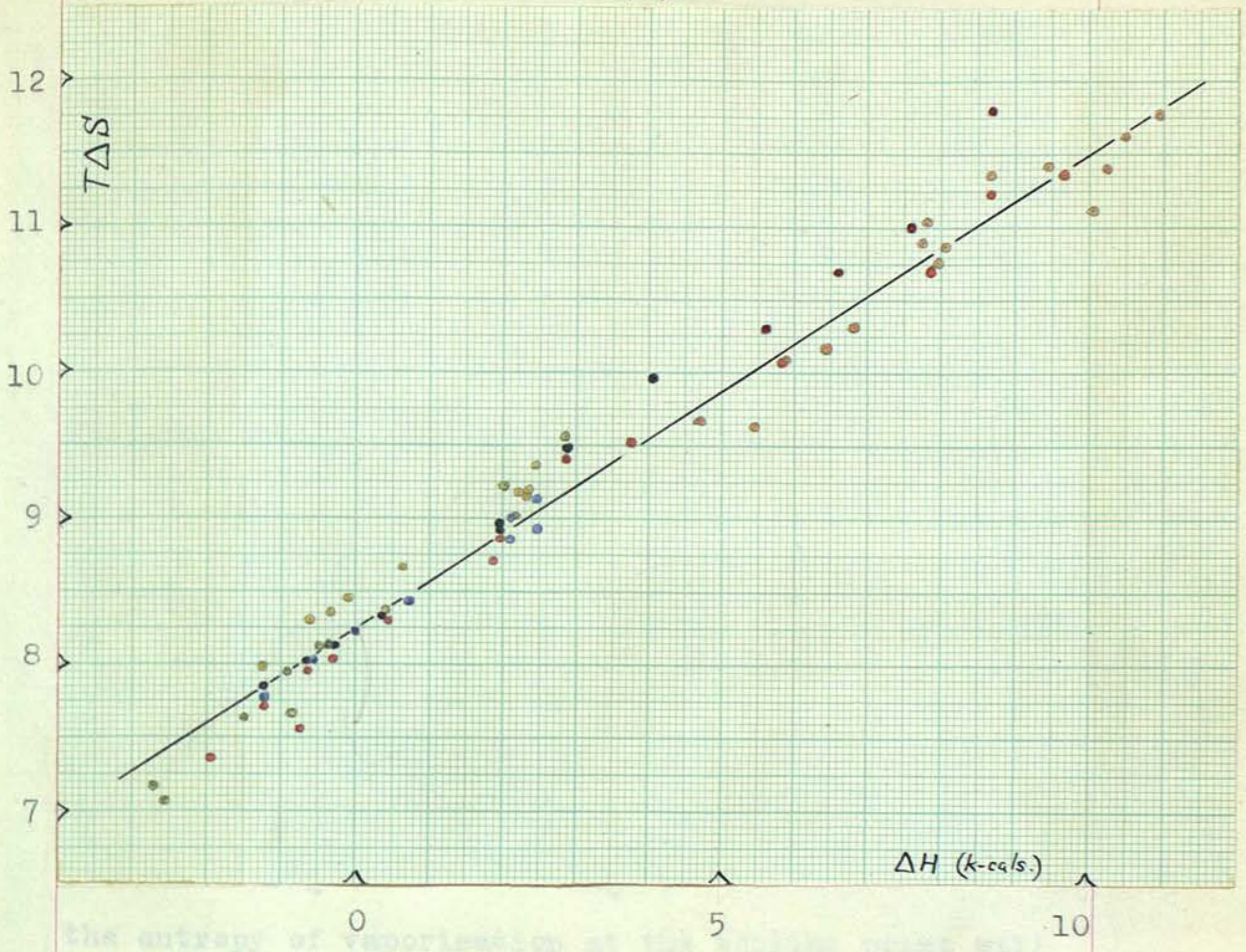


Figure II . Heats and Entropies of Vaporisation from Solutions and Pure Unassociated Liquids.

Key to Figure II .

Gases and Liquids in Acetone	●
Gases in Carbon Tetrachloride	●
Gases in Chlorobenzene	●
Gases in Benzene	●
Gases in Methyl Acetate	●
Alcohols in Benzene	●
Pure Liquids	●

the simple gases and metals, the average variation being of the order of $\Delta S = 16{\cdot}4 + 6{\cdot}5 \times 10^{-4}\,\Delta H$. More complicated molecules including those given in Table I, show no clear regularity.

It is obvious that if the entropy varies linearly with the heat of vaporisation at a constant temperature, the increase will be less marked at the boiling points which also increase linearly with the heat of vaporisation. The following calculation indicates the magnitude of the change.

If at a standard temperature T_o, the relation between the heat and the entropy, be represented by

$$\Delta S_{T_o} = a + b\,\Delta H_{T_o} ,$$

the entropy of vaporisation at the boiling point will be given by

$$\begin{aligned} \Delta S_{T_b} &= a + b\,\Delta H_{T_o} + \int_{T_o}^{T_b} (\Delta C_p/T)\,dT \\ &= a + b\,\Delta H_{T_o} + \Delta C_p \log (T_b/T_o) \end{aligned}$$

For boiling points not far different from T_o, this can be approximated to

$$\Delta S_{T_b} = a + b\,\Delta H_{T_o} + \Delta C_p(T_b - T_o)/T_o .$$

Taking the boiling point T_b as $\Delta H_{T_b}/a'$, where a' is the conventional Trouton ratio, and writing $\Delta H_{T_b} = \Delta H_{T_o} + \Delta C_p(T_b - T_o)$, we obtain

$$\Delta S_{T_b} = a + b\Delta H_{T_b} + \Delta C_p\left(\frac{\Delta H_{T_b}}{a'} - T_o\right)\left(\frac{1}{T_o} - b\right).$$

The variation of ΔS_{T_b} with ΔH_{T_b} is thus represented

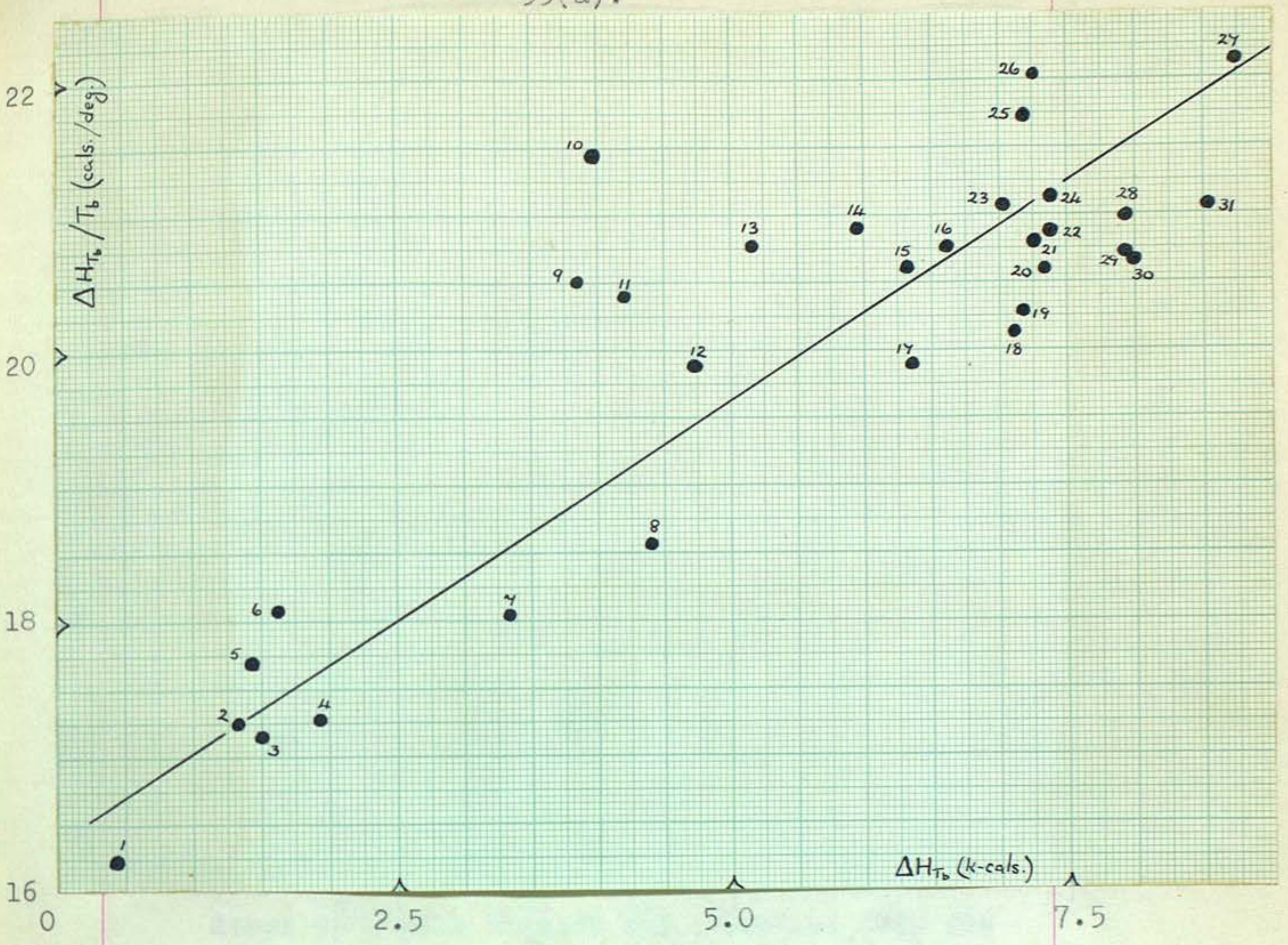


Fig. 3. Trouton Ratios at the Boiling Point.

Key to Diagram given above.

(1) Neon; (2) Nitrogen; (3) Argon; (4) Methane; (5) Carbon Monoxide (6) Oxygen; (7) Ethane; (8) Chlorine; (9) Hydrochloric acid (10) Nitrous oxide; (11) Hydrobromic acid; (12) Hydriodic acid; (13) Methyl Chloride; (14) Ethyl Chloride; (15) Propyl Chloride (iso-) (16) Propyl Chloride (n-); (17) Carbon Disulphide; (18) Acetonitrile; (19) Hexane; (20) Amyl Chloride (t-); (21) Carbon tetrachloride; (22) Benzene; (23) Chloroform; (24) Butyl Chloride (n-) (25) Silicon tetrachloride; (26) Acetone; (27) Amyl Bromide (iso-); (28) Amyl Chloride (n-); (29) Toluene; (30) Stannic Chloride; (31) Chlorobenzene.

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by $$b_{T_b} = b + \frac{\Delta C_p}{a'} \left(\frac{1}{T_0} - b\right).$$

Putting $1/T_0 = 0{\cdot}0033$, $b = 0{\cdot}0011$ and $a' = 20$, we thus find that $b_{T_b} = b + \frac{\Delta C_p}{20} \times 0{\cdot}0022$ i.e. for $\Delta C_p = -10$, $b_{T_b} = 0$; for $\Delta C_p = -6$, $b_{T_b} = 4{\cdot}4 \times 10^{-4}$.

For the simple gases ΔC_p is of the order of -6 and the calculated variation is similar to that observed; for more complicated molecules, ΔC_p is equal to or greater than -10, so that little or no variation of the Trouton ratio with ΔH_{T_b} is to be expected at the boiling point. Some of the divergences may be caused by the variations of ΔC_p, but it is obvious that the constant temperature variation observed above is consistent with the known variations of the conventional Trouton's ratios.

Since both pure liquids and solutions obey the same constant temperature relation, it is thus clear that Trouton's rule will also be valid for solutions to the same extent as for pure liquids, i.e. the entropy of vaporisation from solutions will be constant at suitable comparative temperatures, e.g. adopting Hildebrand's formulation as that giving the best constancy, at temperatures at which the vapour of equally concentrated solutions has equal concentrations. There is thus no important distinction between the behaviour of pure liquids and their solutions.

On the assumption that the rotational states are the same in the liquid as in the gas, Newton and Eyring

(Trans. Far. Soc., 1937, 33, 73) and Lennard-Jones and Devonshire (Proc. Roy. Soc., 1937, A 163, 53; 1938, A 165, 1) express the entropy of vaporisation as, approximately,

$$\Delta S = R \log (V_g / V_f),$$

where V_g is the volume of the vapour and V_f, the free volume of the liquid. The function, free volume, has been defined for equal spherical molecules by Lennard-Jones and Devonshire, as $\int e^{-\psi(r)/kT} d\tau$, where $\psi(r)$ is the potential energy of the molecule, expressed as a function of its distance from the centre of its cavity. This certainly indicates a relation between V_f and the heat of solution; numerical calculations are however extremely complicated and as yet have only been made for monatomic liquids.

Such equations as have been mentioned above apply only to atomic liquids i.e. liquids in which the rotational terms are fully excited. It is well known that the entropy of vaporisation of associated liquids, such as water, alcohols etc., is greater than that of normal liquids. In these cases, the entropy of the liquid compared with the vapour is abnormally small, which is easily accounted for on the consideration that the molecular rotations are incompletely developed in the liquid owing to hydrogen links between molecule and molecule. It is now necessary to account for the fact that not only have associated liquids abnormally low entropies, but also that non-polar solutes dissolved in them have low partial entropies. It was suggested, in discussing the entropies of solution in water (Butler and Read, J. Chem. Soc., 1936, 1171) that this is connected with the entropy of cavity formation in the associated liquid. One of the early tests of association in liquids was provided by the Ramsay-Eötvos rule, according to which the temperature coefficient of the molecular surface free energy is a constant for normal liquids (except near the critical temperature), and for associated liquids has lower values. This means that the molecular surface entropy, which is the excess entropy of a molecule in the surface layer over that of molecules in the interior, is a constant for normal liquids and lower for associated liquids. This may be interpreted as indicating that the rotations of molecules of associated liquids are more hindered in the surface layer than in the interior of the liquid, a result which is quite feasible, for intermolecular links may be expected to produce a greater degree of orientation at the surface than in the interior of an associated liquid.

To introduce a non-polar molecule into an associated liquid, it is necessary to form a cavity in the latter. This cavity will be associated with a low surface entropy, and thus when the solute molecule is removed from the liquid, in addition to the normal entropy of vaporisation, it will be necessary to restore the loss of entropy in the formation of the cavity, hence the entropy of vaporisation will be exceptionally great.

SUMMARY.

(1) The entropies of solution of four solutes in acetone and seven solutes in ethyl alcohol have been determined at 25°C.

(2) The values in acetone extend the linear relation between the entropy and heat of solution from $\Delta H = 4$ to 10 k-cals. The values in alcohol are appreciably higher than those in acetone for the same heats of solution.

(3) It is pointed out that all the entropies of vaporisation of solutes from non-associated solvents now available, as well as those of pure non-associated liquids themselves, approximate to a single linear relation between the entropy and heat of vaporisation. This relation is shown to be equivalent to the known fact that the Trouton ratio (entropy of vaporisation at the boiling point) increases slightly with the boiling point. Dilute solutions and pure liquids thus obey the same relation.

(4) The abnormally high entropies of vaporisation of solutes from associated liquids are connected with the abnormal surface entropies of cavities in those liquids, indicated by deviations from the Ramsay-Eötvos relation.

In conclusion I wish to express my gratitude to Dr. J. A. V. Butler for his most valuable guidance and encouragement during the course of this research.

Finally I wish to acknowledge my indebtedness to the Carnegie Trust for the grant of a Research Scholarship, during the tenure of which, this work was performed.