A SIMULTANEOUS INTERPRETATION OF EXISTING DATA ON NON-
IDEALITY OF GASES AND SOLUTIONS: SIMPLE EQUATIONS OF
STATE WITHOUT EMPIRICAL CONSTANTS AND PARAMETERS; LAN-
GUARD 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 $\Pi,V,T$ properties of
gases and solutions are described by two simple analogous
equations of state, Eqs. (32) 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 conducti-
vity, 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 c.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 occu-
pation of space, obtained by rearrangement of the equations
of state, Eqs. (31) and (32). As a consequence of the above,
representation of nonideality by activity and fugacity co-
efficients is not necessary.
INTRODUCTION

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

\[ PV = RT \]  

and (2)

\[ \Pi V = \Pi V_{RT} \]  

(\text{All for association/dissociation}),

was established nearly a century ago by van’t Hoff\(^1\) (see also\(^2\)) for very low pressures of gases and very dilute solutions of electrolytes and non-electrolytes. The ratios \(PV/RT\) and \(\Pi V_{RT}\) (called compression factor \(Z\) \(\equiv \frac{PV}{RT}\) and van’t Hoff’s factor \(\Pi V_{RT}\) respectively) are equal to unity and \(\Pi\) for the ideal laws. That the properties of gases and solutions are analogous even at higher pressures and concentrations can be seen\(^3\) from Figs 1 and 2 where \(PV\) and \(\Pi V\) products are plotted as functions of \(P\) and \(T\). It is evident from these Figs that Eqs (1) and (2) are best approximations for very low \(P\) and \(T\) values and that at all other values of \(P\) and \(T\) 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 \(P, V, T\) \(\equiv \rho V, r T\) and \(\Pi, V, T\) \(\equiv \rho V, r T\) 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.,

\[ PV/RT = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots \]  

(3)

\[ \Pi V/RT = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots \]  

(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, \( \gamma \), and
by the molal activity coefficient, \( \gamma^* \), which are inter-re-
lated\(^{12,24}\) by Eq. (3) through the Gibbs-Duhem relation,
\[
\frac{\Pi V^0_s}{RT} = 1 + \frac{\gamma^*}{\gamma} = \frac{\gamma^*}{\gamma} = \frac{n}{n_s} \ln \gamma^*_s
\]
where \( V^0_s \) is\(^{25}\) the volume of solvent \( s \) used for dissolving
each mole of solute \( B \) i.e. \( \varphi \) can be obtained\(^{26,11b}\) from mea-
surements of osmotic pressure, vapor pressure, changes in
freezing and boiling points, etc.; \( \gamma \) is obtained from \( \gamma^* \) by
integration using Eq. (3) or from e.m.f. measurements, say,
of concentration cells without transport\(^{26,11c}\), from the
"deficit" free energy\(^{26,10b,11c}\) attributed to non-ideality
as in Eq. (6):
\[
\Delta H(\text{actual}) = \Delta H(\text{ideal}) = \Delta H(\text{non-ideal})
\]
Conversely, the tables of \( \gamma \) and \( \gamma^* \) data in the literature
are considered as "measured" from which the actual osmotic
pressure, vapor pressure, changes in freezing and boiling
points, e.m.f. of cells etc., can be back-calculated. This
method was used for calculating \( \Pi \) from the \( \gamma^* \) values for
\( \text{NaCl}_s \).
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 \( B_{eq} \) (the undissociated electrolyte is
here\(^26\) denoted by \( B_{eq} \), e.g., Na\(^{+}\)Cl\(^-\)), since 'free ions'
associate to form 'hundt ions', see also\(^{12}\) dissociating
into a total of \( \gamma \) number of cations and anions according to
\[ \text{Eq. (7)}: \]

\[ n_{\infty} = n_0 \beta \]  

\[ n_{\infty} = n_0 \beta \]  

\[ \text{where } \alpha \text{ is the degree of dissociation, } i \text{ is given by Eq. (8)}: \]

\[ i = 1 + (\alpha - 1) \beta \]  

Thereby an excess number, \( (\alpha - 1) \beta \), of moles are created by the dissociation of \( B \). At infinite dilution, an electrolyte is completely dissociated and therefore \( \alpha = 1 \) and \( i = \beta \). In the case of solutes which associate to form dimers or polymers in the given solvent, \( i < 1 \) since \( \alpha < 1 \). 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 \( \alpha \) from experiments, like from measurements of electrical conductivity. The use of the Arrhenius ratio \( (\Lambda / \Lambda_0) \) or other modifications \( 10 \text{a} \) for the calculation of \( \alpha \), which approximately satisfied the law of mass action or the Gouy-Chapman dilution law, Eq. (9),

\[ \lambda_0 = (1 + \alpha) / (\alpha^2 a) = [1 - (\Lambda / \Lambda_0)] / (\Lambda / \Lambda_0)^2 \]  

for weak acids, gave neither the correct values of \( \alpha \) nor the association constant, \( \lambda_0 \), independent of concentration for strong electrolytes. In order to steer through the apparent anomalous behavior 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 \( \alpha \), the physical-chemical degree of dissociation. Despite the fact
that the $\gamma$ vs $a$ curves exhibit minima and pass through the $\gamma = 1$ values twice (as in definition 1a only for infinite dilution), subsequent theories of non-ideality, especially of electrolyte solutions, have largely converged upon explaining the concentration and temperature dependence of $\gamma$ and the thermodynamic properties of solutions are interpreted in terms of $\ln \gamma$ of Eq. (8). For a comparison with various other theories for the non-ideal part of free energy of solutions see 10c. The interionic attraction theory 20, 21a, 11c, 12a formulated on the assumption of complete dissociation ($\kappa = 1$) of strong electrolytes predicted the $\ln \gamma_{1/1}$ dependence and explained the $\ln \gamma_{1/1}$ relation found empirically by Koltunow 20, 10c. Despite the considerable support 12, 17, 20a 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 0.0M (about), they were extended or modified by the successive additions of more terms, parameters, and theories to fit the data at higher concentrations 20, 21a, 11c, 12a, 13a. At the same time theories of ionic association were also worked out by Bjerrum and others 20a, 11c, 13a, 14c, 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 solute in the solution. These theories show that ion pairs can be formed (although to a small extent) even in aqueous LiCl electrolyte 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^{158,9,20} provides a growing evidence for ion association even in aqueous strong electrolytes, especially of bulky ions. Thus, in the theory of solutions in cases where incomplete dissociation and formation of complex ions were evident, \( x \) was incorporated^{54,112,159,23-25} into the equations for \( \Phi \), \( \gamma \) and \( \Lambda \) while retaining the Debye-Hückel-Chargaff terms for the free ions.

As in the case of solutions, there exist two different interpretations of the non-ideality of gases:^{36,102} 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 in found^{26,36,102} in the case of vapours of nonpolar substances (e.g., \( \text{CH}_4 \)), nonpolar substances (e.g., \( \text{H}_2 \), \( \text{N}_2 \), dihydrogen halides of \( \text{H}_2 \), \( \text{Ar} \), \( \text{H}_2 \), oxides of \( \text{P}_4 \), and organic compounds (e.g., acetic and formic acid) and even in gases like helium.

Solvation of dissolved solutes as one of the important causes of non-ideality has long been recognized^{24}. Even since, there has been an increasing awareness of its importance in the interpretation of the properties of solutions^{54,112,116,154,159,25}. However, there is no concurrence^{104,106} in the reported values of the solvation numbers obtained by different methods, mainly because of the use of unsatisfactory theories of non-ideality.
In the whole, one finds that the equations explaining the non-ideality of gases and solutions (e.g., the \( P/\gamma \rightarrow T \)) relations and the concentration dependences \(^5,11,13,18\) of equivalent conductivity, of diffusion and viscosity coefficients and of \( \gamma \) and \( \gamma'^2 \) 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 \( 35^\circ\) of \( H_2 \) and aqueous sucrose and at \( 30^\circ\) of \( H_2 \) and aqueous NaCl), proposes 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; however, this treatment should hold for other solvents and solutes as well. For the preliminary work in this direction see \(^5,11\). 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.

1. A simple extension of the ideal gas and solution laws to higher pressures and concentrations: \( PV = \gamma^4 ST \) and \( \gamma V^3 = k \)

- Determination of \( \gamma \); the value of gas molecules and \( V \);
- 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 \( \Pi \), both \( PV \) and \( \Pi V^3 \) increase linearly with \( P \) and \( \Pi \). From amongst the equations
of state in the literature, the linearity is as expected according to Eqs (10) and (II)

\[ P(V-b) = RT \]  \hspace{1cm} (10)

\[ PV = bRT \]  \hspace{1cm} (II)

proposed by Kim,\textsuperscript{50} and Seeker, Porter and others\textsuperscript{51} respectively. The slopes of these linear regions give the volume \( b \) of one mole of gas molecules as Kim interpreted and the volume \( V_{\text{so}}^0 \) of solvent \( A \) bound as solvation\textsuperscript{52}(cf., the primary or inner solvation sphere\textsuperscript{23a}) to one mole of \( A \) (and not the volume \( b \) of solute molecules as supposed\textsuperscript{53} in Eqs (II)). The values of \( b \), \( V_{\text{so}}^0 \), \( b/V_{\text{so}}^0 \)

and the molar volume\textsuperscript{2} of the solidified gases are given in Figs 1 end 2. The hydration numbers obtained here are slightly less than the measured ones in the literature.\textsuperscript{54} Both \( b \) and \( V_{\text{so}}^0 \) decrease 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\textsuperscript{54} 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 gas closer\textsuperscript{55}, 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-vapor-liquid triple point

In the case of gases, the range of pressures over which \( b \) is \( P/V \) is linear decrease diminishes as the temperature is lowered\textsuperscript{56} until at \( T_g \), 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 \( T \), as in
Fig. 14. On compressing the gas from C to D, at $P_{CR}$, beyond the region of linearity of Fig. 10 or of the horizontal region $P_{CR}$ of Fig. 14, the slope decreases (as in the above case of solutions with highly hydrated solutes) as the gas turns directly into vapour. Since the liquid begins to appear at $T_{C}$ and $P_{CR}$, the critical point $T_{CR}, P_{CR}$ can be considered as the 'gas-vapour-liquid triple point'. (In the literature $^{20, 21, 10}$ 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 $P_{CR}$, although uncondensable (see $^{20}$ and also section VII).  

(e) if the van't Hoff's factor, approximated for $b$ and $P_{C}$.

Considering now the intercepts at $P_{C}$ and $T_{C}$ of the extrapolated linear regions in Figs 1 and 2, these, in general, have the values $i_{v, b}$, where $i_{v, b}$ (gases) and $i_{v, b}$ (solutions), and not just $P_{C}$ as implied by Eqs (10) and (11). In the case of gases, only at and above a sufficiently high temperature designated $^{20}$ as the 'lim point', $T_{lim}$ which is much higher than the Boyle point, $T_{B}$. Eq. (10) becomes valid for all $P$ and for $T > T_{lim}$, i.e., $i_{v, b} = 1.04$ etc. see the straight lines for $H_{2}$ at $200^\circ C$ and $90^\circ C$ at $500^\circ C$. In the case of solutions, substances, a non-electrolyte, give the linear dependence like gases at $T_{lim}$ and $i_{v, b} = 1.0$. On the other hand, for solutions of electrolytes $i_{v, b}$ is and for gases at $T_{lim}$, $i_{v, b} = 1.1$ etc., see the cases of $H_{2}$ at $50^\circ C$ and of aqueous NaCl.

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

\[
\begin{align*}
\Pi (v-b) &= \Pi P = \Pi x_{b}^{2} \\
\Pi (v_{A}^{B} - v_{A}^{E}) &= \Pi v_{A}^{B} = \Pi / \Pi m = \Pi^{1/2} 
\end{align*}
\]
can be written\(^3\) as for gases and solutions, where \(V_f\) and \(V_{f+}\) are the volumes of 'free space' and 'free solvent' (not bound to solute) respectively per mole of gas and solute taken, and \(m^a\) is the number of moles of solute \(A\) dissolved in one litre of 'free solvent' and is thus a new unit of concentration. It is related to \(\alpha\) by Eq. (15a)
\[
\frac{m^a}{\mu} = \frac{m_A}{(1-\frac{m_B}{m_A})}
\] (15a)
\(i^a\) is the van't Hoff factor corrected for 'bound volume'.

The latter volume is not available for the molecular and ionic movements. Assuming the constancy of the values of \(b\) \(\mu\) for pressures down to zero (which is justified for solutions by the support from literature\(^5\)) and by the correlation of \(i^a\) or \(\alpha\) with \(\lambda\) in section IV, and for gases, by the analogy with solutions) the values of \(i^a\) were calculated using Eqs (12) and (15) and are shown as functions of \(P\) and \(\pi\) in Fig. 5 and 6. It can be seen that \(i^a = 1.0\) for gases at \(P?=P_H\) at all \(\pi\) and for non-electrolytes at all \(\pi\). For gases at \(\pi<\pi_H\) and for electrolyte solutions \(i^a\) decreases from the value of unity (gases) or of \(\alpha\) (electrolytes) at zero \(P\) and \(\pi\) down to the constant value \(\lambda_H^a\) (mentioned earlier) at higher \(P\) and \(\pi\).

In Figs 3 and 4 the examples chosen demonstrate the general validity of the above dependences. Temperature does not influence much the value of \(i^a\) for solutions, whereas it has a great effect on gases as can be seen in Fig. 5 and in Fig. 6 which has the same ordinate.

An equation similar to Eq. (12) has been suggested by amoget\(^2\) for gases (see Eq. (39) section 8) where symbol \(x\) is used instead of \(i^a\). It is supposed to indicate mutual attraction between molecules, a decrease of \(x\) implying increase of attraction (see section VII).
II. Demonstration that $i^W = 1 + (v-1)x$ represents the actual number of moles present in the solution due to association/dissociation.

a) Relation between $i^W$ and the degree of dissociation, $x$.

Since Figs. 3 and 4 for $i^W$ show no initial decrease followed by an increase as in Figs. 1 and 2, the next step was to check whether $i^W$ and not $i$ of Eq. (6) represents the total number of moles actually present in the solution per mols of solute dissolved. In the absence of any exact method of obtaining $x$ from equivalent conductivity or other data, $x$ was directly calculated from $i^W$ presuming the validity of Eq. (14)

$$\Pi'_{ion}/x = i^W = 1 + (v-1)x \quad \therefore x = (i^W-1)/(v-1)$$

(14)

and these values were then correlated with equivalent conductivity, Fig. 5 shows the dependence of $x$ on $\Pi'$ (as account of the constancy of $v$ this figure is similar to Fig. 4). It can be seen that $x$ diminishes gradually from the value of unity at infinite dilution to a minimum value $x_m$ which remains constant in the region of high concentrations.

The possibility of a constant degree of dissociation has been suggested before as an interpretation of the conformity with Debye's law of light absorption by CuSO$_4$ solutions. It is pointed out here that in Bjerrum's theoretical treatment of ion association, since the degree of association, $1-x$, is directly proportional to concentration, it does not account for the constancy of $x_m$ observed here. Referring to his diagram of the degree of association as a function of the distance of approach of ions of 1:1 electrolyte, the constant $x_m$ found here is suggestive of a minimum cut-off distance which the ions cannot trespass and get closer. Such a minimum dis-
tance has been reported for the case of lanthanum ferrioxalate.

b) Correlation of $\alpha$ with equivalent conductivity $\Lambda$

As $\Lambda$ is proportional to mobility, by analogy with the pressure dependence of the velocity of gas molecules, the influence of $\Pi$ on $\Lambda$ was investigated rather than that of concentration on $\Lambda$ as is usually done in the literature. Fig. 5 shows the dependence of $\Lambda$ on $\Pi$. Alternately, because of Eq. (13), $\Lambda$ vs $\Pi^{1/3}$ can be plotted. It can be seen that this graph is linear in the range of $\Pi$ values where the degree of dissociation is constant, see Fig. 9a. Denote the slope of this region by $\Lambda_{\Pi}^{-1/3}$ (which is negative), the value of $\Lambda^{\infty} = \Lambda + \frac{\Delta \Lambda}{\Pi^{1/3}}$ can be calculated to check if $\Lambda^{\infty}$ is proportional to $\alpha$. $\Lambda^{\infty}$ is the equivalent conductivity corrected for the effect of osmotic pressure (see below). Fig. 7a shows the variation of $\Lambda^{\infty}$ with $\Pi$ from which its similarity to Figs. 3 and 5 is evident. Fig. 7c shows that $\Lambda^{\infty}$ is indeed directly proportional to $\alpha$, and that it reaches a constant value $\Lambda^{\infty}_{\alpha}$ when $\alpha = \alpha_{\infty}$. The equivalent conductivity at infinite dilution, $\Lambda_{\infty}$, is obtained as the intercept at $\alpha = 1.0$ of the $\Lambda^{\infty}$ vs $\alpha$ straight line. (The conventional method of obtaining $\Lambda_{\infty}$ is to extrapolate to $\alpha = 0$ the $\Lambda$ vs $\sqrt{C}$ graph for very dilute solutions). Thus, the dependence of equivalent conductivity on $\Pi$ (=$\Pi^{1/3}$) and $\alpha$ is given by the simple Eq. (15)

$$(\Lambda_{\infty} - \Lambda^{\infty}) = \lambda_{\Pi}^{\infty}(1-\alpha)$$

where $\lambda_{\Pi}^{\infty}$ (written as $\lambda_{\Pi}^{\infty}$ in ref. 8a) is characteristic of the ionic pair, $\Pi_{\infty}$, in the given solvent and is obtained as slope of Fig. 7a. This equation also shows that $\Lambda_{\infty} - \Lambda^{\infty}$ is directly proportional to the degree of association, $1-\alpha$. Eq. (15) is written in the full form in Eq. (18).
\[ \Lambda = \Lambda_0 - \lambda^C_p(1-\alpha) - \mu \frac{\Delta \mu}{\Delta N} \]

where \( \lambda^C_p(1-\alpha) \) is the reduction in equivalent conductivity due to ion pair formation and the last term can be considered as the reduction in conductivity due to the osmotic pressure or equivalently, due to the combined effects of Eq. 15, see Eq. 11. The validity of Eq. 16 for dilute as well as concentrated solutions is demonstrated in Fig. 8. Eq. 16 can be compared with these in the literature. Thus, the above correlation of \( \alpha \) values, calculated from osmotic pressure using Eq. 16, with the equivalent conductivity data confirms Eq. 14 for electrolyte solutions.

a) Determination of \( \Lambda \) and \( \lambda^C_p \) from the linear dependence of \( \Lambda \) on \( (1-\alpha) \) for very dilute solutions.

According to the simple kinetic theory of gases, the root-mean-square velocity is related to the pressure and density \( \rho \) of the gas by Eq. (17):

\[ \sqrt{v} = \sqrt{\frac{3kT}{\pi m \rho}} \]  

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 \( \Lambda \sqrt{v} \) linear dependence empirically found by Kohlrausch is a manifestation of the gas-solution ideal gas analogy.

The Debye-Hückel-Onsager (D-H-O) limiting law, Eq. (18):

\[ \Lambda_0 - \Lambda = \left( \gamma^\infty \frac{\Lambda_0^2}{R_0} \right) \frac{e^2}{h} = \alpha \ln \gamma = \alpha \frac{\Lambda_0^2 \Lambda}{R_0} \]  

which interprets Kohlrausch's observation, suggests that the conductivity decreases \( \Lambda_0 - \Lambda \) is due to the interionic forces between free ions (assuming complete dissociation) in the given solvent. In this equation \( R_0 \) and \( \Lambda_0 \) are Onsager constants.
and \( \lambda', \lambda'' \) are proportionality constants, \( \sigma \) is the inter-ion interaction energy and \( \sigma' \) is the reciprocal thickness of the ion atmosphere.

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

\[
\Lambda_0 - \Lambda = \Lambda_0(1 - \alpha)
\]

The present work shows that for dilute solutions Eq. (19) reduces to Eq. (20)

\[
\Lambda_0 - \Lambda'^{\infty} = \Lambda_0 - \Lambda = \lambda'^{\infty}(1 - \alpha)
\]

and thus supports Arhenius' idea, except that \( \lambda'^{\infty} \), the equivalent conductance characteristic of the ion pair, has to be used in Eq. (19) in place of \( \Lambda_0 \), the sum of the conductivities of the free ions, \( \lambda'^{\infty} \) and \( \lambda''^{\infty} \).

On comparing Eq. (20) with Eq. (19), one can see that \( 1 - \alpha \) must be proportional to \( \sqrt{\sigma'} \) in the range of validity of the Boltzmann and S-C-G's \( \sqrt{\sigma} \) law. Figs. 1, 2 and 3 show the dependence of \( \Lambda' \) on \( \sqrt{\sigma'} \), of \( 1 - \alpha \) on \( \sqrt{\sigma} \), and of \( \Lambda \) on \( 1 - \alpha \) respectively. It is obvious that the S-C-G relation gives the tangential slope at infinite dilution whereas the present limiting Eq. (20) gives the best fit. Therefore, using Eq. (20) both \( \Lambda'_0 \) and \( \lambda'^{\infty} \) can be obtained from the intercept and slope of a plot of \( \Lambda' \) vs. \( 1 - \alpha \) for dilute solutions.

On combining Eqs. (20) and (19), one gets Eq. (21)

\[
\lambda'^{\infty}(1 - \alpha) = \lambda''^{\infty} n/2 \lambda
\]

from which one can see that ion association, naturally, is a direct result of the interionic attractive forces between free ions. Thus, 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 a 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 DIILUTE AND CONCENTRATED SOLUTIONS OF ELECTROLYTES AND NON-ELECTROLYTES, \( \Pi^\gamma = RT \) OR \( \Pi = 1^m \cdot RT \)

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

\[ \Pi^\gamma = RT \]  

where \( \gamma = V_{avg}/1^m = 1/(1^m \cdot N) \) is the average volume of free solvent per mole of solute species in the dissolved state and \( 1^m \) 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 \( 1^m = 1 \) at all concentrations. By writing the equation in this form, the definition of partial molar free energy, \( \Pi \), (or \( N \), per molecule) at any temperate of \( T \), Eq. (23):

\[ d\Pi = M \Delta H = \Delta H = -\Delta H = \Delta H = \Delta H (1^m \cdot N) \]  

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

\[ \Delta S = M \ln N = -\Delta H \ln \Pi \]  

giving the corresponding change in entropy. Thus, non-ideality can be explained completely by the association/dissociation and solvation of solute. The arbitrary concept 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 iso-osmotic since for both \( V = 1^m \cdot N \), \( \gamma = \frac{1^m \cdot \phi}{C} \)) at a given temperature \( \gamma \) is the same and, consequently, Eq. (24) holds

\[ 1^m \cdot N = 1^m \cdot N = \ldots \quad \text{(constant \( \Pi/T \))} \]
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 $V_{As}$ per mole of A 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. 2. When the concentration (and hence the osmotic pressure) increases beyond that corresponding to point C, coalescence of the solvation sheets 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. 2. Although these different types of solvation have in general been considered plausible in the literature, the $K_{A}^{B}$ vs $\Pi$ plot of Fig. 2 enables exact location of the concentration corresponding to point C (cf. Fig. 2c) until which $V_{As}$ 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 SOLUTION, $n_{o}^{o}$, $n_{o}^{s}$, AND $n_{o}^{s}$.

The mole fractions $n_{o}^{o}$, $n_{o}^{s}$ and $n_{o}^{s}$ are given by Eqs (29)

\[ n_{o}^{o} = n_{o}^{s} = \frac{x}{\lambda} \quad n_{o}^{s} = \frac{1-x}{\lambda} \]

\[ n_{o}^{o} + n_{o}^{s} + n_{o}^{s} = 1 \]  

The corresponding partial osmotic pressures are given by Eqs (26)
\[ \Pi_\alpha = \Pi_\beta = \Pi_\gamma = \Pi = \alpha \Pi \quad \Pi_{\alpha \beta} = \Pi_{\alpha \gamma} = \Pi_{\beta \gamma} = \Pi = (1-\alpha) \Pi \quad (25a, b) \]
\[ \Pi_\alpha + \Pi_\beta + \Pi_\gamma = \Pi \quad (25c) \]

Eq. (25c) demonstrates that Dalton's law is applicable for the ionic components of electrolyte solutions. The partial molar volumes are defined by Eqs. (27)
\[ V_\alpha = V_\beta = V_\gamma = V = \frac{1}{1-\alpha} \quad \text{and} \quad V_{\alpha \beta} = V_{\alpha \gamma} = V_{\beta \gamma} = \frac{1}{1-\alpha} \]
\[ \frac{1}{V_\alpha} + \frac{1}{V_\beta} + \frac{1}{V_\gamma} = \frac{1}{V} \quad (27a, b) \]

In Figs. 10 a, b, c, and d the actual ionic concentrations of the dissociated forms, \( n_\alpha \) and \( n_\beta \), or the associated form, \( n_{\alpha \beta} \), of the actual total solute concentration, \( m_\alpha^{\text{II}} \), and \( m_\beta \) itself are plotted vs the solubility, \( m \). Historically, these were considered as undeterminable quantities. Moreover, the mean ionic activity \( n_\alpha \) was assumed\(^{28}\) 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 all electrolytes, and that the concentration of the associated form, \( n_{\alpha \beta} \), 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 recognized by the values of \( m_\alpha \) 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 \( K_\Pi \) (if solubility is used) by Eq. (28). In terms of partial osmotic pressures it can be written as \( K_\Pi = K_{\alpha \beta} \), Eq. (28):
\[ K_\Pi = \frac{\Pi_{\alpha \beta}}{\Pi_{\alpha} \Pi_{\beta}} = \frac{\Pi_{\alpha \beta}}{(\Pi_\alpha \Pi_\beta)} = \frac{(1-\alpha^2)}{\alpha^2} \quad (28) \]
whereas use of mole fractions gives \( K_\Pi \), Eq. (29):
\[ K_\Pi = \frac{n_{\alpha \beta}}{n_\alpha n_\beta} = \frac{(1-\alpha^2)}{\alpha^2} = K_\Pi \]
Fig. 11 a, b show the variations of \( k_\alpha \) and \( k_\beta \) with activity. It can be seen that while \( k_\alpha \) and \( k_\beta \) decrease with increasing concentration, \( k_\gamma \) increases from the value of zero at infinite dilution to a constant value at high concentrations where \( \alpha = \alpha_0 \). Since \( k_\gamma \) increases as the degree of association increases, Eq. (29) seem more appropriate for the definition of the association constant. The reported \( k_\alpha \) increases of the dissociation constant, \( K_0^{-1} \) (see Eq. (9)) of 2,4-dinitrophenol (obtained from extinction coefficient) with concentration in the high concentration range shows that \( \alpha \) indeed attains a constant value, see also \( ^{27} \). Since ionic association increases with decreasing dielectric constant of the solvent, \( k_\gamma \) must also increase.

Eq. (28) is similar to that used for gases, e.g., in association/dissociation of phosphorus chlorides, \(^{102}\) formation of double molecules in the vapour state, \(^{132}\), etc. (Increase of temperature increases the dissociation of PCl\(_3\), whereas increase of water concentration increases the dissociation of electrolytes).

From Eqs. (28) and (29) the dependence of \( \alpha \) on \( \Pi \) is given by Eq. (30) which is analogous to that for gases \(^{101}\).

\[
\frac{1}{\alpha} = \left(1 + k_0 \Pi \right)^{1/2} = \left(1 + k_0 \Pi \right)^{1/2} \quad (30)
\]

**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_0 \Delta (= \frac{1}{2} k_0 \Pi) \quad \Delta = \frac{D_0}{D} \quad \text{(Stokes' factor, \( \pi \), \( \Delta \))}
\]
governs the Brownian motion in solutions and describes the concentration dependence of the product of coefficients of diffusion and viscosity (ν represents noise) for dilute and concentrated solutions, see Fig. 2. This relation supports the original idea of Frenkel that diffusive flow is a result of osmotic force. Eq. (31) reduces to Eq. (31a):

\[ \nu^2 \eta = \nu_0 \eta_0 \]

for infinite dilution (cf. Stokes–Einstein's relation for Brownian motion, \( B \eta = \nu_0 / \eta_0 \)).

Eq. (31) can be compared with those in the literature, in which 1) the term with activity coefficient forms a major fraction of the concentration dependence of \( B \eta \), where \( \eta \) is introduced as a correction factor, and 2) the interpretation is based on irreversible thermodynamics.

b) Relation between \( \Delta F^{\text{osm}} \) and osmotic pressure

The free energy change \( \Delta F^{\text{osm}} \), associated with change of ionic concentration (cf. Eq. (32)) for \( \Delta F^{\text{osm}} \), measured as the corresponding change in the e.m.f. of concentration cells without transport was found to obey Eq. (32),

\[ \Delta F^{\text{osm}} = R \ln \frac{\bar{\mu}}{\bar{\mu}_0} = \frac{K_{2,1} \bar{\mu}}{\bar{\mu}_0} \]

where \( K_{2,1} \) is a constant. Fig. 13 shows the linear dependence of \( \bar{\mu} \) on \( \ln \frac{\bar{\mu}}{\bar{\mu}_0} \). The slope gives the constant \( K_{2,1} \), which has values ranging between 1.63 and 1.80 for 1:1 electrolytes and between 1.27 and 1.76 for 2:1 electrolytes. \( K_{2,1} \) can be tentatively interpreted in terms of solvent polarization as follows: writing the equation of Eq. (32) as \( \alpha_p \frac{\partial \mu}{\partial \bar{\mu}} = \alpha_p \frac{\partial \mu}{\partial \bar{\mu}} \), \( \alpha_p \) (\( = \frac{\nu_0}{(K_{2,1} \bar{\mu})} \)) can be considered as the factor by which the ionic charge of is changed by the polarization of the bound solvent. Thus \( \alpha_p = 1.073 \) for 1:1 electrolytes and 1.154 for...
21 l electrolytes. For an account of charge density rearrangements accompanying ion solvation see \(26, 27\). Eq. (32) can be compared with Eq. (5) from which the activity coefficient is calculated.

a) and b) are discussed in more detail in \(24\) and \(25\).

c) Interpretation of cryoscopic

The cryoscopic of all halides in nitrobenzene has been treated in terms of solvation and degree of association without \(\gamma\); see \(25\) for details.

VII. CORRELATION OF \(\gamma^m\) WITH THE DEGREE OF MOLECULAR ASSOCIATION, \(\alpha\), IN GASES

The striking resemblance of the \(\gamma^m\) vs \(\alpha\) and \(\gamma^m\) vs \(\Pi\) graphs for gases and solutions (Figs. 3 and 4) suggests that \(\gamma^m\) 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 \(T = T_0\) can be considered to produce a certain degree of association.

This association increases as the temperature is lowered and pressure is increased and the gas first turns into aggregates of vapour molecules at pressures near \(P_0\) and temperatures near \(T_0\), and finally into liquid itself at \(T = T_0\) and \(P = P_0\); see also section 12. Support for this view can be found in the concept of association of gas molecules and formation of molecular clusters and aggregates prior to condensation\(36, 37, 38\). Also, attention can be drawn to the fact that the van der Waals' attraction term, \(a/r^2\), for free gas molecules, represents the cohesive pressure for liquids\(22\).

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

\[
B \rightleftharpoons (1/n)B_n
\]

(33)
1 - \alpha = \alpha / n

1^m \text{ is given by Eq. (34) analogous to Eq. (14)}

\[ 1^m = 1 + (3-2)\alpha, \quad \alpha = 1/n \]

(34)

and is decrease from the value of unity at P=0 to a constant value, \( i^m_{\text{av}} \), at high P. Here (1-\alpha) represents the degree of dissociation. Thus, for gases, Eq. (12) can be written as Eq. (35)

\[ PV / RT = 1^m = 1 + (3-2)\alpha \]

(35)

Since \( i_{\text{av}} \), and \( i_{\text{av}} \) are in accordance with the observations in Fig. 7. Consequently, the smaller the value of \( i^m \), the higher is the degree of association; this is in agreement with Arrhenius view of increased mutual attraction (see sect. 1). One can see from Fig. 8 that at any given \( P_{\text{av}} \), gradual isothermal compression of one mole of a gas decreases the total number of molecules from its initial value of \( N_{\text{av}} \) (at 0°C) to a minimum value \( i^m_{\text{av}} \) which remains constant over a large range of pressures (see Fig. 8 for the analogy with electrolytes). The lower the temperature, the smaller the values of \( i^m \) as well as the range of pressures over which \( i^m \) is constant. At \( T = 0°C \), the cohesive forces become strong enough for the gas to liquefy by compression. The values of \( i^m \) at \( P_o \), \( V_o \), and \( F_o \), calculated using Eq. (35) for some common gases are: \( i^m \) for \( \text{H}_2: 0.469; \text{N}_2: 0.191; \text{O}_2: 0.196; \text{Cl}_2: 0.152 \) mole.

As \( P_{\text{av}} \) increases, the gas molecules do not cohere or associate on compression in the pressure region investigated, and therefore \( i^m = 1.0 \) at all \( P_{\text{av}} \) 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 18 only between the temperatures \( Z_{\text{av}} \) and \( F_o \).

Fig. 9A shows the degree of association, \( \alpha \) as a function of
pressure for $N_2$ at 50°C, for an arbitrary value of $\gamma = 1/2$
in Eq. (33). As in the corresponding Fig. 2a for electrolytes, 
$\alpha$ reaches a constant value $\alpha _m$ in the high pressure region.

VIII. THE ACTUAL EQUATION OF STATE FOR LOW AND HIGH PRESSURE
OF GASES. $\Psi = NT$

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

$$\Psi = NT$$

(36)

where $\Psi = \frac{V}{M} - M/\rho$. This is analogous to Eq. (22) for
solutions. Eq. (36) differs in significance from the ideal law,
Eq. (1), in that $\Psi$ 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)

$$d\Psi = d\Omega - dW = -RT d\ln V$$

(37)

as for the ideal law but with $\Psi$ in place of $V$. The correspond-
ing change in entropy is given by Eq. (37a)

$$dS = R d\ln V$$

(37a)

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

The mole fractions, partial pressures and partial molar vol-
umes of the dissociated and associated (subscripts $da$ and $ea$)
forms of the gas molecules are expressed by Eqs. (38 a,b and c)

$$H_{da} = (1-\alpha)\frac{V}{M}, \quad H_{ea} = \alpha \frac{V}{M}; \quad H_{da} + H_{ea} = 1$$

$$P_{da} = \frac{V}{M} P, \quad P_{ea} = \frac{V}{M} P; \quad \frac{V}{M} + \frac{V}{M} = P$$

$$\frac{V}{M} = \frac{1}{V} \rho \frac{V}{M}$$

(38a)

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

The association constant defined in terms of mole fraction
by Eq. (38a)
\[
K_m = \frac{\alpha}{m(1-\alpha)}
\]

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

The above equations demonstrate the necessity of taking into consideration the presence of associated gas molecules, either to neglected in the literature, when investigating the physicochemical properties of gases like, e.g., gas kinetics, adsorption, etc. For detailed expressions for \(\alpha\) in terms of the dissociation energy of gaseous dimers and \(\alpha\) see [18].

Finally, from Eq. (34) follows Eq. (38a)

\[
\frac{V_{f,1}/V_1}{V_{f,2}/V_2} = \cdots
\]

showing that at any given \(T/P\), \(V\) is the same for all gases.

Inversely, the number of moles per unit volume of free space is constant at constant \(T/P\).

1. COMPARISON OF HIS 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 \(P = \frac{N(V-b)/RT}{E} \):

\[
1^* = 1 + (v-1)\alpha
\]

present work (39a), (39)

\[
= x
\]

Lagasse (39) (39)

\[
= \frac{1}{1+\frac{a}{V}}
\]

Linn (40a)

\[
= \frac{1}{1+\frac{a}{V}}
\]

van der Waals (41a)

\[
= \exp(-a/RT)
\]

Bierstitter (42a)

\[
= \frac{1}{1 + \frac{b}{V} + \frac{a^2(V-b)}{2RT^2}}
\]

Wohl (43a)

\[
= \frac{1}{1 - \frac{b}{V} + \frac{a}{V^2} + \frac{c}{V^3} + \cdots}
\]

Virenia (44a)

\[
= \exp\left[\ln \frac{V}{b} - b/(V-b) - 2a/RT^2\right]
\]

Fugacity (47a)
In Eq. (43) \( k \) is the dissociation constant which has been equa-
ted to \( B \), the second virial coefficient of Eq. (46).

II. THE IDEAL LAWS, Eqs. (1) and (2), AS LIMITING CASES OF
Eqs. (46) AND (49)

Eqs. (36) and (22) for gases and solutions reduce to the ideal
laws, Eqs. (1) and (2), for very low values of \( P \) and \( \Pi \), when
\[ T = 28 \text{ and } 1^{m} = 1 \text{ for gases; and } \Pi = 28 \text{ and } 1^{m} = \chi \text{ for}
solutions, where \( \chi \) is for electrolytes and \( \Pi \) is for non-electrolytes
(non-associating/dissociating). Thus, relations (43)
and (49) hold

\[
\lim_{\Pi \to 0}(PV) \approx PV = \Pi
\]

\[
\lim_{\Pi \to 0}(\Pi V) \approx \Pi V = \Pi^{m}
\]

II. 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 \( \Pi^{m} \) of an equation for surface layers simi-
lar to the Langmuir's equations for gases. In the present
work the Langmuir isotherm for 2 dimensions is extended to
3 dimensions by rearranging Eqs. (22) and (36).

The Langmuir isotherm \( \Pi^{m} \) for surface coverage valid for
moderate concentrations is in the familiar Eq. (30)

\[
\theta/(1-\theta) = n_{a} P, \quad n_{a} = \text{constant}
\]

for the coverage ratio where \( \theta \) is the fraction of covered
surface and the coverage ratio is directly proportional to \( P \).

For three-dimensional coverage, the ratio of 'occupied'
space to 'free space' for gas molecules can be written \( \theta \)
from Eq. (25) as Eq. (31)
\[
\Phi_e/(1-\Phi_e) = b/V_e = \beta_e (P/\Pi^M)
\]

where the volume fraction \( \Phi_e = b/V_e \) is the ratio of 'occupied' to 'total' space per mole of gas and \( b_e = b/\Pi^M \) = constant. (Note that \( 1^M \) corresponds to \( \Pi \) of Eq. (36)).

Correspondingly, for solutions Eq. (38) holds

\[
\Phi_s/(1-\Phi_s) = \frac{V^3_{AB}}{V^3_s} \frac{V^3_{s}}{V^3_{AB}} = \beta_s (P/\Pi^M)
\]

for the ratio of the volumes of 'bound solvent' to 'free solvent', where the volume fraction \( \Phi_s = V^3_{AB} / V^3_s \) is the ratio of 'bound' to 'total' solvent per mole of solute and \( \beta_s = V^3_{AB} / V^3_s \) = constant.

Figs. 14a and 14b show the linear dependence of \( \Phi/(1-\Phi) \) for gases and solutions (for dilute as well as concentrated solutions) on \( P/\Pi^M \) and \( \Pi/\Pi^M \) respectively, the latter being the 'actual' pressures per mole. \( \beta_s \) and \( \beta_e \) are obtained from the slopes. In the region of moderately high concentrations when \( \Pi^M = \Pi^M = \) constant, the occupation ratio becomes directly proportional to \( P \) as in Eq. (36). Thus Figs. 14 demonstrate that filling of three-dimensional space by molecules is Langer-
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LEGENDS FOR FIGURES

FIG. 1
Dependence of PV product on P for gases; PV data \( \frac{\text{atm}}{\text{cm}^2} \) from [1] at 298 K. Horizontal broken lines passing through the points at PhO represent extrapolation of the ideal law at that temperature; the broken line shown is for PhO. Dashed lines pass through the points at 300, 600, 900, and 1200°C respectively. (For 1,2 coordinate scale is on the right side.) 1, 2, 3: N\(_2\) at 150, 250, and 350°C respectively; 5, 6, 10: CO\(_2\) at 150, 250, and 350°C respectively; 7: O\(_2\) at 100°C; 9: He at 298°C.

He(298°C) N\(_2\) (298°C) N\(_2\) (200°C) (200°C) (200°C) O\(_2\) (298°C) CO\(_2\) (298°C)

b (1 mol\(^{-1}\)) 0.211 0.203 0.203 0.211 0.203 0.203 0.203 0.203

\( v \) (solid) 0.211 0.203 0.203 0.211 0.203 0.203 0.203 0.203

\( b/V^* \) 0.18 0.24 0.33 0.34 0.39

FIG. 2
Dependence of the ratio PV/\( n^2 \) on P for gases. 1, 2, 3, 4: \( \text{N}_2\) at 600, 1000, 1500, and 2000°C; critical point; 5, 6: CO\(_2\) at 1500 and 2000°C respectively. Note: in the region 69 the gas is in the form of vapour for \( \text{N}_2 \) and in the form of liquid at \( \text{CO}_2\). The critical point is therefore in fact the gas-vapour-liquid triple point.

FIG. 3
Dependence of the molal osmotic coefficients \( \Phi \) (\( \text{mol} \text{ osm} \text{liter}^{-1} \)) for aqueous solutions at 298 K (except 6, 100°C). \( \Phi_{\text{ide}, \text{sol}} \) (solid); \( \Phi \) data \( \text{mol} \text{ osm} \text{liter}^{-1} \). (Ordinate scale is on the right side.)

and 3). Hydrogen numbers are in parentheses below. 1. sucrose (4, 10), 1. InCl\(_3\) (21), 2. NaCl (11, 17), 3. BaCl\(_2\) (10, 5), 4. KCl (10, 5), 5. NaCl (10, 5), 6. KCl (10, 5), 7. NaCl (10, 5) at 20°C, \( 2.05 \) at 100°C, 8. NaCl (10, 5), 9. KBr (10, 5), 10. NaCl (10, 5). Graphs not shown: LiCl (10, 1), KCl (10, 1), NaCl (10, 1), NaBr (10, 1).
Main (4.25), 302L (10-8). Note: 1, 2, 3, 4 deviate from linearity at high concentrations.

FIG. 3

Dependence of $\ln a$ on $\Pi$ (or $\Pi$ or $a^*$) on the actual solute concentration in mole per liter of free solvent. Note: At $A$, only the solvated free ions are present. In the region $AB$, $a^*$ is constant and the association/dissociation equilibrium (1)$\equiv(3)$ 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, $a^*$ decreases further and 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. (Mac for ion pair, etc.)

FIGS 3 AND 4

$1^m$ vs $P$ for gases and $1^{m*}$ vs $\Pi$ for solutions. a) gases at $35^\circ C$ (e.g., $H_2$, $O_2$, $N_2$ at 250 atm); b) gases at $35^\circ C$ (e.g., $H_2$ at 250 atm); c) solutions at $25^\circ C$, $m$, aqueous at $25^\circ C$, $mc$ at $25^\circ C$.

FIG. 5

$a^*$ vs $\Pi$ for solutions (aqueous at $25^\circ C$); b) $\alpha$ vs $P$ for gases ($H_2$ at $25^\circ C$), $\alpha$ for gases ($H_2$ at $25^\circ C$), $\alpha$ for gases ($H_2$ at $25^\circ C$).

FIG. 6

$\Lambda$ vs $\Pi$ for aqueous at $25^\circ C$. Slope of the linear region $= k_1\Pi = -0.0938 \text{ cm}^2 \text{ atm}^{-1}$; $\Lambda$ data.

FIG. 7

$\Lambda$ data at $25^\circ C$: a) $\Lambda^m$ vs $\Pi$, b) $\Lambda^m$ vs $\alpha$ intercept at $\alpha = 0$ gives $\Lambda^m = \Lambda^0 = 151.5$ and slope gives $\Lambda^m = 151.5$.

FIG. 8

a) $(\Lambda - \Lambda)/\Pi$ vs $(1 - \alpha)/\Pi$ for aqueous at $25^\circ C$; slope $= \lambda_{\alpha} = \ldots$
(132, intercept $= \left| \frac{K_{\text{ion}}}{I} \right| = 0.0956$; b) $(\alpha - \lambda) \times 10^6$ vs $(1 - \alpha) / I$ for general at $25^\circ\text{C}$; c) data $\lambda_1^0 = 170$, slope $= \lambda_1^0 = 170$, intercept $= 5 \times \left| \frac{K_{\text{ion}}}{I} \right| = 4 \times 10^6$, $\lambda_1^0 = 235$ from a plot of $\lambda^0$ vs $\alpha$; $\lambda_1^0$ vs $1 - \alpha$ $= 0.243$.

FIG. 9

Aqueous at $25^\circ\text{C}$: a) $A$ vs $1 - \alpha$, b) $(1 - \alpha) / \sqrt{\alpha}$, c) $A_1$ vs $(1 - \alpha)$ d) $A_0 - 0$ square root law ($\lambda_1^0$ = 151.7 by extrapolation). Slope and intercept of c) give $\lambda_1^0$ = 132 and $\lambda_1^0$ = 131.19.

FIG. 10

Actual concentrations of $A^+$, $B^-$, and $AB^2$ in aqueous at $25^\circ\text{C}$ a) $K_a = \left[ A^+ \right] \times [B^-] \times [AB^2]$ vs a; b) $(1 - \alpha) / I = \left[ A^+ B^- \right]$ vs $\alpha$; c) $K_a = \left[ A^+ \right] + \left[ A^+ B^- \right]$ vs $\alpha$; d) $K_a^0 = \left[ A^+ B^- \right]$ vs $\alpha$; e) $\lambda^0$ vs $\alpha$ $(\alpha < 0.5)$. If $\alpha = 1$, there are actually a total of 4.8 mol of solute, out of which 2.6 mol are as ion pairs, $A^+ B^-$, and 0.77 mol each as $A^+$ and $B^-$.

FIG. 11

Association constants for aqueous at $25^\circ\text{C}$; a) $K_a$ vs $\alpha$; b) $B^-$ vs $\alpha$ ($K_a$ increases from zero and reaches a constant value of 0.75 at high concentrations).

FIG. 12

Linear dependence of $\rho$ (dysmole/cm$^{-2}$) vs $\Pi$ (atm) for aqueous KBr at $25^\circ\text{C}$ from 0 to 44. Data: $\rho^o \times 10^2$, $\rho^o$, $\Pi^o$, $\Delta = 45.6$; $\rho^o$ (from $\Delta$ and Eq. (28a)) = 2.417 cm$^2$ atm$^{-1}$ (lit. 1, 2.16 and 3.236).

FIG. 13

Linear dependence of c.a.f. of concentration cells without transport on a) $\log \Pi$; and b) $\log \Pi^2$, for aqueous KBr at $25^\circ\text{C}$ from 0.05 to 4.8 data 35. Slope a) 0.109 V, b) 0.411 V.

For other electrolytes (graphs not shown) 25/100 = 0.0046, $\Pi_1^o$, $\Pi_2^o$, 0.1090, NaCl 0.1112, KCl 0.1110, NaCl 0.1111, CaCl$_2$ 0.0978, BaCl$_2$ 0.0799, FeCl$_2$ 0.0478. (Note: Instead of
$E$ vs log $\Pi$, log $\eta$ vs log $\Pi$ can be plotted, cf. Eq. (6).

Fig. 14

Linear dependence of the coverage ratio $b/V$, on $P/\Pi$ for gases and $V_{H^+}^{B}/V_{H^+}^{M}$ on $P/\Pi$ for solutions; $a_2$ aqueous at 25°C, $a_1$ aqueous at 25°C (0 to 4.75 l); $b_1$ H₂ at 25°C, $b_2$ and $b_3$ H₂ at 50°C and 600°C respectively. (Langmuir plot for 3 dimensions, slope = $b/RT$ (gases), $V_{H^+}^{B}/RT$ (solutions).
LIST OF SYMBOLS

\( R \) Boltzmann constant
\( \mathcal{R} \) standard molar gas constant
\( T \) temperature in \( ^\circ \text{C} \)
\( N_A \) Avagadro number

\( P \) pressure
\( V \) total volume of 1 mole of gas
\( b \) volume of 1 mole of gas molecules
\( V_b = V - b \) volume of ‘free space’ per mole of gas

\( T_b \) Boyle point
\( T_f \) firm point

\( \sqrt{\frac{\mathcal{R}}{M}} \) root mean square velocity of gas molecules

\( x_a \), \( x_b \) mole fractions of the associated and dissociated molecules of gas

\( \rho \) density of gas

\( 1 - \alpha \) degree of dissociation of gas

\( \frac{V}{V_b} \) total number of moles of gas actually present per mole of gas taken

\( V = \frac{V}{V_b} \) volume of free space per mole of gas actually present

Solutions

\( \Pi \) osmotic pressure
\( V \) volume of solution per mole of solute 3

\( d = \frac{1}{V} \) molar concentration

\( c \) moles per lit

\( a \) molality

\( \rho_3 \) density of solvent 3

\( \nu_3 = \frac{1}{a_3} \) volume of solvent 3 used for dissolving one mole of solute 3

\( \nu_3^0 \) volume of solvent 3 bound as solution by one mole of 3.
\[ V^0_f = V^0_A V^0_s \text{ volume of 'free solvent'} \]
\[ V = V^0_A / V^0\text{ actually present} \]
\[ n^M = 1/V^0_A \text{ moles of solute per l of free solvent} \]
\[ \phi \] van't Hoff's factor
\[ \gamma_+ \gamma_- \text{ activity coefficients} \]
\[ \alpha \] degree of dissociation of solute
\[ \alpha = \alpha n^M (1-\alpha)n^M \text{ actual concentrations of the free ions } \]
\[ \text{ or } \text{ and of the ion pair } \]
\[ \lambda \text{ equivalent conductivity} \]
\[ K_+ K_- \text{ mole fractions of the free ions and ion pair} \]
\[ \Pi^+ \Pi^- \Pi^{+ -} \text{ corresponding partial osmotic pressures} \]
\[ \Psi^+ \Psi^- \Psi^{+ -} \text{ corresponding partial molar volumes} \]
\[ K_a K_t K_w \text{ association constants} \]
\[ D \text{ coefficient of diffusion} \]
\[ \eta \text{ coefficient of viscosity} \]
\[ E \text{ e.m.f. of concentration cell} \]
\[ \alpha_p \text{ polarization of 'bound solvent'} \]