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A SIMULTANEOUS INTERPRETATION OF EXISTING DATA ON NON-IDEALITY OF GASES AND SOLUTIONS; SIMPLE EQUATIONS OF STATE WITHOUT EMPIRICAL CONCEPTS AND PARAMETERS; LANGMUIR ISOTHERM FOR THREE DIMENSIONS

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Dedicated to the memory of J.H.van't Hoff

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Existing data on the actual P,V,T and Π,V,T properties of gases and solutions are described by two simple analogous equations of state, Eqs (22) and (36), valid for low as well as high concentrations. Deviations from ideality are ascribed to a) the volume of gas molecules, b) solvation and c) molecular and ionic association/dissociation as a result of intermolecular and interionic forces. Other main findings supporting the above conclusions are 1) a simple quantitative relation between equivalent conductivity, degree of dissociation and osmotic pressure, Eq.(16), 2) linear dependence of the product of concentration and the coefficients of diffusion and viscosity on the osmotic pressure, Eq.(31), 3) linear dependence of the e.m.f. of concentration cells on the logarithm of osmotic pressure, Eq.(32), with the slope depending on solvent polarisation and 4) quantitative fit of the Langmuir isotherm for occupation of space, obtained by rearrangement of the equations of state, Eqs (51) and (52). As a consequence of the above, representation of nonideality by activity and fugacity coefficients is not necessary.

INTRODUCTION

The basic analogy of the gas and solution ideal laws, Eqs(1)

$$PV = RT \qquad (1)$$

and (2)

$$\Pi V = \nu RT \quad (\nu \neq 1 \text{ for association/dissociation}), \qquad (2)$$

was established nearly a century ago by van't Hoff[1] (see also[2a]), for very low pressures of gases and very dilute solutions of electrolytes and non-electrolytes. Accordingly, the ratios PV/RT and $\Pi V_A^B/RT$ (called compression factor Z [6a,7a,8a] and van't Hoff's factor i [1,8a] respectively) are equal to unity and ν for the ideal laws. That the properties of gases and solutions are analogous even at higher pressures and concentrations can be seen[3a] from Figs 1 and 2 where PV and ΠV_A^B products are plotted as functions of P and Π. It is evident from these Figs that Eqs (1) and (2) are best approximations for very low P and Π values and that at all other values of P and Π the chemical entities do not obey the ideal laws. Various equations of state have been formulated in the literature to interpret in general the actual P,V,T [2b,7b,8b,9a,10a] and Π,V,T [8c,10b] data, but the suggested equations have limited applicability and have a smaller or larger number of empirical parameters with no exact physical significance. The virial forms, Eqs (3) and (4), e.g.,

$$PV/RT = 1 + B/V + C/V^2 + \ldots \qquad (3)$$

$$\Pi V/\nu RT = 1 + B/V + C/V^2 + \ldots \qquad (4)$$

contain an indefinite number of terms and temperature-dependent parameters B, C, etc., of which the coefficient B is given special importance.

The virial form is more widely used for gases, whereas in the case of solutions deviations from ideality are more usually expressed by the molal osmotic coefficient, ϕ, and by the molal activity coefficient, γ, which are inter-related[11a,5b] by Eq.(5) through the Gibbs-Duhem relation,

$$\Pi V_A^B/RT = i = \nu\Phi = (1/m)\int \nu m d\ln m\gamma_{\pm} \tag{5}$$

where V_A^B is[3a] the volume of solvent A used for dissolving one mole of solute B. i or Φ ~~are~~ is obtained[5c,11b] from measurements of osmotic pressure, vapour pressure, changes in freezing and boiling points, etc.; γ is obtained from ϕ by integration using Eq.(5) or from e.m.f. measurements, say, of concentration cells without transport[5d,11c], from the 'deficit' free energy[5e,10c,11c] attributed to non-ideality as in Eq.(6):

$$\begin{array}{ccccc} nF(E-E^0) & - & \nu RT\ln m_{\pm} & = & \nu RT\ln\gamma_{\pm} \\ \Delta\bar{G}(\text{actual}) & - & \Delta\bar{G}(\text{ideal}) & = & \Delta\bar{G}(\text{non-ideal}) \end{array} \tag{6}$$

Conversely, the tables of ϕ and γ data in the literature can be considered as 'stores' from which the actual osmotic pressure, vapour pressure, changes in freezing and boiling points, e.m.f. of cells etc., can be back-calculated. This method was used for calculating Π from the ϕ values for Fig.2.

van't Hoff[1] interpreted i as the total number of moles of solute actually present in the solution due to dissociation /association of one mole of dry solute B dissolved in the given solvent at the given concentration. Thus, for one mole of an electrolyte B_{+-} (the undissociated electrolyte is here[5b] denoted by B_{+-}, e.g. Na^+Cl^-, since 'free ions' associate to form 'bound ions', see also[12]) dissociating into a total of ν number of cations and anions according to

Eq.(7):

$$\underset{1-\alpha}{B_{+-}} \rightleftharpoons \underset{\nu\alpha}{B_{+} + B_{-}} \qquad (7)$$

where α is the degree of dissociation, i is given by Eq.(8):

$$i = 1 + (\nu-1)\alpha \qquad (8)$$

Thereby an excess number, $(\nu-1)\alpha$, of moles are created by the dissociation of B. At infinite dilution, an electrolyte is completely dissociated and therefore $\alpha=1$ and $i=\nu$. In the case of solutes which associate[8a] to form dimers or polymers in the given solvent, $i<1$ since $\nu<1$. Eq.(8) did not gain much attention since it appeared to be at variance with experiment : Fig.2 shows for an electrolyte an initial decrease and then an increase of i and in the case of a non-dissociating solute like sucrose in water $i>1$! Moreover, there has not been an exact way of determining α from experiments, like from measurements of electrical conductivity. The use of the Arrhenius ratio (Λ/Λ_0) or other modifications[10d] for the calculation of α, which approximately satisfied the law of mass action or the Ostwald's dilution law, Eq.(9),

$$K_c = (1-\alpha)/(\alpha^2 c) = \left[1-(\Lambda/\Lambda_0)\right]/(\Lambda/\Lambda_0)^2 c \qquad (9)$$

for weak acids, gave neither the correct values of i nor the association constant, K_c, independent of concentration for strong electrolytes[13]. In order to steer through the apparent anomalous behaviour of strong electrolytes, the formal concepts and conventions of activity and activity coefficient (fugacity and fugacity coefficient for gases) were introduced[13] arbitrarily for a unified representation of all deviations from ideality, circumventing the question of α, the physico-chemical degree of dissociation. Despite the fact that the γ vs c curves exhibit minima and pass through the $\gamma = 1$ value twice (~~by~~ and thereby contradict the definition that $\gamma = 1$ only for infinite dilution), subsequent theories of non-ideality, especially of electrolyte solutions, have largely converged upon explaining the concentration and temperature dependence of γ, and the thermodynamic properties of solutions are interpreted in terms of $\ln \gamma$, cf. Eq. (6). For a comparison with various other theories for the non-ideal part of free energy of solutions see[10c]. The interionic attraction theory[5e, f, 11d, 14, 15a] formulated on the assumption of complete dissociation ($\alpha = 1$) of strong electrolytes predicted the $\ln \gamma, \sqrt{m}$ dependence and explained[16] the $\Lambda, \sqrt{c}$ relation found empirically by Kohlrausch[5g, 10e]. ~~Despite~~ Disregarding the considerable support[12, 17, 18a] for Arrhenius' and van't Hoff's hypotheses of incomplete dissociation of electrolytes, the interionic attraction theory gained a wide acceptance since the square-root laws were found to hold for dilute solutions of many electrolytes in different solvents. However, as these were unsatisfactory for concentrations above 0.01m (about), they were extended or modified by the successive additions of more terms, parameters and theories to fit the data at higher concentrations[5e, g, 11d, 15a, 18b, 19]. At the same time theories of ionic association were also worked out by Bjerrum and others[5h, 10f, 11e, 15b, 18c], according to which free ions of opposite charge getting closer than a certain critical distance form separate associated entities thereby changing the total number of moles in the solution. These theories show that ion pairs can be formed (although to a small extent) even in aqueous 1:1 electrolytes where the critical distance is 3.57 Å at 25°C, and that for higher valent ions in solvents of lower dielectric constant, as the predicted critical distance is larger, associated ions are more likely. In fact, the literature[15b,c,20] provides a growing evidence for ion association even in aqueous strong electrolytes 1:1, especially of bulky ions. Thus, in the theory of solutions, in cases where incomplete dissociation and formation of complex ions were evident, α was incorporated[5i,11f,15c,21-23] into the equations for ϕ, γ and Λ while retaining the Debye-Hückel-Onsager terms for the free ions.

As in the case of solutions, there exist two different interpretations of the non-ideality of gases[9b,10g]; one (corresponding to the theory of complete dissociation in solutions) is that of attributing all deviations from ideality to various types of intermolecular forces between free (separate) molecules (as, e.g., in van der Waals' equation), and the other explains non-ideality in terms of formation of associated entities (corresponding to the theory of incomplete dissociation in solutions). Experimental evidence for association/dissociation is found[2c,9b,10g] in the case of vapours of monoatomic metals (e.g. K), non-metals (e.g., S, halogens, halides of Al, Fe, HF, oxides of P,As,Sb) and organic compounds (e.g., acetic and formic acids) and even in gaseous helium.

Solvation of dissolved solutes as one of the important causes of non-ideality has long been recognized[24]. Ever since, there has been an increasing awareness of its importance in the interpretation of the properties of solutions[5j,10i,11g,15d,18a,25]. However, there is no concordance[18d,26a] in the reported values of the solvation numbers obtained by different methods, mainly because of the use of unsatisfactory theories of non-ideality.

On the whole, one finds that the equations explaining the non-ideality of gases and solutions (e.g., the P,V,T relations and the concentration dependences[5,11,15,18] of equivalent conductivity, of diffusion and viscosity coefficients and of Φ and γ) are fairly complicated and that there is no simple and unified interpretation of the properties of dilute and concentrated solutions. Therefore, the present author, struck by the analogy of gas and solution properties evident in Figs 1 and 2 (e.g., the similarity of the behaviour at 25° of N_2 and aqueous sucrose and at 50°C of N_2 and aqueous NaCl!) ~~[illegible]~~ decided to interpret directly the actual experimental results as such rather than the deviations of the experimental results from ideality. The scheme of the paper is presented in the titles of the several main sections and the matter is discussed in a logical sequence with relevant support from the existing data and literature. In the case of solutions, attention is mainly paid to aqueous strong electrolytes since these are considered anomalous[13]; however, this treatment should hold for other solvents and solutes as well. For the preliminary work in this direction see[3a-f]. As for the references to literature, only the minimum necessary to support the arguments are given; in view of the large amount of literature in the field the reference list could not be exhaustive.

I. A SIMPLE EXTENSION OF THE IDEAL GAS AND SOLUTION LAWS TO HIGHER PRESSURES AND CONCENTRATIONS: $PV_g = i^*RT$ AND $\Pi V^B_{As} = i^*RT$

a) Determination of b, the volume of gas molecules and of V^B_{As}, the volume of 'bound solvent' (solvation) from Figs 1 and 2

A comparison of Figs 1 and 2 shows that, in general, over a considerable range of moderately high P and Π, both PV and ΠV^B_A increase linearly with P and Π. From amongst the equations of state in the literature, the linearity is as expected according to Eqs (10) and (11)

$$P(V-b) = RT \qquad (10)$$

$$\Pi(V-b) = RT \qquad (11)$$

proposed by Hirn[9c] and Sackur, Porter and others[2d] respectively. The slopes of these linear regions give the volume b of one mole of gas molecules as Hirn interpreted and the volume V_{As}^{B} of solvent A bound as solvation[3a](cf.: the primary or inner solvation sphere[26a]) to one mole of B (and not the volume b of solute molecules as supposed[2d] in Eq.(11). The values of b, V_{As}^{B}, b/V_s and the molar volumes (V_s) of the solidified gases[4b] are given in Figs 1 and 2. The hydration numbers obtained here are slightly less than the presumed ones in the literature[5j]. Both b and V_{As}^{B} decrease ~~only~~ slightly with increasing temperature. The constancy of the hydration over a large range of concentrations (the larger the solvation, the smaller this range) observed here justifies the assumption[5j] of a constant hydration number in the theory of activity coefficient. At higher concentrations, as can be seen clearly in the case of highly hydrated solutes, the slope begins to decrease gradually implying a decrease of the solvation due to overlapping of the solvation sheaths as the solvated ions get closer[3a], until at saturation the solid solute begins to separate from the solvent either in the hydrated or non-hydrated form as the case may be.

b) The gas-vapour-liquid triple point

In the case of gases, the range of pressures over which ~~b is~~ PV vs P is linear ~~constant~~ diminishes as the temperature is lowered[3a] until at T_c it is reduced to a minimum or a point. This is illustrated best by the horizontal region BC of the plot of $P(V-b)/RT$ vs P, as in

Fig.1a. On compression of the gas from C to D, at $T>T_c$, beyond the region of linearity of Fig.1 or of the horizontal region BC of Fig.1a, the slope decreases (as in the above case of solutions with highly hydrated solutes) as the gas turns directly into vapour[3a]. Since the liquid begins to appear at $T=T_c$ and $P=P_c$, the critical point T_c, P_c, V_c can be considered as the 'gas-vapour-liquid triple point'. (In the literature[2e,9d,10j] the term 'vapour' is used for the gaseous form of matter at temperatures only below T_c; however, liquids do turn totally into vapour at temperatures and pressures just above T_c and P_c, although uncondensable (see[2e] and also section VII).

c) i^*_m, the van't Hoff's factor, corrected for b and V^B_{As}

Considering now the intercepts at $P=0$ and $\pi=0$ of the extrapolated linear regions in Figs 1 and 2, these, in general, have the value $i^*_m RT$, where $i^*_m \leq 1$ (gases) and $\leq \nu$ (solutions), and not just RT as implied by Eqs (10) and (11). In the case of gases, only at and above a sufficiently high temperature designated[3e] as the Hirn point, T_H, which is much higher than the Boyle point, T_B, Eq.(10) becomes valid for all P and for $T \geq T_H$, i.e., $i^*_m = 1.0$; e.g., see the straight lines for He at 0°C, H_2 at 25°C and N_2 at 500°C. In the case of solutions, sucrose, a non-electrolyte, gives the linear dependence like gases at $T \geq T_H$ and $i^*_m = 1.0$. On the other hand, for solutions of electrolytes $i^*_m < \nu$ and for gases at $T < T_H$, $i^*_m < 1$; e.g., see the cases of N_2 at 50°C and of aqueous NaCl.

In general, therefore, instead of Eqns (10) and (11), the following Eqs (12) and (13)

$$P(V-b) = PV_f = i^* RT \tag{12}$$

$$\pi(V^B_A - V^B_{As}) = \pi V^B_{Af} = \pi/m^* = i^* RT \tag{13}$$

can be written[3a,e] for gases and solutions, where V_f and V^B_{Af} are the volumes of 'free space' and 'free solvent' (not bound to solute) respectively per mole of gas and solute taken, and m^* is the number of moles of solute B dissolved in one litre of 'free solvent' and is thus a new unit of concentration. It is related to m by Eq.(13a)

$$m^* = md_A/(1-md_A V^B_{As}) \tag{13a}$$

i^* is the van't Hoff's factor corrected for 'bound volume'. The latter volume is not available for the molecular and ionic movements. Assuming the constancy of the values of b V^B_{As} for pressures down to zero (which is justified for solutions by the support from the literature[5j] and by the correlation of i^* or α with Λ in section IIb, and for gases, by the analogy with solutions) the values of i^* were calculated using Eqs (12) and (13) and are shown as functions of P and π in Figs 3 and 4. It can be seen that $i^* = 1.0$ for gases at $T>T_H$ at all P and for non-electrolytes at all π. For gases at $T<T_H$ and for electrolyte solutions i^* decreases from the value of unity (gases) or of ν (electrolytes) at zero P and π down to the constant value i^*_m (mentioned earlier) at higher P and π. In Figs 3 and 4 the examples chosen demonstrate the general validity of the above dependences. Temperature does not influence much the value of i^* for solutions, whereas it has a great effect on gases as can be seen in Fig.3 and in Fig.1a which has the same ordinate.

An equation similar to Eq.(12) has been suggested by Amagat[2f] for gases (see Eq.(39) section X) where the symbol x is used instead of i^*; it is supposed to indicate mutual attraction between molecules, a decrease of x implying increase of attraction (see section VII).

II. DEMONSTRATION THAT $i^{*} = 1 + (\nu-1)\alpha$ REPRESENTS THE ACTUAL NUMBER OF MOLES PRESENT IN THE SOLUTION DUE TO ASSOCIATION/DISSOCIATION

a) Relation between i^{*} and the degree of dissociation, α

Since Figs 3 and 4 for i^{*} show no initial decrease followed by an increase as in Figs 1 and 2, the next step was to check whether i^{*} and not i of Eq.(8) represents the total number of moles actually present in the solution per mole of solute dissolved. In the absence of any exact method of obtaining α from equivalent conductivity or other data, α was directly calculated from i^{*} presuming the validity of Eq.(14)

$$\Pi V^{B}_{Af}/RT = i^{*} = 1 + (\nu-1)\alpha \; ; \; \alpha = (i^{*}-1)/(\nu-1) \qquad (14)$$

and these values were then correlated with equivalent conductivity. Fig.5a shows the dependence of α on Π (on account of the constancy of ν this figure is similar to Fig.4). It can be seen that α diminishes gradually from the value of unity at infinite dilution to a minimum value α_m which remains constant in the region of high concentrations[5c].

The possibility of a constant degree of dissociation has been suggested[27] before as an interpretation of the conformity with Beer's law of light absorption by $CuSO_4$ solutions. It is pointed out here that in Bjerrum's theoretical treatment of ion association[5h], since the degree of association, $1-\alpha$, is directly proportional to concentration, it does not account for the constancy of α_m observed here. Referring to his diagram of the degree of association as a function of the distance of approach of ions of 1:1 electrolytes, the constant α_m found here is suggestive of a minimum cut-off distance which the ions cannot trespass and get closer. Such a minimum distance has been reported[5k] for the case of lanthanum ferricyanide.

b) Correlation of α with equivalent conductivity, Λ

As Λ is proportional to mobility, by analogy with the pressure dependence of the velocity of gas molecules, the influence of π on Λ was investigated rather than of concentration on Λ as is usually done in the literature. Fig.6 shows the dependence of Λ on π. Alternately, because of Eq.(13), Λ vs i^*m^* can be plotted. It can be seen that this graph is linear in the range of π values where the degree of dissociation is constant, see Fig.5a. Denoting the slope of this region by $K_{\Lambda,\pi}$, (which is negative), the value of $\Lambda^* = \Lambda + (K_{\Lambda,\pi})\pi$ was calculated to check if Λ^* is proportional to α. Λ^* is the equivalent conductivity corrected for the effect of osmotic pressure (see below). Fig. 7a shows the variation of Λ^* with π from which its similarity to Figs 3 and 5 is evident. Fig.7b shows that Λ^* is indeed directly proportional to α, and that it reaches a constant value Λ^*_m when $\alpha = \alpha_m$. The equivalent conductivity at infinite dilution, Λ_0, is obtained as the intercept at $\alpha = 1.0$ of the Λ^* vs α straight line. (The conventional method of obtaining Λ_0 is to extrapolate[5l] to $\sqrt{c} = 0$ the Λ vs $\sqrt{c}$ graph for very dilute solutions). Thus, the dependence of equivalent conductivity on π ($= i^*m^*RT$) and α is given by the simple Eq.(15)

$$(\Lambda_0 - \Lambda^*) = \lambda^0_{+-}(1-\alpha); \quad \alpha = 1-(\Lambda_0 - \Lambda^*)/\lambda^0_{+-} \qquad (15)$$

where λ^0_{+-} (written as $K_{\Lambda,\alpha}$ in ref.[3c,f]) is characteristic of the bound ion pair, B_{+-}, in the given solvent and is obtained as slope of Fig.7b. This equation also shows that $\Lambda_0 - \Lambda^*$ is directly proportional to the degree of association, $1-\alpha$. Eq. (15) is written in the full form in Eq.(16)

$$\Lambda = \Lambda_0 - \lambda^0_{\pm\infty}(1-\alpha) - \pi|E_{\Lambda,\pi}| \qquad (16)$$

where $\lambda^0_{\pm\infty}(1-\alpha)$ is the reduction in equivalent conductivity due to ion pair formation[3a] and the last term can be considered as the reduction in conductivity due to the osmotic pressure or equivalently, due to the combined effects[3d] of $D\eta C$, see Eq.(31). The validity of Eq.(16) for dilute as well as concentrated solutions is demonstrated in Fig.8. Eq.(16) can be compared with those in[5g,11h,15e]. Thus, the above correlation of α values, calculated from osmotic pressure using Eq.(14), with the equivalent conductivity data confirms Eq.(14) for electrolyte solutions.

e) Determination of Λ_0 and $\lambda^0_{\pm\infty}$ from the linear dependence of Λ on $(1-\alpha)$ for very dilute solutions

According to the simple kinetic theory of gases, the root-mean-square velocity is related[9a] to the pressure and density ρ of the gas by Eq.(17)

$$\sqrt{\overline{v^2}} = \sqrt{3P/\rho} \qquad (17)$$

In dilute solutions, since 1) the equivalent conductivity is proportional to the sum of the velocity of the ions, 2) the osmotic pressure is proportional to the concentration and 3) the density of solution is nearly equal to that of solvent, the Λ, $\sqrt{c}$ linear dependence empirically found by Kohlrausch is a manifestation of the gas - solution ideal law analogy. The Debye-Hückel-Onsager (D-H-O)[16] limiting law, Eq.(18)

$$\Lambda_0 - \Lambda = (B_1\Lambda_0 + B_2)\sqrt{c} = A\ln\gamma = A'\varkappa = A''u/kT \qquad (18)$$

which interprets Kohlrausch's observation, suggests that the conductivity decrease $\Lambda_0 - \Lambda$ is due to the interionic forces between free ions (assuming complete dissociation) in the given solvent. In this equation B_1 and B_2 are Onsager constants and A, A′ and A′′ are proportionality constants, u is[10k] the inter-ionic interaction energy and $\varkappa$ is[10k] the reciprocal thickness of the ionic atmosphere.

According to Arrhenius, the change in conductivity is directly proportional to the degree of association as shown in Eq.(19)

$$\Lambda_0 - \Lambda = \Lambda_0(1-\alpha) \qquad (19)$$

The present work shows that for dilute solutions Eq.(15) reduces to Eq.(20)

$$\Lambda_0 - \Lambda^* \simeq \Lambda_0 - \Lambda = \lambda^0_{\pm}(1-\alpha) \qquad (20)$$

and thus supports Arrhenius′ idea, except that $\lambda^0_{\pm}$, the equivalent conductivity characteristic of the ion pair, has to be used in Eq.(19) in place of Λ_0, the sum of the conductivities of the free ions, λ^0_+ and λ^0_-.

On comparing Eq.(20) with Eq.(18), one can see that $1-\alpha$ must be proportional to $\sqrt{c}$ in the range of validity of the Kohlrausch′s and D-H-O′s $\sqrt{c}$ law. Figs 9a,b and c show the dependences of Λ on $\sqrt{c}$, of $1-\alpha$ on $\sqrt{c}$ and of Λ on $1-\alpha$ respectively. It is obvious that the D-H-O relation gives the tangential slope at infinite dilution whereas the present limiting Eq.(20) gives the best fit. Therefore, using Eq.(20) both Λ_0 and $\lambda^0_{\pm}$ can be obtained from the intercept and slope of a plot of Λ vs $1-\alpha$ for dilute solutions.

On combining Eqs (20) and (18), one gets Eq.(21)

$$\lambda^0_{\pm}(1-\alpha) = A'\varkappa = A''u/kT \qquad (21)$$

from which one can see that ion association, naturally, is a direct result of the interionic attractive forces between free ions. Thereby, the two different schools of thought, of complete and incomplete dissociation of strong electrolytes, can be bridged together. (It should be pointed out here that u can, in general, represent intermolecular energy of association of any two ions or molecules, see section VII.

III. THE ACTUAL EQUATION OF STATE VALID FOR DILUTE AND CONCENTRATED SOLUTIONS OF ELECTROLYTES AND NON-ELECTROLYTES, $\Pi\bar{V} = RT$ OR $\Pi = i^*m^*RT$

The equation of state valid for both dilute and concentrated solutions can, therefore, be written as Eq.(22)

$$\Pi\bar{V} = RT \qquad (22)$$

where $\bar{V} = v^S_{Af}/i^* = 1/(i^*m^*)$ is the average volume of free solvent per mole of solute species in the dissolved state and i^*m^* is the actual number of moles of solute present in the dissolved state per litre of free solvent. For a non-associating/dissociating solute like sucrose (a non-electrolyte) in water $i^* = 1$ at all concentrations. By writing the equation in this form, the definition of partial molar free energy, $\bar{G}$, (or $\bar{\mu}$, per molecule) at any temperatute T, Eq.(23),

$$d\bar{G} = \bar{V}d\Pi = RTd\ln\Pi = -\Pi d\bar{V} = -RTd\ln\bar{V} = RTd\ln(i^*m^*) \qquad (23)$$

remains in line with the existing thermodynamic relations for the ideal law, except that $\bar{V}$ here has a different significance than the molar volume V of the ideal law. Eq.(23a)

$$d\bar{S} = Rd\ln\Pi = -Rd\ln\bar{V} \qquad (23a)$$

gives the corresponding change in entropy[10ℓ]. Thus, non-ideality can be explained completely by the association/dissociation and solvation of solutes. The arbitrary concepts of activity and activity coefficient are therefore not necessary.

It follows from Eq.(22) that for different solutions exerting the same osmotic pressure (note that isotonic solutions are also isopiestic since for both $\nu_1 m_1\phi_1 = \nu_2 m_2\phi_2$) at a given temperature $\bar{V}$ is the same and, consequently, Eq.(24) holds

$$i_1^*m_1^* = i_2^*m_2^* = \ldots \qquad (\text{constant } \Pi/T) \qquad (24)$$

for the total number of moles per unit volume of the free solvent.

Regarding solvation in particular, the constancy of the volume of bound solvent V_{As}^{B} per mole of B over a large range of concentrations (from zero until that corresponding to the end of the linearity in Fig.2) irrespective of the state of dissociation/association of the solute, suggests formation of solvated ion pairs without loss of solvation, as shown in Fig. 2a. When the concentration (and hence the osmotic pressure) increases beyond that corresponding to point C, coalescence of the solvation sheaths of the ion pairs and subsequent decrease of solvation begins to occur; it is also possible that the degree of association and of complex ion formation increases in the region CD. The 'contact ion pairs', with no solvent in between, possibly form only at concentrations nearing saturation when the solute begins to separate out as shown in Fig.2a. Although these different types of solvation have in general been considered plausible in the literature[20f,29], the ΠV_{A}^{B} vs Π plot of Fig.2 enables exact location of the concentration corresponding to point C (cf.Fig.2a) until which V_{As}^{B} is constant and above which coalescence and solvent squeezing occurs.

IV. MOLE FRACTIONS, PARTIAL OSMOTIC PRESSURES, PARTIAL MOLAR VOLUMES AND ACTUAL CONCENTRATIONS OF THE THREE COMPONENTS OF SOLUTE, B_{+}, B_{-} AND B_{+-}

The mole fractions N_{+}, N_{-} and N_{+-} are given by Eqs (25)

$$N_{+} = N_{-} = N_{\pm} = \alpha / i^{*} \; ; \; N_{+-} = (1-\alpha)/i^{*} \qquad (25a,b)$$

$$N_{+} + N_{-} + N_{+-} = 1 \qquad (25c)$$

The corresponding partial osmotic pressures are given by Eqs (26)

$$\Pi_{+} = \Pi_{-} = \Pi_{\pm} = N_{\pm}\Pi = \alpha m^{*}RT; \; \Pi_{+-} = N_{+-}\Pi = (1-\alpha)m^{*}RT \qquad (26a,b)$$

$$\Pi_{+} + \Pi_{-} + \Pi_{+-} = \Pi \qquad (26c)$$

Eq.(26c) demonstrates that Dalton's law is applicable for the ionic components of electrolyte solutions. The partial molar volumes are defined by Eqs (27)

$$\bar{V}_{+} = \bar{V}_{-} = \bar{V}_{\pm} = \bar{V}/N_{\pm} = 1/(\alpha m^{*}) \; ; \; \bar{V}_{+-} = \bar{V}/N_{+-} = 1/(1-\alpha)m^{*} \qquad (27a,b)$$

$$1/\bar{V}_{+} + 1/\bar{V}_{-} + 1/\bar{V}_{+-} = 1/\bar{V} \qquad (27c)$$

In Figs 10 a,b,c and d the actual ionic concentrations of the dissociated forms, B_{+} and B_{-}, of the associated form, B_{+-}, of the actual total solute concentration, $i^{*}m^{*}$, and m^{*} itself are plotted vs the molality, m. Hitherto, these were considered as undeterminable quantities. Moreover, the mean ionic molality $m_{\pm}$ was assumed[5a] to be a constant multiple of the concentration of the dissolved solute on the basis of the theory of complete dissociation of strong electrolytes. The present work shows that this is not true even for 1:1 electrolytes, and that the concentration of the associated form, B_{+-}, must be taken into account or allowed for in the electrochemical, physico-chemical and interfacial properties of solutions. Formation of complex ions, dimers and polymers can also be recognised by the values of i^{*} and their concentrations can be calculated precisely; these cases will be treated in detail separately.

V. THE ASSOCIATION CONSTANT

The law of mass action defines the association constant K_{c} (K_{m} if molality is used) by Eq.(9). In terms of partial osmotic pressure it can be written as K_{π}, Eq.(28):

$$K_{\pi} = \Pi_{+-}/\Pi_{+}\Pi_{-} = N_{+-}/(N_{+}N_{-}\Pi) = (1-\alpha^{2})/\alpha^{2}\Pi \qquad (28)$$

whereas use of mole fractions gives K_{N}, Eq.(29):

$$K_{N} = N_{+-}/(N_{+}N_{-}) = (1-\alpha^{2})/\alpha^{2} = K_{\pi}\Pi \qquad (29)$$

Figs 11 a, and b show the variations of K_C, K and K_N with molality. It can be seen that while ~~both~~ K_C and K decreases with increasing concentration, K_N increases from the value of zero at infinite dilution to a constant value at high concentrations where $\alpha = \alpha_m$. Since K_N increases as the degree of association increases, Eq.(29) seems more appropriate for the definition of the association constant. The reported[18e] linear increase of the dissociation constant, K_c^{-1} (see Eq.(9)) of 2,4-dinitrophenol (obtained from extinction coefficient) with concentration in the high concentration range shows that α indeed attains a constant value, see also[27]. Since ionic association increases with decreasing dielectric constant of the solvent, K_N must also increase.

Eq.(28) is similar to that used for gases, e.g., ~~in~~ association/dissociation of phosphorous chlorides[10ℓ], formation of double molecules in the vapour state[10g], etc.(Increase of temperature increases the dissociation of PCl_5 whereas increase of water concentration increases the dissociation of electrolytes).

From Eqs (28) and (29) the dependence of α on π is given by Eq.(30) which is analogous to that for gases[10m]

$$1/\alpha = (1+K_\pi \pi)^{1/2} = (1+K_N)^{1/2} \qquad (30)$$

VI. OTHER EVIDENCE SUPPORTING THE INTERPRETATION OF PROPERTIES OF SOLUTIONS WITHOUT ACTIVITY COEFFICIENT

a) Relation between coefficients of diffusion and viscosity, osmotic pressure and concentration

The simple Eq.(31)

$$\pi = D\eta c\Delta \ (= i^* m^* RT) \ ; \ \Delta = 6\pi r \ \text{(Stokes' factor, } \pi = 3.14) \qquad (31)$$

governs[3d] the Brownian motion in solutions and describes[3d] the concentration dependence of the product of coefficients of diffusion and viscosity ($D\eta$ represents force) for dilute and concentrated solutions, see Fig.12. This relation supports the original idea of Nernst[31] that diffusive flow is a result of osmotic force. Eq.(31) reduces to Eq.(31a) for

$$D^0\eta^0 = NkT/\Delta \tag{31a}$$

for infinite dilution (cf.Stokes´-Einstein´s relation for Brownian motion[10m] $D\eta = kT/\Delta$).

Eq.(31) can be compared with those in the literature[5o,15f,32] in which 1) the term with activity coefficient forms a major fraction of the concentration dependence of $D\eta$, where η is introduced as a correction factor, and 2) the interpretation is based on irreversible thermodynamics.

b) Relation between e.m.f. and osmotic pressure

The free energy change $\Delta\bar{G}_{\pm}$, associated with change of ionic concentration (cf.Eq.(23) for $\Delta\bar{G}$) measured as the corresponding change in the e.m.f. of concentration cells without transport was found[3f] to obey Eq.(32),

$$\Delta\bar{G}_{\pm} = RT\ln\pi_{\pm} = F\Delta E/K_{E,\pi_{\pm}} \tag{32}$$

where $K_{E,\pi_{\pm}}$ is a constant. Fig.13 shows the linear dependence of E on $\log\pi_{\pm}$. The slope gives the constant $K_{E,\pi_{\pm}}$ which has values ranging between 1.83 and 1.89 for 1:1 electrolytes and between 1.27 and 1.36 for 2:1 electrolytes. $K_{E,\pi_{\pm}}$ can be tentatively interpreted in terms of solvent polarization as follows: writing the coefficient of ΔE of Eq.(32) as $\alpha_p zF/\nu$, α_p ($= \nu/(zK_{E,\pi_{\pm}})$) can be considered as the factor by which the ionic charge zF is changed by the polarization of the bound solvent. Thus $\alpha_p \simeq 1.075$ for 1:1 electrolytes and 1.154 for

2:1 electrolytes. For an account of the charge density rearrangements accompanying ion solvation see[26b,34]. Eq.(32) can be compared with Eq.(6) from which the activity coefficient is calculated.

a) and b) are discussed in more detail in[3d] and [3f].

c) Interpretation of cryoscopy

The cryoscopy of Al halides in nitrobenzene has been treated in terms of solvation and degree of association without γ; see [35] for details.

VII. CORRELATION OF i^* WITH THE DEGREE OF MOLECULAR ASSOCIATION, α IN GASES

The striking resemblance of the i^* vs P and i^* vs π graphs for gases and solutions (Figs 3 and 4) suggests that i^* for gases might have the same significance as in the case of solutions. In fact, the attractive/cohesive forces operating between the gas molecules at $T<T_H$ can be considered to produce a certain degree of association. ~~Support for this view~~ This association increases as the temperature is lowered and pressure is increased and the gas first turns into a dispersion of aggregates of vapour molecules at temperatures nearing T_c and pressures greater than P_c and finally into liquid itself at $T=T_c$ and $P \geq P_c$; see also section Ib and Fig.(a). Support for this view can be found in the concepts[10g] of association of gas molecules and formation of molecular clusters and aggregates prior to condensation[36a,b]. Also, attention can be drawn to the fact that the van der Waals' attraction term, a/V^2, for free gas molecules, represents the cohesive pressure for liquids[9f].

Assuming an association/dissociation equilibrium of the type represented by Eq.(33)

$$B \rightleftharpoons (1/n)B_n \qquad (33)$$

$1-\alpha$ α/n

i^* is given by Eq.(34) analogous to Eq.(14)

$$i^* = 1 + (\nu-1)\alpha, \quad \nu = 1/n \qquad (34)$$

and it decreases from the value of unity at P=0 to a constant value, $i_m^* < 1$ at high P. Here $(1-\alpha)$ represents the degree of dissociation. Thus, for gases, Eq.(12) can be written as Eq.(35)

$$PV_f/RT = i^* = 1 + (\nu-1)\alpha \qquad (35)$$

Since $n \geqslant 1$, $\nu \leqslant 1$ and $i^* \lesssim 1$ in accordance with the observations in Fig.3. Consequently, the smaller the value of i^*, the higher is the degree of association; this is in agreement with Amagat's view of increased mutual attraction (see sec.Ic). One can see from Fig.3 that at any given $T < T_H$, gradual isothermal compression of one mole of a gas decreases the total number of molecules from its initial value of N_{Av} $(=6.02 \times 10^{23})$ at P=0 down to a minimum value $i_m^* N_{Av}$ which remains constant over a large range of pressures (see Fig.4 for the analogy with electrolytes). The lower the temperature, the smaller the values of i^* and i_m^* as well as the range of pressures over which i_m^* is constant (see Fig.1a). At $T = T_c$, the cohesive forces become strong enough for the gas to liquefy by compression. The values of i_c^* at T_c, V_c and P_c, calculated using Eq.(35) for some common gases are : H_2, 0.253; O_2, 0.194; N_2, 0.191; and CO_2, 0.158 moles.

At $T > T_H$, the gas molecules do not cohere or associate on compression in the pressure region investigated, and therefore $i^* = 1.0$ at all P (as in the case of the non-electrolyte, sucrose, where association does not occur). Thus, compression can bring about the direct gas - vapour conversion referred to in section Ib only between the temperatures T_H and T_c.

Fig.5b shows the degree of association, α as a function of pressure for N_2 at 50°C, for an arbitrary value of $\psi = 1/2$ in Eq.(35). As in the corresponding Fig.5a for electrolytes, α reaches a constant value α_m in the high pressure region.

VIII. THE ACTUAL EQUATION OF STATE FOR LOW AND HIGH PRESSURE OF GASES, $P\bar{V} = RT$

The equation of state valid for both low and high pressures of gases can be written in the simple form, Eq.(36),

$$P\bar{V} = RT \tag{36}$$

where $\bar{V} = V_f/i^M = RT/P$. This is analogous to Eq.(22) for solutions. Eq.(36) differs in significance from the ideal law, Eq.(1), in that $\bar{V}$ here represents the average volume of free space per mole of gas molecules dispersed in the associated and dissociated forms. The isothermal free energy change (see Eq.(33) for solutions) is given by Eq.(37)

$$d\bar{G} = \bar{V}dP = RTdlnP = -Pd\bar{V} = -RTdln\bar{V} \tag{37}$$

as for the ideal law but with $\bar{V}$ in place of V. The corresponding change in entropy is given by Eq.(37a)

$$d\bar{S} = RdlnP = -Rln\bar{V} \tag{37a}$$

IX. PARTIAL PRESSURES OF THE ASSOCIATED AND DISSOCIATED MOLECULES AND THE ASSOCIATION CONSTANT

The mole fractions, partial pressures and partial molar volumes of the dissociated and associated (subscripts ds and as) forms of the gas molecules are expressed by Eqs (38 a,b and c)

$$N_{ds} = (1-\alpha)/i^M, \quad N_{as} = \alpha/ni^M \;;\; N_{ds} + N_{as} = 1 \tag{38a}$$

$$P_{ds} = N_{ds}P, \quad P_{as} = N_{as}P \;;\; P_{ds} + P_{as} = P \tag{38b}$$

$$\bar{V}_{ds} = \bar{V}/N_{ds}, \quad \bar{V}_{as} = \bar{V}/N_{as} \;;\; 1/\bar{V}_{ds} + 1/\bar{V}_{as} = 1/\bar{V} \tag{38c}$$

Eq.(38b) shows the applicability of Dalton's law for the dissociated and associated molecules of the same gas.

The association constant defined in terms of mole fraction by Eq.(38d)

$$K_M = \alpha/n(1-\alpha) \qquad (35a)$$

increases from a value of 0 at P=0 to a constant value $\alpha_m/n(1-\alpha_m)$ in the region of high P.

The above equations demonstrate the necessity of taking into consideration the presence of associated gas molecules, hitherto neglected in the literature, when investigating the physico-chemical properties of gases like, e.g., gas kinetics, adsorption, etc. For detailed expressions for K in terms of the dissociation energy of gaseous dimers and α see [10g].

Finally, from Eq.(36) follows Eq.(36a)

$$\bar{V}_{f,1}/i_1^* = \bar{V}_{f,2}/i_2^* = \dots \qquad (36a)$$

showing that at any given T/P, $\bar{V}$ is the same for all gases. Inversely, the number of moles per unit volume of free space is a) constant at constant T/P.

X. COMPARISON OF THE PRESENT EQUATION OF STATE FOR GASES WITH SOME EXISTING ONES

A convenient way of comparing Eq.(36) with some existing equations of state is to write the equivalent expressions for $i^* = P(V-b)/RT$:

$$i^* = 1 + (\nu-1)\alpha \qquad \text{present work} \qquad (35),(36)$$

$$= x \qquad \text{Amagat}^{2f} \qquad (39)$$

$$= 1 \qquad \text{Hirn} \qquad (40a)$$

$$= \left[1 + (r/P)\right]^{-1} \qquad \text{Hirn}^{9c} \text{ (later)} \qquad (40b)$$

$$= \left[1 + a/PV^2\right]^{-1} \qquad \text{van der Waals}^{9a} \qquad (41)$$

$$= \exp(-a/RTv) \qquad \text{Disterici}^{9a} \qquad (42)$$

$$= 1 - Pb/RT + (2\pi N/V)\int_0^\infty (1-e^{-\Phi/kT})\, a^2 da \qquad \text{Rayleigh}^{10p} \qquad (43)$$

$$= 1 - a/RT^2V + c(V-b)/RT^3V^3 \qquad \text{Wohl}^{10a} \qquad (44)$$

$$= 1 - Pb/RT - K/V \qquad \text{Moelwyn Hughes}^{10g} \qquad (45)$$

$$= 1 - Pb/RT + B/V + C/V^2 + \dots \qquad \text{virial}^{10a} \qquad (46)$$

$$= \exp-\left[\ln\gamma - b/(V-b) + 2a/RTV\right] \qquad \text{fugacity}^{9a} \qquad (47)$$

In Eq.(45)

In Eq.(45) K is the dimerisation constant which has been equated[10g] to B, the second virial coefficient of Eq.(46).

XI. THE IDEAL LAWS, EQS (1) AND (2), AS LIMITING CASES OF EQS (22) AND (56)

Eqs (56) and (22) for gases and solutions reduce to the ideal laws, Eqs (1) and (2), for very low values of P and Π, when $\bar{V} \simeq V \gg b$ and $i^* = 1$ for gases; and $V \simeq V^{B}_{x} \gg V^{B}_{AS}$ and $i^* = \nu$ for solutions, where $\nu \neq 1$ for electrolytes and $\nu = 1$ for non-electrolytes (non-associating/dissociating). Thus, relations (48) and (49) hold

$$\lim_{P \to 0}(P\bar{V}) \simeq PV = RT \qquad (48)$$

$$\lim_{\Pi \to 0}(\Pi\bar{V}) \simeq \Pi V = RT \qquad (49)$$

XII. THE LANGMUIR ISOTHERM FOR THREE DIMENSIONS AS A NATURAL CONSEQUENCE OF THE PRESENT EQUATIONS OF STATE FOR GASES AND SOLUTIONS

The analogy of the equations of state for 3 dimensions and for surface coverage is well known. Particular mention is made here of the use[2f] of an equation for surface layers similar to the Amagat's equations for gases. In the present work the Langmuir isotherm for 2 dimensions is extended to 3 dimensions by rearranging Eqs (22) and (56).

The Langmuir isotherm[37] for surface coverage valid for moderate concentrations is the familiar Eq.(50)

$$\theta/(1-\theta) = B_L P, \quad B_L = \text{constant} \qquad (50)$$

for the coverage ratio where θ is the fraction of covered surface and the coverage ratio is directly proportional to P. P. For three-dimensional coverage, the ratio of 'occupied space' to 'free space' for gas molecules can be written[3e] from Eq.(55) as Eq.(51)

$$\Theta_g/(1-\Theta_g) = b/V_f = B_g(P/i^*) \qquad (51)$$

where the volume fraction $\Theta_g = b/V$ is the ratio of 'occupied' to 'total' space per mole of gas and $B_g = b/RT$ = constant. (Note that i^* corresponds to x of Eq.(39)).

Correspondingly, for solutions Eq.(52) holds[3e]

$$\Theta_s/(1-\Theta_s) = V^B_{As}/V^B_{Af} = B_s(\pi/i^*) \qquad (52)$$

for the ratio of the volumes of 'bound solvent' to 'free solvent', where the volume fraction $\Theta_s = V^B_{As}/V^B_A$ is the ratio of 'bound' to 'total' solvent per mole of solute and $B_s = V^B_{As}/RT$ = constant.

Figs 14a and 14b show the linear dependences of $\Theta/(1-\Theta)$ for gases and solutions (for dilute as well as concentrated solutions) on P/i^* and π/i^* respectively, the latter being the 'actual' pressures per mole[3e]. B_g and B_s are obtained from the slopes. In the region of moderately high concentrations when $i^* = i^*_m$ = constant, the occupation ratio becomes directly proportional to P as in Eq.(50). Thus Figs 14 demonstrate that filling of three-dimensional space by molecules is Langmuirian.

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LEGENDS FOR FIGURES

FIG. 1

Dependence of PV product on P for gases; PV data [4a]; PV=1 at S.T.P. Horizontal ~~broken~~ lines passing through the points at P=0 represent extrapolation of the ideal law at that temperature; the broken line shown is for 0°C. ●, gases at $T>T_H$; ○, Φ, ⊖, ●, gases at $T<T_H$. 1, 2, 4, 8 : N_2 at 700°, 600°, 50° and −100°C respectively; (for 1,2 ordinate scale is on the right side); 3, 6, 10 : H_2 at 150°, 25° and −175°C respectively; 5 : CO_2 at 100°C; 7 : O_2 at 0°C; 9 : He at 0°C

	He(0°)	H_2(25°)	N_2(600°&50°),	(−100°)	O_2(0°)	CO_2(100°)
b (l mole^{-1})	0.011	0.0165	0.030	0.031	0.0255	0.036
V_s [4b] (solid)	0.021	0.023		0.029	0.022	0.027
b/V_c	0.18	0.24		0.33	0.34	0.39

FIG. 1a

Dependence of the ratio $P(V-b)/RT$ on P for gases. 1, 2, 3, 4 : N_2 at 600°, 100°, 0° and −100°C; ✱ critical point; 5, 6 : CO_2 at 100° and 30°C respectively. Note: in the region CD the gas is in the form of vapour for $T_H>T>T_c$ and in the form of liquid at $T<T_c$ (e.g. CO_2 at 30°C). The critical point is therefore in fact the 'gas-vapour-liquid triple point'.

FIG. 2

Dependence of the molal osmotic coefficient ϕ $(\pi V_A^B = \nu RT\phi)$[3a] on $m\phi$ $(\pi = \nu RTd_A m\phi)$[3a] for aqueous solutions at 25°C (except ⊗, 100°C); $\phi=1.0$, ideal; ϕ data[5a]. (Ordinate scale on the right is for (curves 3 and 8). Hydration numbers are in parentheses below. ● sucrose (4.45), 1) $LaCl_3$ (21), 2) $CaCl_2$ (11.7), 3) $BeSO_4$ (10.6), 4) HCl (6.9), 5) NaI (4.3), 6) NaOH (3.6), 7) NaCl (2.95 at 25°, 2.85 at 100°), 8) Na_2SO_4 (4.7), 9) KBr (1.5), 10) CsCl (1.15); graphs not shown: LiCl (5.1), KCl (1.8), RbCl (1.3), NaBr (3.5), NaAc (4.25), $FeCl_2$(12.8). Note: 1, 2, 3, 4 deviate from linearity at high concentrations.

FIG. 2a

Dependence of V^B_{As} on $m\Phi$ (or Π or i^*m^*, the actual solute concentration in mole per l of free solvent). Note: At A, only the solvated free ions are present. In the region ABC, V^B_{As} is constant and the association/dissociation equilibrium (1)$\rightleftharpoons$(2) exists. At C, solvent begins to get squeezed out as the ions get closer and solvated ion pairs of the type (3) are formed, with less bound solvent. At D nearing saturation, V^B_{As} decreases further and contact ion pairs of the type (4) are probably formed before the solute separates from the solvent. The reverse sequence, (4), (3), (2), (1) corresponds to the dilution of saturated solutions. (n=1 for ion pair, n=2 for ion pair dimer, etc.).

FIGS 3 AND 4

i^* vs P for gases and i^*/ψ vs Π for solutions. 3a, gases at $T>T_H$ (e.g., H_2 600°, H_2 25°C); 3b, gases at $T<T_H$ (e.g., N_2 at 50°C); 4a, aq. sucrose at 25°C, 4b, aq.KBr at 25°C.

FIG. 5

a, $(1-\alpha)$ vs Π for solutions (aq.KBr at 25°C); b, α vs P for gases (N_2 at 50°C), ($\alpha/2$ corresponds to gaseous dimer).

FIG. 6

Λ vs Π for aq.KBr at 25°C; slope of the linear region = $K_{\Lambda,\Pi}$ = -0.0958 $cm^2\Omega^{-1}g.equiv.^{-1}atm^{-1}$; Λ data[28a].

FIG. 7

Aq.KBr at 25°C : a) Λ^* vs Π, b) Λ^* vs α ; intercept at $\alpha=1.0$ gives $\Lambda^* = \Lambda_0$ (= 151.15) and slope gives λ°_{+-} (= 132).

FIG. 8

a) $(\Lambda_0-\Lambda)/\Pi$ vs $(1-\alpha)/\Pi$ for aq.KBr at 25°C; slope = λ°_{+-} =

132, intercept = $|K_{\Lambda,\pi}|$ = 0.0958; b) $(\Lambda_0 - \Lambda)/i^* m^*$ vs $(1-\alpha)/i^* m^*$ for aq.NaCl at 25°C; Λ data [26b]; slope = λ^0_{+-} = 176, intercept = $RT|K_{\Lambda,\pi}|$ = 4 . $|K_{\Lambda,\pi}|$ = −0.164. Λ_0 = 133 from a plot of Λ^* vs α ; $(1-\alpha_m)$ = 0.245 .

FIG. 9

Aq.KBr at 25°C ; a) Λ vs $\sqrt{c}$, b) $(1-\alpha)$ vs $\sqrt{c}$, c) Λ vs $(1-\alpha)$ d) D-H-O square root law (Λ_0 = 151.7 by extrapolation). Slope and intercept of c) give λ^0_{+-} = 132 and Λ_0 = 151.15.

FIG. 10

Actual concentrations of B_+, B_- and B_{+-} in aq.KBr at 25°C; a) $\alpha m^* = [K^+] = [Br^-]$ vs m; b) $(1-\alpha)m^* = [K^+Br^-]$ vs m ; c) $i^* m^* = [K^+] + [Br^-] + [K^+Br^-]$ vs m ; d) m^* vs m . (E.g., at $m^* \simeq m = 1$, there are actually a total of 1.8 moles of solute, out of which 0.25 moles are as ion pairs, K^+Br^-, and 0.77 moles each are as K^+ and Br^- .)

FIG. 11

Association constants for aq.KBr at 25°C; a) K_c vs c , b) K_N vs c (K_N increases from zero and reaches a constant value of 0.754 at high concentrations).

FIG. 12

Linear dependence of $D\eta c$ (dyne.mole.cm^{-3}) vs π (atm) for aq. KBr at 25°C from 0 to 4m. Data: D^{30a}, η^{30b}. Slope, Δ = 45.6 Å; D^0 (from Δ and Eq.(3a)) = 2.017 cm^{2}s^{-1} (lit.: 2.016 and 2.018)

FIG. 13

Linear dependence of e.m.f. of concentration cells without transport on a) log π , and b) log $\pi_{\pm}$, for aq.KBr at 25°C from 0.05 to 4 m ; data [33]. Slope a) 0.109 V, b) 0.111 V . For other electrolytes (graphs not shown) dE/dlog π : KBr 0.1087, KCl 0.1090, NaBr 0.1112, NaCl 0.1100, HCl 0.1116, CaCl$_2$ 0.0773, BaCl$_2$ 0.0755, FeCl$_2$ 0.0776. (Note: instead of

E vs $\log \pi$, $\log m\gamma$ vs $\log \pi$ can be plotted, cf.Eq.(6)).

FIG. 14

Linear dependence of the coverage ratio b/V_f on P/i^* for gases and V^B_{As}/V^B_{Af} on π/i^* for solutions; a_1: aq.sucrose at 25°C, a_2: aq.KBr at 25°C (0 to 3.75 M); b_1: H_2 at 25°C, b_2 and b_3 : H_2 at 50° and 600°C respectively. (Langmuir plot for 3 dimensions), slope = b/RT (gases), = V^B_{As}/RT (solutions).

LIST OF SYMBOLS

k	Boltzmann constant
R	standard molar gas constant
T	temperature in °K
N_{Av}	Avogadro number

Gases

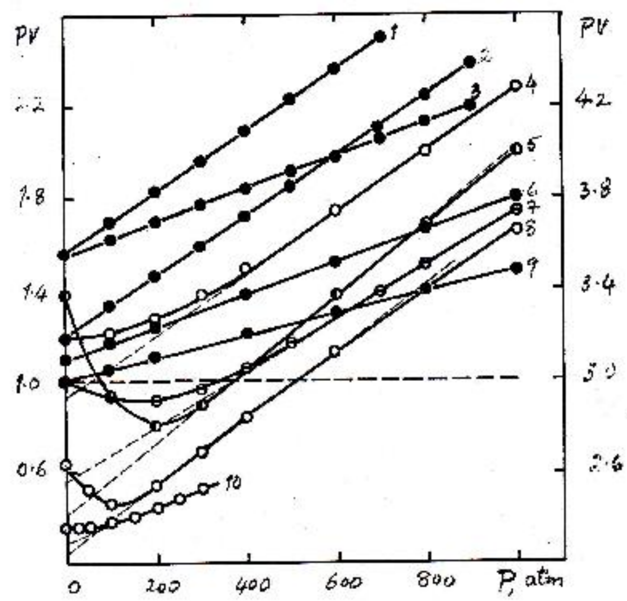
P, V	pressure and total volume of 1 mole of gas
b	volume of 1 mole of gas molecules
$V_f = V-b$	volume of 'free space' per mole of gas
T_B	Boyle point
T_H	Hirn point
$\sqrt{\bar{v}^2}$	root mean square velocity of gas molecules
N_{as}, N_{ds}	mole fractions of the associated and dissociated molecules of gas
ρ	density of gas
$1-\alpha$	degree of dissociation of gas
i^*	total number of moles of gas actually present per mole of gas taken
$\bar{V} = V_f/i^*$	volume of free space per mole of gas actually present

Solutions

Π	osmotic pressure
V	volume of solution per mole of solute B
$C = 1/V$	molar concentration
c	moles per ml
m	molality
d_A	density of solvent A
$V_A^B = 1/md_A$	volume of solvent A used for dissolving one mole of solute B
V_{As}^B	volume of solvent A bound as solvation by one mole of B.

$V^{B}_{Af} = V^{B}_{A} - V^{B}_{As}$	volume of 'free solvent'
$\bar{V} = V^{B}_{Af}/i^{*}$	volume of free solvent per mole of solute actually present
$m^{*} = 1/V^{B}_{Af}$	moles of solute per l of free solvent
i	van't Hoff's factor
ϕ	osmotic coefficient
$\gamma, \gamma_{\pm}$	activity coefficients
α	degree of dissociation of solute
αm^{*}, $(1-\alpha)m^{*}$	actual concentrations of the free ions B_{+} or B_{-} and of the ion pair B_{+-} respectively
Λ	equivalent conductivity
N_{+}, N_{-}, N_{+-}	mole fractions of the free ions and ion pair
$\Pi_{+}, \Pi_{-}, \Pi_{+-}$	corresponding partial osmotic pressures
$\bar{V}_{+}, \bar{V}_{-}, \bar{V}_{+-}$	corresponding partial molar volumes
K_{c}, K_{m}, K, K_{N}	association constants
D	coefficient of diffusion
η	coefficient of viscosity
E	e.m.f. of concentration cell
α_{p}	polarisation of 'bound solvent'

Fig (4) (R.H.)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2.2
1.8
1.4
1.0
0.6
PV
4.2
3.8
3.4
3.0
2.6
0
200
400
600
800
P, atm
1
2
3
4
5
6
7
8
9
10

247

Fig (1a) (R. H.) 37

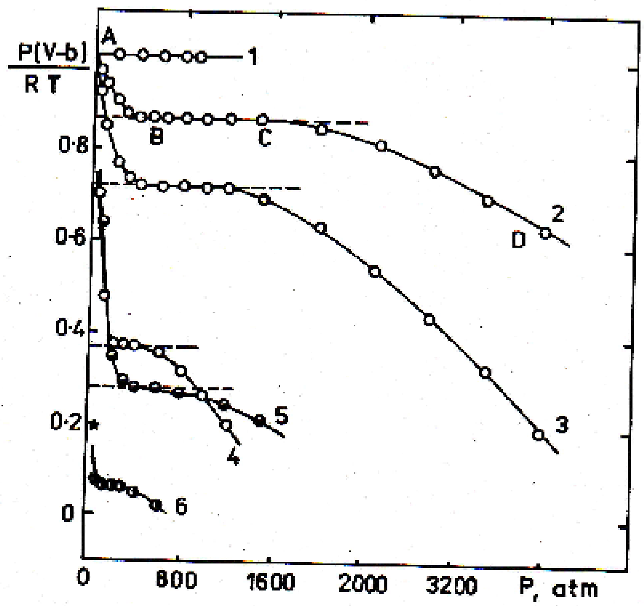
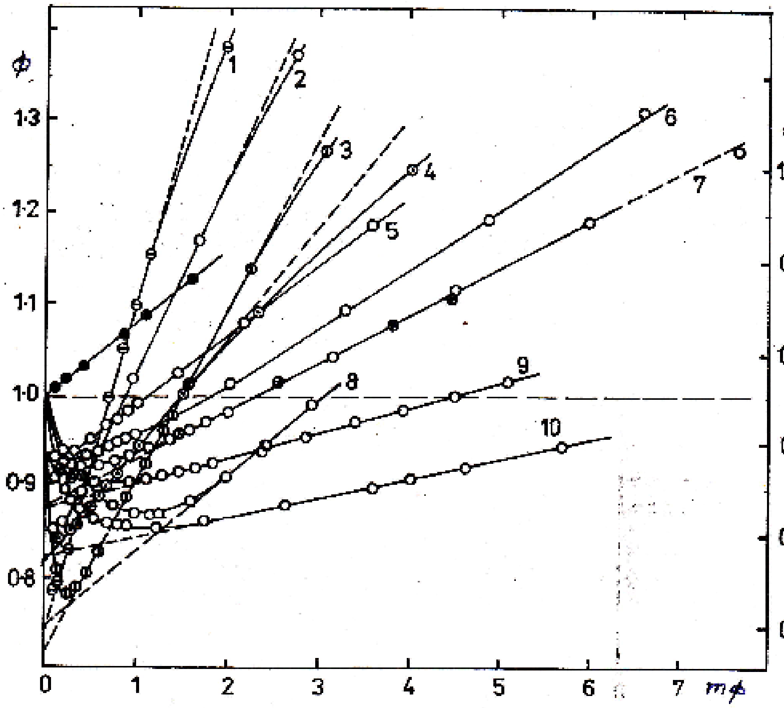
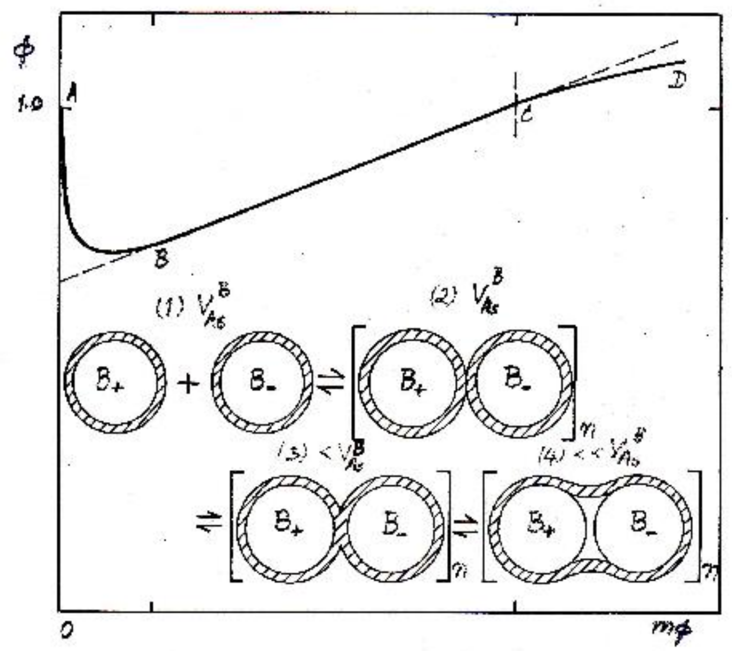
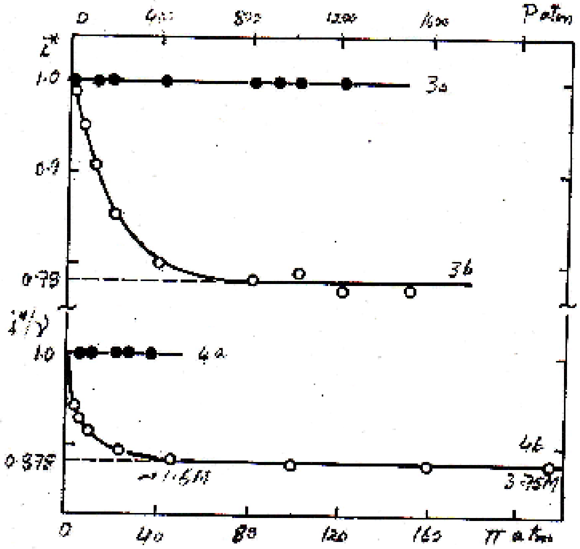


Fig (2) (R.H.)



Fig(2a) (R.H.)





Figs (3) & (4)

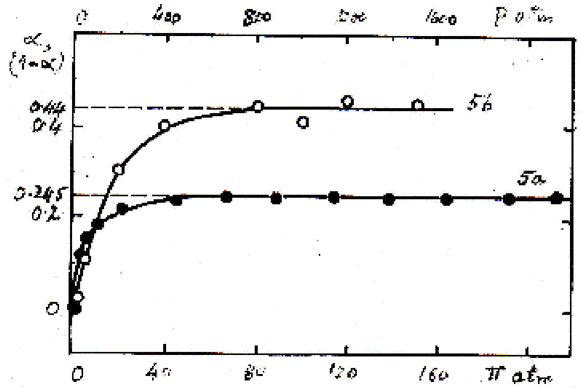


Fig (5)

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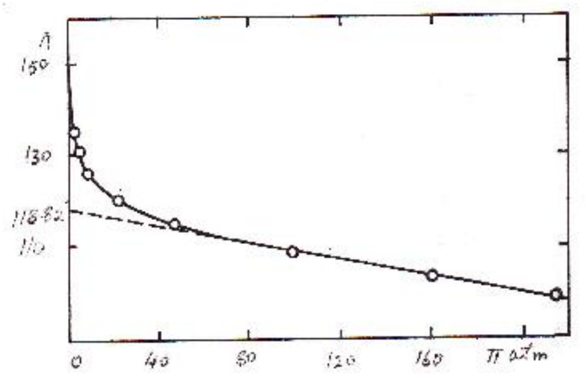


Fig (6) (R.H.)[41]

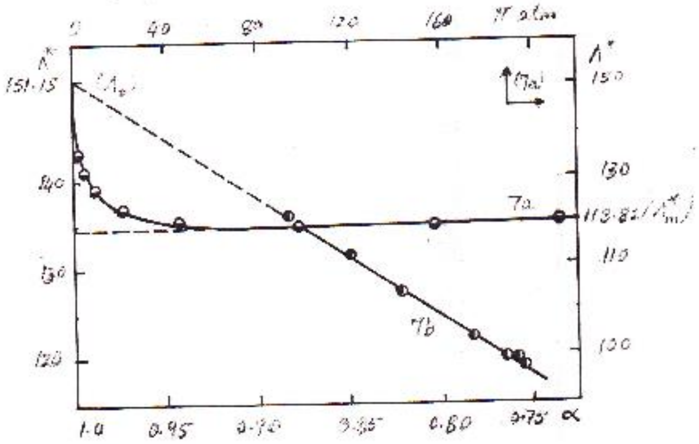


Fig (7)

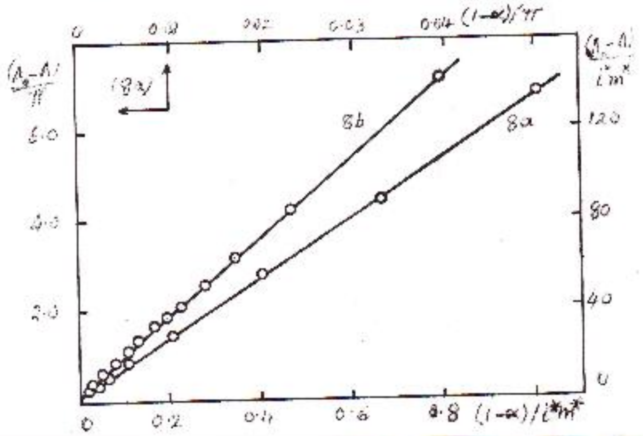
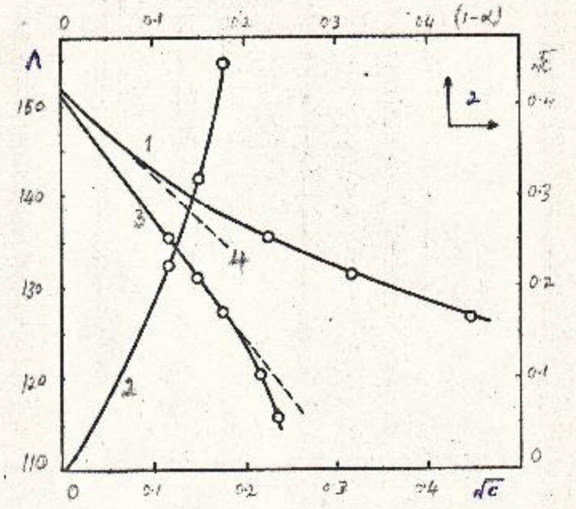


Fig (8)

2·0

㊷
(R-H)
Fig. (9)


0
0.1
0.2
0.3
0.4
(1-α)
Λ
150
140
130
120
110
√c
0.4
0.3
0.2
0.1
0
2
1
3
4
2
0
0.1
0.2
0.3
0.4
√c

294

$(R.H.)^{43}$ [illegible]

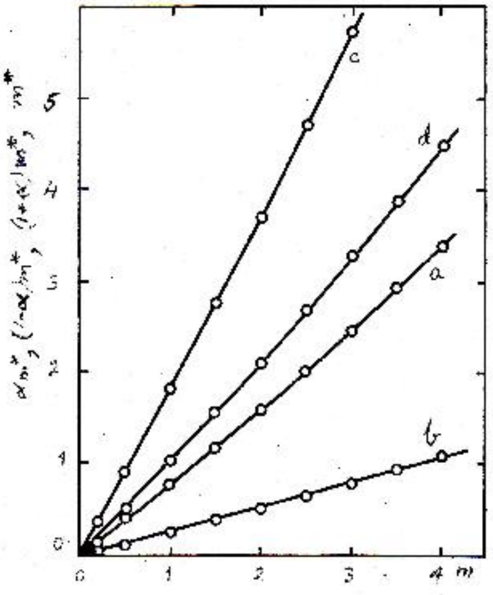


Fig.(10)

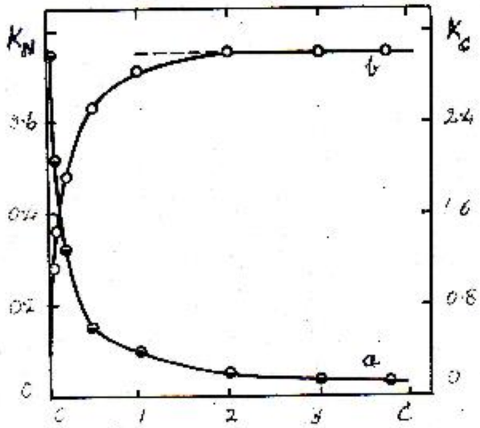


Fig.(11)

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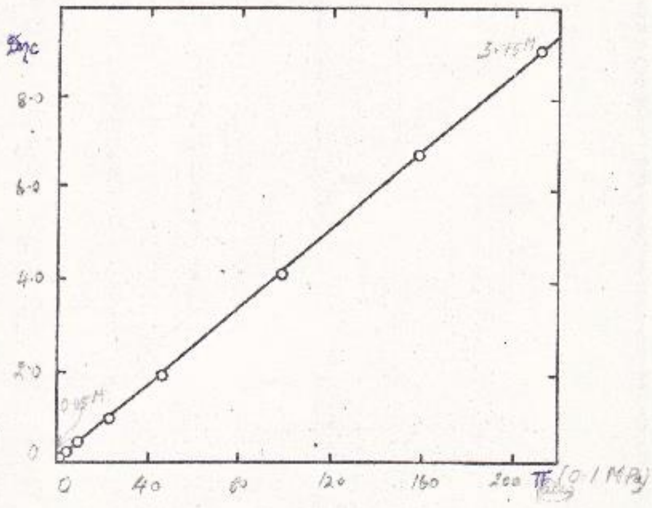

Fig (12)

(45)
(R.H.)

Fig (8)

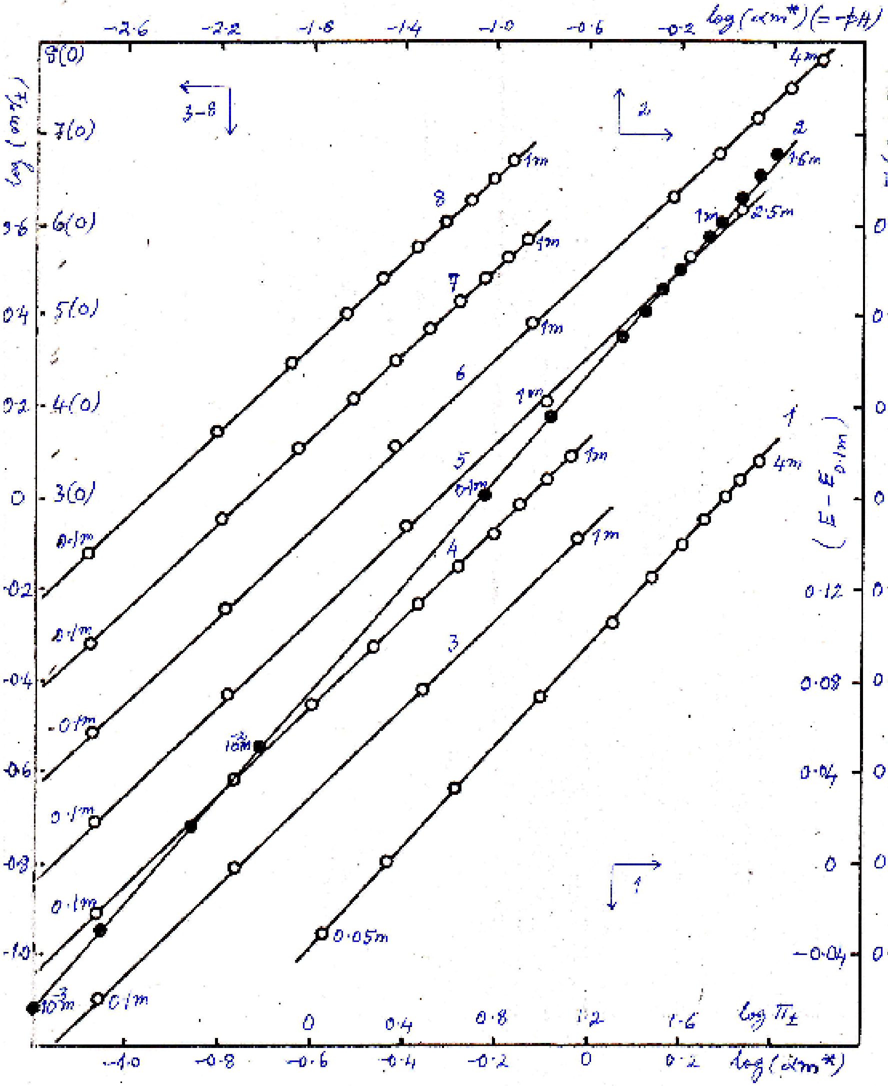

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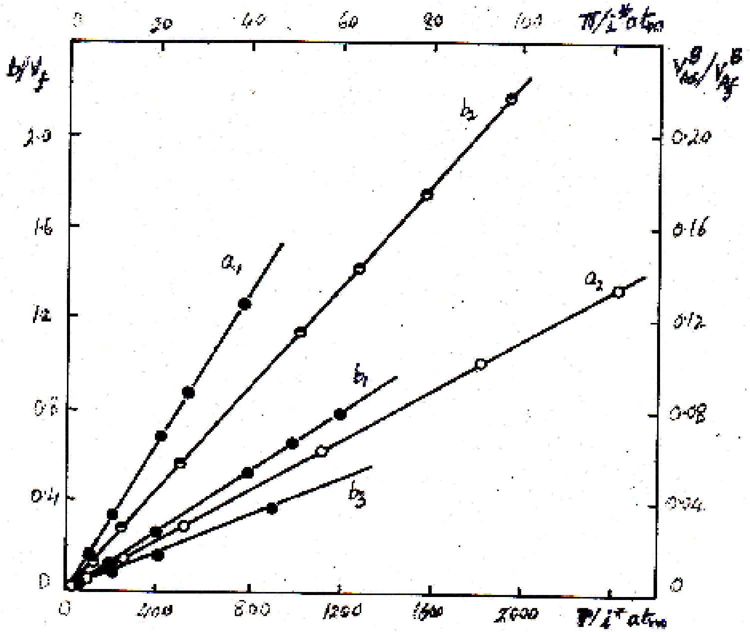
Fig. (14) (R.H.) 46



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