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THE ROLE OF ELECTROSTRICTION IN HIGH PRESSURE CHEMISTRY

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This article gives a partly historical review of the role that is played in high-pressure chemistry by electrostriction (the contraction of solvent that occurs around dissolved ions and charged groups).

It has emerged that the high-pressure behaviour of many ionic reactions in solution is governed primarily by the changes of electrostriction that accompany the reactions, and that the pressure effects can be predicted, at least qualitatively and to some extent quantitatively, by the simple continuum electrostatic theory of Drude and Nernst and of Born. More detailed molecular models are now being developed by the methods of computer simulation and these should ultimately be capable of predicting chemical behaviour over a very wide range of pressures and temperatures.

1. Author's Preamble

I am honoured to have been invited to contribute to this, the fiftieth, volume of the *Review of Physical Chemistry of Japan* — and sobered by the thought that, when I first embarked upon high-pressure research, the journal had scarcely reached its twentieth volume! I have, ever since, found it to be a constant source of new and interesting results in high-pressure chemistry.

On this commemorative occasion, I have felt it appropriate to give my review something of an historical flavour. I think it also appropriate that it should be concerned with the subject of electrostriction, for the *Review of Physical Chemistry of Japan* was founded by Professor Shinkichi Horiba, a distinguished scientist who had, some years earlier, made the first accurate measurements of the separate apparent molar volumes of both salts and water in aqueous electrolyte solutions, over a range of temperatures and concentrations, and discussed them in terms of the contraction of water around the dissolved ions.¹ I shall refer to this important contribution by Professor Horiba in Section 4.

2. Pressure Effects and Volume Changes

In beginning a discussion of high-pressure chemistry, it is natural to ask what thermodynamics can tell us about the influence of pressure on simple chemical reactions.

The earliest contribution on this question was made in 1861, when James Thomson (Lord Kelvin's elder brother) wrote²:

"If any substance, or any system of substances, be in a condition in which it is free to

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change its state... of molecular arrangement... and if mechanical work be applied to it... in such a way as that the occurrence of the change of state will make it lose... that mechanical work... *then the substance or system will pass into the changed state*".*

This rule was later restated by Le Chatelier³¹ in 1884 and by Braun³¹ in 1887, and is now almost universally (although unfairly to Thomson) referred to as the Le Chatelier or Le Chatelier-Braun principle. Applied to pressure effects, the principle is almost a truism, for in effect it simply says that:

"If a thing can shrink, it *will* shrink if you squeeze it".

And one way in which a thing can shrink is by undergoing an internal chemical reaction that reduces its total volume. It follows that an increase in pressure will favour those reactions that are accompanied by a decrease of volume. This is a useful rule, but of course it is only a qualitative one: it says nothing about the *degree* of any pressure-induced change.

However, in the same year that Braun's paper appeared, Planck⁴¹ derived an important quantitative relationship between the volume change ΔV accompanying a reaction and the influence of pressure P on its equilibrium 'constant' K (which is not really a constant, because it varies with temperature and pressure). Unfortunately, in later years, his relationship has often been misunderstood and misapplied, and it is therefore worthwhile to consider its precise meaning. Planck assumed that the reactants mix ideally, so that for a general reaction



he could write the equilibrium constant simply in terms of the mole fractions x of the reactants, in a form equivalent to

$$K'_x = \frac{x_L^l x_M^m \dots}{x_A^a x_B^b \dots} \quad (2)$$

(the prime ' is here intended to indicate the assumption of ideal mixing). Then, on the basis of the second law of thermodynamics, he was able to derive a relationship equivalent to

$$\frac{\partial}{\partial P} RT \ln K'_x = aV_A^\circ + bV_B^\circ + \dots - lV_L^\circ - mV_M^\circ - \dots \quad (3)$$

$$= -\Delta V^\circ \quad (4)$$

where R denotes the gas constant, T is the absolute temperature, and the V° are the molar volumes of the pure reactants. That this is a quantitative statement of Le Chatelier's principle is clear from the fact that if ΔV° is negative, K'_x increases with increasing pressure: and conversely.

More generally, we can allow for the non-ideality of real mixtures and write the complete

* I have taken the liberty of omitting a large number of parenthetical clauses from this passage, without, I hope, altering its general meaning.

equilibrium constant as

$$K_x = \frac{x_L^L x_M^M \dots f_L^L f_M^M \dots}{x_A^A x_B^B \dots f_A^A f_B^B \dots} \quad (5)$$

where the f are activity coefficients on the mole fraction scale, defined to be unity for each species in its pure state. We then find^{5,6)} that

$$\frac{\partial}{\partial P} RT \ln K_x = aV_A^o + bV_B^o + \dots - lV_L^o - mV_M^o - \dots \quad (6)$$

$$= -\Delta V^o \quad (7)$$

where the V^o are the molar volumes of the pure reactants. However, if we adopt Planck's simplifying assumption of ideality and suppose that all the activity coefficients in Eq. (5) are unity, so that K_x is written as K'_x , we find that

$$\frac{\partial}{\partial P} RT \ln K'_x = aV_A^* + bV_B^* + \dots - lV_L^* - mV_M^* - \dots \quad (8)$$

$$= -\Delta V^* \quad (9)$$

where the V^* are now the partial molar volumes of the reactants at their actual concentrations in the equilibrium mixture. In other words, allowance for non-ideality shows that the V^o in Planck's formula (3) should be replaced by V^* .

For reactions in dilute solution, it is convenient to employ concentration units, not of mole fractions, but of molalities m (moles per kilogramme of solvent) and write the molal equilibrium constant as

$$K_m = \frac{m_L^L m_M^M \dots \gamma_L^L \gamma_M^M \dots}{m_A^A m_B^B \dots \gamma_A^A \gamma_B^B \dots} \quad (10)$$

where the γ are molal activity coefficients, defined to approach unity as the total molality of all the solute species approaches zero. We then find^{5,6)} that

$$\frac{\partial}{\partial P} RT \ln K_m = aV_A^\infty + bV_B^\infty + \dots - lV_L^\infty - mV_M^\infty - \dots \quad (11)$$

$$= -\Delta V^\infty \quad (12)$$

where the V^∞ denote the partial molar volumes of the solute species at infinite dilution in the pure solvent [if the solvent, S, itself takes part in the reaction, it contributes a term $sV_S^\infty = sV_S^o$ (V_S^o is the molar volume of the pure solvent)]. If we make the simplifying assumption of ideal solution behaviour, and define K'_m analogously with K'_x by omitting the terms γ from Eq. (10), we find^{5,6)} that

$$\frac{\partial}{\partial P} RT \ln K'_m = aV_A^* + bV_B^* + \dots - lV_L^* - mV_M^* - \dots \quad (13)$$

$$= -\Delta V^* \quad (14)$$

where the V^* are once more the partial molar volumes of the species at the actual concentra-

tion of the equilibrium mixture [cf. Eq. (8)].

Rather regrettably, equilibrium constants are often expressed in molar concentration units (moles per cubic decimetre of solution), which vary with the temperature and pressure, rather than mole fraction or molality units, which are independent of the temperature and pressure. Equilibrium constants K_c of this kind, are defined as

$$K_c = \frac{c_L^l c_M^m \cdots y_L^l y_M^m \cdots}{c_A^a c_B^b \cdots y_A^a y_B^b \cdots} \quad (15)$$

where the c denote molarities and the y are molar scale activity coefficients. Since the c are proportional to x/V and to m/V , where V denotes the total volume of the mixture, it follows from Eqs. (6) and (11) that

$$\frac{\partial}{\partial P} RT \ln K_c = -\Delta V^\infty + (l+m+\cdots - a-b-\cdots) RT \kappa^* \quad (16)$$

where ΔV^∞ is the molar volume change for reaction at infinite dilution, and $\kappa^* [= -(1/V)(\partial V/\partial P)]$ is the isothermal compressibility of the reaction mixture, which in very dilute solutions approaches the compressibility of the solvent κ_s^* . For water at 25°C and atmospheric pressure, the factor $RT\kappa_s^*$ equals 1.12 cm³ mol⁻¹, which is often not negligible in comparison with ΔV^∞ . Omission of the activity coefficients from Eq. (15) gives a relationship

$$\frac{\partial}{\partial P} RT \ln K_c' = -\Delta V^c + (l+m+\cdots - a-b-\cdots) RT \kappa^* \quad (17)$$

where ΔV^c is the partial molar volume change for reaction at the finite concentrations of the reaction mixture.

It is in relation to the term involving the compressibility κ^* in Eqs. (16) and (17) that most of the confusion over Planck's relationship has arisen. Many workers have ignored it*—probably unconsciously—and a few have even advanced fallacious arguments for doing so. For instance, Rice⁷⁾ 'derived' a formula

$$RT \cdot \frac{d \log K_c}{dP} = V_1 - V_2 \quad (18)$$

where $V_2 - V_1$ is the "change of volume due to the reaction". But it is clear that he did so by following a cycle of the kind that G. N. Lewis described as "eccentric and not quite completed", and, as Williams⁸⁾ has shown, by misinterpreting his symbols. An even more specious derivation later appeared in Taylor's *Treatise on Physical Chemistry*,⁹⁾ where the writer's mistakes arose because he supposed that his free energy differential $d\bar{F}$ was equal both to the term on the right hand side of his formula (100) and to that on the right hand side of his (101). In fact, though, it is equal to the *sum* of these two terms, and it is therefore impossible to eliminate it in the way that he did.

* As they have ignored the corresponding term, involving the coefficient of thermal expansion, in the temperature dependence of K_c .

More recently, Marshall¹⁰⁹ has advocated the use, for some kinds of reactions, of an expression for $\partial(RT \ln K)/\partial P$ that involves the compressibility of the solvent κ_s , but *not* the volume change for reaction ΔV ! It is contrary to the laws of thermodynamics¹¹⁻¹³¹ and it does not work in practice.

Finally in this section, it must be mentioned that the molar volumes V^* , V' and V^∞ , that enter into the above relationships, are by no means independent of pressure, and the equations can not be integrated in any general form. The predictive power of thermodynamics is therefore limited to the conditions under which these volumes are known or can be measured easily — which usually mean normal temperature and pressure.

3. Contributions to ΔV for Reactions in Solution

This review is concerned with reactions occurring in molecular solvents in the liquid or dense-gas state (the effect of pressure on reactions in ionic solvents — molten salts — is an interesting¹⁴⁰ but almost unexplored field).

We have seen in Section 2, how the influence of pressure on such reactions is related to the change ΔV that occurs in the total partial molar volumes of the dissolved species when they react. These volumes in turn are related, for each species, to:

- (i) the size of its molecules or ions, that is, to its van der Waals or 'intrinsic' volume,
- (ii) its interaction with the solvent,
- (iii) its interaction with all the solute species, including itself.

The last of these contributions (iii) is unimportant in dilute solutions, and the first (i) is usually defined to be independent of the solvent and concentration (that is almost true of the actual partial molar volumes of organic non-electrolytes).

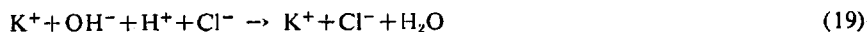
In general, the contribution from (ii) is a complex one, because the solute molecules or ions exert repulsive forces on the solvent molecules at close separations and attractive forces at larger distances, and both these tend to alter the average orientation and packing of the solvent molecules, and hence their average local densities. However, if the solute is ionic rather than molecular, the attractive forces are overwhelmingly dominant. The ions exert very strong electrostatic forces of attraction on the surrounding solvent molecules and pull them in in a manner that 'compresses' them locally to a higher density than they have in the bulk liquid. This contraction of solvent in the fields of the ions is known as *electrostriction*. It is extremely important and is often so large that it completely counterbalances the contribution from (i), of the intrinsic volumes of the ions, so that they actually have net negative partial molar volumes in solution.

The remainder of this article will be concerned with experimental and theoretical aspects of electrostriction and its role in high-pressure chemistry. Most of it will deal with aqueous solutions, but a few non-aqueous ones will be discussed.

4. Early Experimental Evidence of Electrostriction

One of the earliest, and certainly one of the most spectacular, discoveries in solution chemistry was made over 250 years ago, when Emanuel Swedenborg¹⁵⁾ found that the addition of soluble salts to water seemed to cause no increase in its volume. The phenomenon was rediscovered several times in the 18th and 19th centuries and, when John Dalton observed it, he declared it to be "the greatest discovery that I know of next to the atomic theory". It led to a belief that water was 'porous' and could absorb salts like a sponge. However, in 1770, Watson¹⁶⁾ showed that the volume of the liquid did change by a small but measurable amount, and in 1844, Holker¹⁷⁾ demonstrated that the change could actually be negative for some salts [*e. g.*, metal(II) sulphates], so that their solutions occupied less volume than the original water. Such behaviour was in striking contrast to that of organic compounds like alcohol and sugar, whose addition to, and dissolution in, water increased the volume of liquid by roughly the amount of their own volume.

A further important discovery came in 1878, when Ostwald¹⁸⁾ showed that if an aqueous solution of a strong acid was mixed with an equivalent amount of an aqueous solution of a strong base, there was a constant expansion of about $19.5 \text{ cm}^3 \text{ mol}^{-1}$, irrespective of the constitutions of the acid and base. This result became completely understandable a few years later, when Arrhenius advanced his theory of electrolytic dissociation [Arrhenius sent a copy of his doctoral dissertation (Uppsala) to Ostwald at Riga, who later described how he had "got on the same day this dissertation, a toothache, and a nice daughter, and it was too much for one day"]. The theory showed that for the neutralization, say, of potassium hydroxide by hydrochloric acid in water, the reaction is really

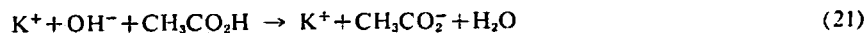


which is equivalent to



and is clearly independent of the composition of the acid and base, provided they are both strong. The observed expansion of about $19.5 \text{ cm}^3 \text{ mol}^{-1}$ meant that the self-ionization of water involved an equal and opposite contraction.

Ostwald also found that if one of the electrolytes was weak, and at a concentration high enough to ensure that it was almost completely unionized, then the volume change was smaller and varied from one electrolyte to another. For example, the neutralizations



occurred with volume changes of $+9.5$ and $-6.6 \text{ cm}^3 \text{ mol}^{-1}$, respectively. Subtracting Eq. (19) from Eq. (21) and from Eq. (22), we find that for the ionization reactions





must involve volume changes of -10.0 and $-26.1 \text{ cm}^3 \text{ mol}^{-1}$, respectively, and in confirmation of this Ostwald showed that the volume change for the mutual neutralization of the two weak electrolytes



was $-16.3 \text{ cm}^3 \text{ mol}^{-1}$, which is very close to the value obtained by summing the changes for reactions (19), (23) and (24). (It should be noted that although subsequent density measurements have shown Ostwald's values to be wrong by a few $\text{cm}^3 \text{ mol}^{-1}$, they have confirmed his general conclusions.)

Much of the subsequent evidence of electrostriction has come from density measurements of the apparent molar volumes and partial molar volumes of salts in solution. Millero¹⁹⁾ has published two excellent reviews of the results, and it will be sufficient here to cite just a few early examples that are fairly typical of the behaviour of salts in general.

In 1916, Horiba¹⁾ found that the apparent molar volumes of NaCl, KCl and NH_4Cl in water increased with increasing concentration of salt between 0 and 4 mol kg^{-1} , and with increasing temperature between 0 and 50°C , whereas the apparent molar volume of the solvent water decreased with increasing salt concentration. His results for NH_4Cl were later used by Fajans and Johnson²⁰⁾ in their attempt to separate the contributions of cation and anion volumes.

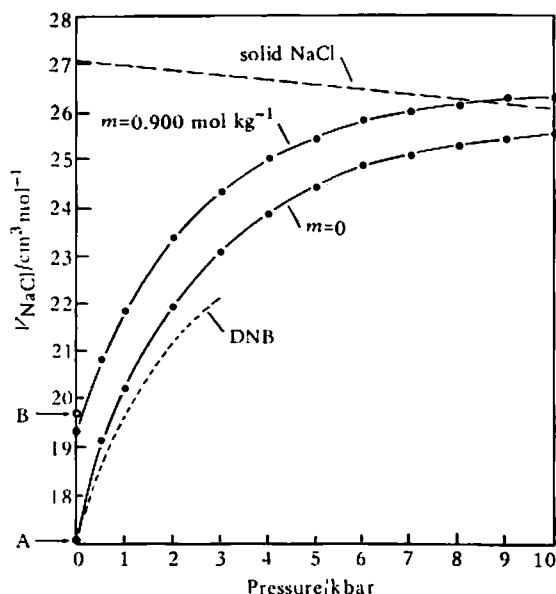


Fig. 1. The partial molar volume V_{NaCl} of NaCl in water at 25°C and (experimental points from Adams²¹⁾). The curve marked DNB was calculated from the Drude-Nernst-Born model for $m=0$ (see p. 156). The point B is a theoretical value for $m=0.900 \text{ mol kg}^{-1}$ at atmospheric pressure, calculated from the value A for $m=0$ using the Debye-Hückel relationship (34).

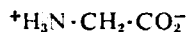
Adams²¹⁾ (who was apparently unaware of Horiba's work) confirmed his results for NaCl at 25°C, and also showed that the partial molar volume V_{NaCl} of the salt *increased* with increasing pressure — a surprising result which, as it turns out, is only explicable in terms of electrostriction of the solvent (see Section 5). Some of Adams's results are shown in Fig. 1, where it will be seen that V_{NaCl} was initially about 10 cm³ mol⁻¹ less than the molar volume of the solid salt, but that it approached that volume at about 10 kbar. At concentrations greater than $m=3$ mol kg⁻¹, the value of V_{NaCl} began to decrease when the pressure was raised above 8 kbar.

In non-aqueous systems, Butler *et al.*²²⁾ observed, in the early 1930's that the partial molar volumes of salts are very much smaller in aliphatic alcohols than in water, a fact which they correctly attributed to the greater electrostriction of the alcohols*. They also found that the apparent molar volumes ϕ increased more rapidly with increasing concentration than they did in water, although they all obeyed the simple relationship

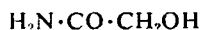
$$\phi = \phi^\infty + ac^{1/2} \quad (26)$$

where c was the molar concentration of salt and the factor a was about six times larger than for water. Later work showed that this kind of behaviour is true in general of salts in organic solvents.

A rather direct estimation of the volume change involved in electrostriction, not around free ions but around *zwitterions* (dipolar ions), was made in about 1935 by Cohn, Edsall and McMeekin,²³⁾ who found that the amino acid, glycine



had an apparent molar volume of 43.5 cm³ mol⁻¹ in water at 25°C, whereas the corresponding volume of the isomeric, unionized compound, glycolamide



was 56.2 cm³ mol⁻¹. They argued, from Traube's rules, that in the absence of electrostriction the two volumes would have been nearly equal, and that the difference of -12.7 cm³ mol⁻¹ represented the electrostrictive contraction that occurred around the ionized isomer. They also showed that the contraction increased as the distance between the two charged groups increased in the higher amino acids.

5. Theories of Electrostriction

In 1872, Favre and Valson²⁴⁾, who were the first to observe additivity relationships for the

* A simple and direct demonstration of this difference can be carried out by adding some solid NaOH to two standard flasks, one containing water and the other methanol. The solid initially increases the volume of each mixture, but as it dissolves, the aqueous solution returns to about the volume of the original water, whereas the methanol solution shrinks to considerably less than the original volume of methanol.

apparent molar volumes of related salts, suggested that the volume change that occurs when a salt is dissolved in water is the result of two competing effects: (i), a contraction of the water under the influence of the solute, and (ii), an increase in the volume of the salt due to "the more or less advanced dissociation of its constituent elements". The first effect is what we now refer to as electrostriction, and the second is probably to be likened to the expansion that occurs when a salt melts.

In 1893, Tammann²⁵⁾ pointed out that the effects of strong electrolytes on the physical properties of water were similar to those of an applied hydrostatic pressure, and inferred from this the existence of a high uniform, "internal pressure" (*Binnedruck*) in such solutions, produced by the attraction of water molecules by the dissolved ions. But he had no quantitative theory of the pressure, nor of the volume compression associated with it.

However, in the following year, Drude and Nernst²⁶⁾ developed a sound electrostatic theory of the contraction of solvent around an ion. Their treatment assumed the solvent to be a continuum of dielectric constant ϵ and the ion to be a hard sphere of radius r and of charge z^+e , e being the charge on a proton and z being an integral number. It yielded an expression for the electrostatic change of volume, per ion, of the form

$$V_{el} = -\frac{V\kappa_s z^2 e^2}{2r\epsilon^2} - \frac{\partial \epsilon}{\partial V} \quad (27)$$

or its equivalent

$$V_{el} = -\frac{z^2 e^2}{2r\epsilon^2} - \frac{\partial \epsilon}{\partial P} \quad (28)$$

where V denotes the volume of solvent, κ_s is its compressibility and P is the pressure. The contraction for a mole of ions V_{el} is, of course, given by multiplying V_{el} by the Avogadro constant N . It is interesting that the assumptions and approximations that underlie Eqs. (27) and (28) are precisely those that Born²⁷⁾ used many years later in deriving his well-known formula for the molar free energy of hydration of ions

$$G_{el} = -\frac{Nz^2 e^2}{2r} \left(1 - \frac{1}{\epsilon}\right) \quad (29)$$

Indeed, Krichevskii²⁸⁾ rediscovered Eq. (28) in 1938 by differentiating Born's formula for G_{el} with respect to pressure. A later treatment by Buchanan and Hamann^{29,30)} allowed for the pressure dependence of r and gave, in place of Eq. (28), the expression

$$V_{el} = -\frac{Nz^2 e^2}{2r\epsilon^2} - \frac{\partial \epsilon}{\partial P} + \frac{Nz^2 e^2}{2r^2} \left(1 - \frac{1}{\epsilon}\right) \frac{\partial r}{\partial P} \quad (30)$$

Although more refined treatments of electrostriction have been developed³¹⁾, it remains a fact that the simple Drude-Nernst-Born (DNB) model works surprisingly well — perhaps better than it should. As Friedman and Krishnan³²⁾ have remarked

"The Born model is so simple and the results obtained with it so promising that there

have been a great many efforts to refine it. The general conclusion is that it is hard to improve on the Born model for estimating the part of the solvation energetics that is peculiar to ionic solutes".

Qualitatively, it will be seen that the DNB model predicts (i), that the electrostriction $-V_{el}$ should be proportional to the square of the charge ze on the ions, and this is borne out by the very negative partial molar volumes of multiply-charged ions¹⁹, (ii), that it is inversely proportional to the ionic radius r , which Hepler³³ found to be the case for many ions, and (iii), that it increases in proportion to the value of the derivative $\epsilon^{-2}\partial\epsilon/\partial P$, which, in turn, increases in going from water to organic solvents⁶:

	water	methanol	ethanol	acetone
$10^7 \times \epsilon^{-2}\partial\epsilon/\partial P(\text{bar}^{-1})$ at 25°C and 1 bar	6.01	32.4	37.6	69.1

This explains the experimental results of Butler *et al.*²² (referred to in Section 4), for the partial molar volumes of ions in alcohols. A statement by Kauzmann *et al.*³⁴, that "electrostriction would be much reduced" in a "non-aqueous environment", is wrong, both in theory and fact.

Quantitatively, the model yields values of about $-20 \text{ cm}^3 \text{ mol}^{-1}$ for the two ions of a 1:1 electrolyte in water at 25°C and atmospheric pressure^{6,30}. This is certainly of the same order as the experimental values of $V^\infty - V_{in}$ for the alkali halides if we take the 'intrinsic' volume V_{in} to be the extrapolated volumes of the liquid salts. It is also of an appropriate magnitude to explain the volume changes that Ostwald¹⁸ found for ionization reactions in water, and that Cohn *et al.*²³ found for the electrostriction of *zwitterions* (see Section 4).

A particular advantage of the DNB model is that it allows us to make at least rough predictions of the influence of pressure and temperature on the electrostatic part of the free energy of ions, and if this is dominant in a system, to make some guess as to the behaviour of the system under pressure. As an example of its usefulness, we may consider the results that Adams²¹ obtained for the partial molar volume V_{NaCl} of NaCl in water under pressure, and which are shown in Fig. 1. Adams commented on "the astonishing fact that V_{NaCl} increases with increasing pressure except at the highest pressures and in the most concentrated solutions". But, a few years later Krichevskii²⁸ pointed out that this trend is just what we should expect from the fact that the term $\epsilon^{-2}\partial\epsilon/\partial P$ in Eq. (28) decreases with increasing pressure. Krichevskii did not consider the pressure dependence of the term $1/r$, but this, also, contributes to the increase of V_{el} with increasing pressure, and a calculation based on formula (30) [see Ref. (30), p. 56] yields the curve labelled DNB in Fig. 1, which has been drawn to pass through the experimental value of V_{NaCl} at zero pressure and concentration. It gives quite a good representation of the experimental trend.

An alternative, and more or less equivalent, way of viewing the increase of V_{NaCl} with increasing pressure is to consider that an applied pressure reduces the compressibility of the solvent κ_s and so reduces any contraction induced by the electric fields of the ions. In this

connection, Hamann and Lim³⁵⁾ observed that the partial molar volumes of salts in water and organic solvents were inversely proportional to the values of ϵ_s . Gases are, of course, very much compressible than liquids and it is therefore not surprising that Benson *et al.*³⁶⁾ found some extraordinarily negative partial molar volumes for NaCl in water above its critical point — of the order of $-10^3 \text{ cm}^3 \text{ mol}^{-1}$ at 390°C and a density of 0.45 g cm^{-3} (the initial increase of V_{NaCl} which Horiba¹⁾ observed between 0 and 50°C , reverses at about 60°C : it is, incidentally, a minor failing of the DNB model that although it correctly predicts the high-temperature decrease, it does not explain the low-temperature increase of V_{NaCl}).

The DNB model is concerned only with solute-solvent interactions and therefore strictly applies only at infinite dilution. The solute-solute interactions that become important at higher concentrations are described by the analogous continuum theory of Debye and Hückel (DH), which gives the following limiting relationship for the mean molal activity coefficient γ_{\pm} of a 1:1 salt at fairly low molalities m

$$-\log_{10} \gamma_{\pm} = Am^{1/2} \rho^{1/2} \quad (31)$$

where ρ denotes the density of the solvent and A is the usual DH parameter, containing the dielectric constant of the solvent as a factor $\epsilon^{-3/2}$. The difference between the partial molar volume V' of the two ions at the molality m and that at infinite dilution V^∞ is given by

$$V' - V^\infty = 2 \frac{\partial}{\partial P} \frac{RT \ln \gamma_{\pm}}{\rho} \quad (32)$$

and carrying out this differentiation of Eq. (31), we find that

$$V' - V^\infty = 2 RT A \left(\ln 10 \right) \left(\frac{3}{2} \frac{\partial \ln \epsilon}{\partial P} - \frac{1}{2} \frac{\partial \ln \rho}{\partial P} \right) m^{1/2} \rho^{1/2} \quad (33)$$

which, for water at 25°C and atmospheric pressure, gives

$$V' - V^\infty = 2.79 m^{1/2} \rho^{1/2} \quad (34)$$

where $V' - V^\infty$ is in $\text{cm}^3 \text{ mol}^{-1}$ if m is in mol kg^{-1} and ρ is in g cm^{-3} . We might expect Eq. (34) to be limited in its usefulness to the range of concentrations in which the DH limiting law (31) applies, that is, to the range below $m=0.05 \text{ mol kg}^{-1}$, where the limiting law values of $\log_{10} \gamma_{\pm}$ are already about 30% too high. However, it turns out that Eq. (34) applies quite well at much higher concentrations than that³⁷⁾: for example, it predicts that between $m=0$ and $m=0.900 \text{ mol kg}^{-1}$, the value of V_{NaCl} in water at 25°C and atmospheric pressure should increase from 17.03 to $19.68 \text{ cm}^3 \text{ mol}^{-1}$ (from A to B in Fig. 1), which is within 17% of the change that Adams²¹⁾ found experimentally. It is wrong by only 6% at $m=5.703 \text{ mol kg}^{-1}$. Also, Butler *et al.*²²⁾ showed that it satisfactorily explained their experimental finding that the apparent molar volumes of salts in alcohol solutions increased much more rapidly with increasing concentration than they did in water, and that they obeyed the square root relationship (26) with a factor a that was greater than that for water by about the theoretical DH amount.

By analogy with the simple picture of the influence of pressure that was offered in the

paragraph before last, it could be argued that the electric field of the ions in concentrated solutions also acts to reduce the compressibility of the solvent — which is essentially Tammann's hypothesis.²⁵⁾

The theories discussed above have assumed the solvent to be a dielectric continuum and, in spite of that gross simplification, they have worked surprisingly well. But ultimately they will be supplanted by treatments that take proper account of the molecular and atomic structures of the solvent and solute. These will be, not so much theories, as simulations of the behaviour of systems of molecules and ions by means of computers. There are two distinct methods of approach to this kind of calculation. The *Monte Carlo* (MC) method generates a large number of configurations of the molecules and ions, subject to their interaction by appropriate interparticle potentials, by random displacements at a fixed temperature and density. Quantities like the energy, pressure and radial distribution function are then derived as averages over all configurations in the sequence. In the *Molecular Dynamics* (MD) technique, the classical equations of motion of the molecules and ions are solved by step-by-step methods at a fixed total energy and density, and the other thermodynamic properties are then estimated as averages over time rather than configurations.

A start has recently been made on simulations of ionic solutions by both methods. Watts and his co-workers³⁸⁾ have carried out MC simulations for a number of aqueous solutions, and Heinzinger and his colleagues³⁹⁾ have made similar calculations by the MD method. Although neither group has explicitly derived or discussed the extent of electrostriction of water around the ions, information on this *is* contained in their calculated plots of the average number of water molecules within particular distances from the centre of an ion. Both the MC and MD results show that, for the alkali halides at normal temperature and pressure, the first hydration shell (as defined by Heinzinger and Vogel⁴⁰⁾) contains 1-2 more water molecules than it would if it had the normal density of water, although this rather large contraction is partly counterbalanced by the lower density of the next shell.

Some particularly interesting calculations are those of Watts *et al.*⁴¹⁾ for Li^+F^- ion-pairs at 500 K, but at a low average water density of 0.125 g cm^{-3} , corresponding to a pressure of about

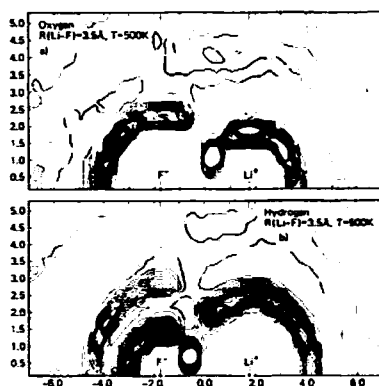


Fig. 2 Calculated (Monte Carlo) densities of O and H atoms of H_2O molecules in the neighbourhood of an Li^+F^- ion-pair (solvent separated) at 500 K and an average water density of 0.125 g cm^{-3} (from Watts *et al.*⁴¹⁾). The numbers on the axes indicate distances in Å from the midpoint between the ions.

200 bar for supersaturated water vapour. The results, based on the use of Hartree-Fock interaction potentials, are shown in Fig. 2 in the form of plots of the density of oxygen and hydrogen atoms around the ions. It will be seen that, in spite of the fairly high temperature and low pressure, a substantial amount of electrostrictive 'condensation' of water has occurred around the ions. There are about ten water molecules within a radius of 5 Å from the centre of each ion, and this 'condensation' corresponds to a contraction of the water at constant pressure by an amount of about -1500 cm^3 per mole of Li^+F^- . It explains the fact that contractions of that order occur when salts dissolve in supercritical water at fairly low pressures.³⁶⁾

6. Chemical Equilibria at High Pressures

6-1. Ionization of weak electrolytes

It will be apparent from the brief history in Sections 2 and 4 that, by the early 1890's the combined thermodynamic contributions of Ostwald, Arrhenius and Planck had led to a clear conclusion that an applied pressure should increase the degree of ionization of a weak electrolyte in solution, and had indicated the extent of that change. And Drude and Nernst had provided a fundamental explanation of the effect in terms of the electrostriction of solvent around the ions that are formed by the electrolytic dissociation of a neutral molecule*.

Soon afterwards, at Arrhenius's suggestion, the pressure effect was observed directly by his student Fanjung,⁴²⁾ who measured the electrical conductivities of aqueous solutions of both strong and weak electrolytes at applied pressures up to 264 bar. Fanjung found that the conductivities of weak carboxylic acids increased much more rapidly with increasing pressure than did those of salts and, from this, he was able to conclude that the molar ionization constants of the acids K'_i increased by an average of 12% between 0 and 264 bar. For acetic acid, the change corresponded to $\partial RT \ln K'_i / \partial P = 10.6 \text{ cm}^3 \text{ mol}^{-1}$, and it follows from formula (17) that $\Delta V^\circ = -9.5 \text{ cm}^3 \text{ mol}^{-1}$, which is quite close to the volume change that Ostwald had estimated from dilatometric data at atmospheric pressure [see under formula (23)].

That pioneering work was followed by some rather more extensive conductivity measurements by Tammann and his colleagues, at pressures up to 3 kbar. The results, which were reviewed by Brander in 1932,⁴³⁾ confirmed Fanjung's observation of a general increase of K'_i for weak electrolytes with increasing pressure, but showed that over the wider experimental pressure range, $\ln K'_i$ was not a simple linear function of the pressure. Instead, $|\Delta V^\circ|$, defined by Eq. (17), decreased steadily — by about 40% between 0 and 3 kbar for weak acids in water.

More recently, since about 1950, there has been a great acceleration of work on this subject

* It is worth noting that Ostwald, Arrhenius, Planck and Nernst all subsequently received Nobel Prizes, as did Born.

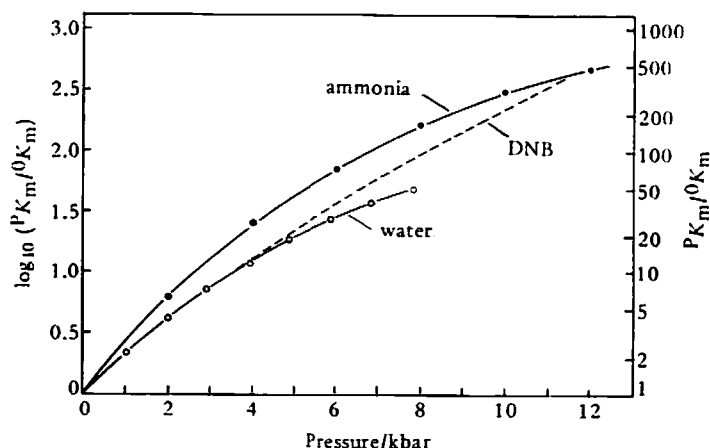


Fig. 3. The effect of pressure on the ionization constant of ammonia in water at 45°C and on the self-ionization constant of water at 25°C. $^P K_m$ is the value of the molal ionization constant at the pressure P and $^0 K_m$ is the value at atmospheric pressure. The curve marked DNB was calculated for the Drude-Nernst-Born model.

and several hundred systems, aqueous and non-aqueous, have now been studied, by a variety of experimental methods: conductimetric, potentiometric and spectroscopic. The methods and results have been fully described and discussed in a review covering work up to 1973⁶⁾ and in a supplementary listing for the years 1973-77⁴¹⁾. Without exception, the results show that the dissociation of ground-state neutral molecules into ions in solution involves a contraction and is favoured by raising the pressure — to the highest pressures that have been reached.

Fig. 3 gives a couple of examples of this general behaviour. It shows the influence of pressure on the molal ionization constant K_m of ammonia in water at 45°C, measured conductimetrically, and on the self-ionization constant of water, measured potentiometrically with a glass electrode⁴⁵⁾. It will be seen that the curves rise continuously, and that a pressure of 12 kbar increases K_m for ammonia by a factor of about 500. The dashed curve DNB represents the result of an attempt to estimate the contribution of electrostriction to the pressure effect. It was calculated³⁰⁾ by applying the Born formula for the free energy of hydration (29) to a pair of small ions, and allowing for the influence of pressure on ϵ and r . It gives at least a qualitative description of the behaviour of the actual weak electrolytes to quite high pressures, as it did also of the behaviour of V_{NaCl} in Fig. 1.

Another, similar, test of the Drude-Nernst-Born model is to see how well it describes the initial pressure-dependence of the standard partial molar volume change ΔV^∞ for the ionization of weak electrolytes. This is often represented by a 'partial molar compressibility' $\Delta \kappa^\infty$, defined as

$$-\Delta \kappa^\infty = \frac{\partial \Delta V^\infty}{\partial P} \quad (35)$$

Table 1.

	$\Delta V^\infty/\text{cm}^3 \text{ mol}^{-1}$ at 25°C and 1 bar	
	water	methanol
phenol	-18.4	-38.5
4-nitrophenol	-10.0	-31.7
picric acid	-10.0	-25
piperidine	-26.8	-53
pyridine	-24.2	-49

If we apply this differentiation to the DNB electrostrictive volume V_{el} [formula (30)], and neglect the pressure-dependence of r , we find the following simple relationship⁶⁾

$$\kappa_{el} = V_{el} \times 1.99 \times 10^{-4} \text{ bar}^{-1} \quad (36)$$

for ions in water at 25°C and atmospheric pressure. Empirically, Lown *et al.*⁴⁶⁾ have observed that a relationship of this kind holds between $\Delta \kappa^\infty$ and ΔV^∞ for the ionization of acetic acid in water, with a proportionality constant of $2.13 \times 10^{-4} \text{ bar}^{-1}$.

The DNB formulae for electrostriction contain the derivative $\epsilon^{-2} \partial \epsilon / \partial P$, which varies considerably from one solvent to another, and has the values listed in Sections 5 for a few common liquids. It is several times greater for methanol than for water and for that reason we might expect that ΔV^∞ for ionization reactions would be more negative and the pressure effects larger for solutions in methanol than for ones in water. That prediction is borne out by the experimental values of ΔV^∞ for the two solvents, listed in Table 1. It is also borne out by the recent measurements of Inoue *et al.*⁴⁷⁾, which show that the ionization constant of trimethylamine in methanol at 25°C is increased by a factor of 11.8 between 0 and 2 kbar, whereas Hamann and Strauss⁴⁸⁾ found that the corresponding factor for water is 6.8. These results are, of course, consistent with the data of Butler *et al.*²²⁾ for the partial molar volumes of salts in alcoholic solutions.

The DNB equations also contain the radius r of the ions (or, more appropriately in a polyatomic ion, the radius of the particular atom or group that carries the bulk of the electric charge) in the denominator, so that ΔV^∞ should be less negative and the pressure dependence of K_∞ correspondingly less for electrolytes that form large ions than for ones that form small ones. This could explain why the first ionization constant of H_2S in water increases by a factor of 2.8 between 0 and 2 kbar, whereas that of H_2O increases by a factor of 4.2.⁶⁾ However, the effect does not always appear where it might be expected: for example it is not apparent in the series of methylamines from ammonia to trimethylamine⁶⁾. There are evidently more subtle structural effects operating here than can be handled by a simple continuum theory.

An effect which is similar to that of ion size arises from charge delocalization in ions. The carboxylic acids provide examples of this effect. If the negative charge in a carboxylate ion were located on one of the two oxygen atoms, it would be expected that ΔV^∞ for the ionization

of these acids would be close to the values for water and phenol, but in fact it is only half those.⁶⁾ The reason is that the charge is distributed equally between the two oxygen atoms, and the effective radius of the charged group is larger than if the charge were wholly on one atom. Other clear examples of the effect are to be seen in the ionization of substituted phenols and benzoic acids containing electron-withdrawing groups. Hamann and Linton⁴⁹⁾ showed, on the basis of Eucken's electrostatic model, that the following relationship should theoretically exist between the ΔV^∞ for substituted and unsubstituted compounds:

$$\Delta V_{\text{sub}}^\infty - \Delta V_{\text{unsub}}^\infty = -2.69(pK_{\text{sub}} - pK_{\text{unsub}}) \text{ cm}^3 \text{ mol}^{-1} \quad (37)$$

for water at 25°C and atmospheric pressure. They found that it did, indeed, describe the high-pressure behaviour of this class of compounds very well.

An alternative way of viewing charge delocalization is to split the electrostriction into parts arising from separated partial charges which act independently on their surroundings. If, in the case of carboxylate ions, it were supposed that each oxygen atom carried half the total negative charge, the electrostrictive effect would be the sum of two terms containing $\epsilon^2/4$, that is, it would be proportional to $\epsilon^2/2$ instead of ϵ^2 , as it would if all the charge were on one atom. This approach is particularly appropriate when the charged centres are a large distance apart.

To conclude this sub-section it should be emphasized that the increase of ionization with increasing pressure is universal and continuous: there is no reason, either theoretical or experimental, to suppose that it may ever stop or reverse. We can confidently expect that all weak electrolytes will become strong if their solutions are compressed sufficiently. Of course, there is a practical problem in doing that, because solvents freeze under isothermal compression and it is necessary to heat them in order to keep them liquid. The most extreme experiments of this kind have been concerned with the self-ionization of water, which has been measured,⁵⁰⁾ conductimetrically in shock-wave compression, to a maximum pressure, temperature and density of 133 kbar, 800°C and 1.73 g cm⁻³, respectively. Under those conditions, the ionic product $(K_w')_\infty = m_{\text{H}^+} m_{\text{OH}^-}$ is 0.089 mol² kg⁻², which is about 10¹³ times greater than its normal value! There is little doubt that at not much higher pressures and temperatures, water becomes fully ionized into H₃O⁺ and OH⁻ ions.^{6,50)} It is then essentially a molten salt, iso-electronic with NH₄F and NaOH. On the theoretical side, it would be very interesting to see whether a computer simulation of water based on Stillinger and David's 'polarization' molecular model⁵¹⁾, which is capable of ionizing, would predict a high degree of ionization in the P - V - T region where it appears to occur experimentally.

6-2. Ionization of charged molecules

The presence of the factor $z^2\epsilon^2$ in the DNB expressions for electrostriction means that the successive ionization steps of a polybasic acid should involve increasingly large decreases in volume and correspondingly greater pressure-induced increases of ionization. This effect is to

be seen in Tables 17 and 18 of reference (6), for example in the data for phosphoric, oxalic, maleic and citric acids and for the base ethylenediamine.

Bjerrum⁵²⁾ proposed a simple electrostatic model for the ionization of polybasic acids which is appropriate when the ionizing groups are structurally identical and which gives the following relationship between the first and second ionization constants K_1 and K_2 of a dibasic acid

$$K_1/K_2 = 4 \exp(e^2/\epsilon a k T) \quad (38)$$

or

$$\ln K_1 - \ln K_2 - \ln 4 = e^2/\epsilon a k T \quad (39)$$

where 4 is a statistical factor (which becomes 3 for a tribasic acid) and the term $e^2/\epsilon a$ is the electrostatic free energy change involved in bringing a second negative charge e from infinity to a distance a from the first charge in the molecule; a is the distance between the two ionizing groups, ϵ is the dielectric constant of the solvent, k is Boltzmann's constant and T is the absolute temperature. To apply Bjerrum's model to pressure effects, we can differentiate Eq. (39) with respect to pressure, assuming that a is independent of pressure, to obtain

$$J V_1^\infty - J V_2^\infty = RT(\ln 10)(pK_2 - pK_1 - \log_{10} 4) \partial(\ln \epsilon)/\partial P \quad (40)$$

Inserting the value of $\partial(\ln \epsilon)/\partial P$ for water at 25°C and atmospheric pressure then gives the result

$$J V_1^\infty - J V_2^\infty = 2.69(pK_2 - pK_1 - \log_{10} 4) \text{ cm}^3 \text{ mol}^{-1} \quad (41)$$

[cf. Eq. (37)], which suggests that $J V_2^\infty$ should be more negative than $J V_1^\infty$ by an amount which is proportional to the difference in the two pK values for the acid. This turns out to be more or less true in practice,⁶⁾ with the correct proportionality factor.

6-3. Dissociation of associated ions

The general effects of compression on the dissociation of ion pairs and ion complexes are of the type to be expected from simple considerations of changes in electrostriction. The separation of two oppositely charged ions in solution involves an increase in the total external field strength and in the electrostriction of solvent, and so is favoured by an increase of pressure. The first evidence of such a change is to be found in the early measurements of Fink,⁵³⁾ in 1885, which showed that the electrical conductances of aqueous solutions of ZnSO_4 increased almost twice as rapidly with increasing pressure as did the conductances of NaCl and HCl solutions. Fink's results were later confirmed by Körber⁵⁴⁾ and subsequently interpreted by Tammann and Rohmann⁵⁵⁾ as implying an increase in the dissociation of ZnSO_4 , consistent with a volume change $\Delta V = -8.2 \text{ cm}^3 \text{ mol}^{-1}$. More recent work has shown that the magnitude of the effect can shed light on the question of whether a particular ion-pair is of the 'solvent separated' or 'contact' type.⁶⁾

The experimental results can be understood quantitatively in terms of Fuoss's⁵⁶⁾ theory of ion-pairing reactions. Assuming that ions of opposite charges $z_1 e$ and $z_2 e$ can be considered

to form ion-pairs when they come within a contact distance a of each other. Fuoss derived the dissociation constant for ion-pairs in the form

$$K_m = 3000[\exp(z_1 z_2 e^2 / a \epsilon k T)] / 4 \pi \rho N a^3 \quad (42)$$

where ρ denotes the density of the solvent and the other symbols have the same meanings as in earlier parts of this paper. If it be assumed that a is independent of the pressure, the pressure effect can be derived in the form

$$-\frac{\partial RT \ln K_m}{\partial P} = \Delta V^\infty = \frac{\partial RT \ln \rho}{\partial P} + \frac{z_1 z_2 e^2 N}{a \epsilon^2} \frac{\partial \epsilon}{\partial P} \quad (43)$$

and for water at 25°C and atmospheric pressure, this gives

$$\Delta V^\infty = 1.12 + 8.35 z_1 z_2 / a(\text{\AA}) \text{ cm}^3 \text{ mol}^{-1} \quad (44)$$

There is no *a priori* way of determining the parameter a , but if it is derived by applying Eq. (42) to a measured value of K_m at atmospheric pressure, then Eqs. (42) and (43) can be used to predict the influence of pressure on the equilibrium. It turns out that they do so with remarkable accuracy. Hamann *et al.*⁵⁷⁾ used Eq. (44) to calculate the values $\Delta V^\infty = -7.4$ and $-9.0 \text{ cm}^3 \text{ mol}^{-1}$ for ion-pairs of $\text{Mg}^{2+}\text{SO}_4^{2-}$ and $\text{La}^{3+}\text{Fe}(\text{CN})_6^{3-}$, respectively, in water at 25°C and 1 bar: the experimental values⁵⁷⁾ are -7.3 and $-8.0 \text{ cm}^3 \text{ mol}^{-1}$. Moreover, as Fig. 4 shows, Eq. (42) gives a good description of the behaviour of K_m for $\text{La}^{3+}\text{Fe}(\text{CN})_6^{3-}$ at high pressures, to at least 2 kbar.

In view of this success of Eq. (42) at normal temperature, it is interesting to see whether it can explain some of the high-temperature, high-pressure (but relatively low-density) results of Franck⁵⁸⁾ and Quist and Marshall.⁵⁹⁾ These authors, respectively, measured the molar dissociation constants K_c of Li^+Cl^- and Na^+Cl^- in water above its critical temperature. Their results are plotted as the solid curves in Fig. 5, together with dashed curves predicted by Fuoss's formula (42) [a has been adjusted to fit the lowest-density values of K_c ; ϵ has been taken from the tables of Helgeson and Kirkham,⁶⁰⁾ and ρ has been omitted from Eq. (42)

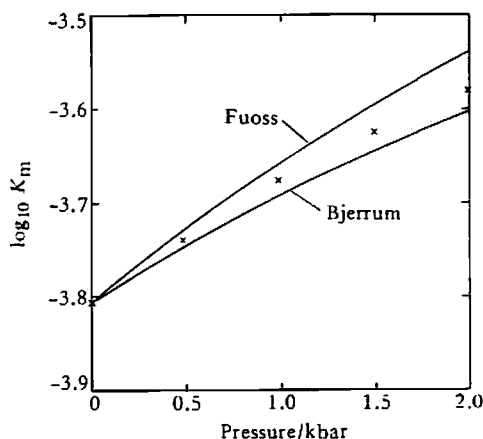


Fig. 4. The molal dissociation constant of ion-pairs of $\text{La}^{3+}\text{Fe}(\text{CN})_6^{3-}$ in water at 25°C. The crosses are experimental points.⁵⁷⁾ The curve marked Fuoss was calculated from formula (42); the curve marked Bjerrum is discussed in Ref. (57).

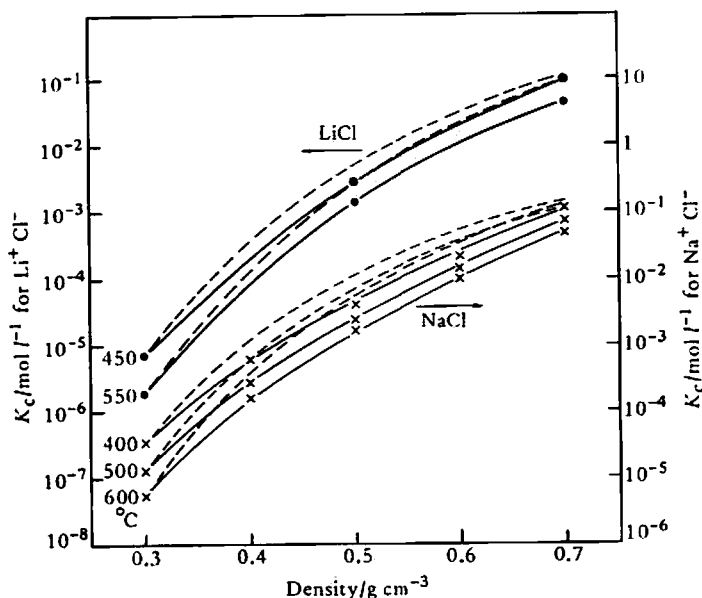


Fig. 5. The molar dissociation constants K_c of ion-pairs of Li^+Cl^- ⁵⁶⁾ and Na^+Cl^- ⁵⁹⁾ at high temperatures and pressures. The dashed curves are given by formula (42).

to convert K_m to K_c]. The agreement is quite surprisingly good.

7. Chemical Reaction Rates at High Pressures

One of the most important advances in the theory of chemical reaction rates was made in 1935, when Eyring, in the U. S. A. and Evans and Polanyi, in England, independently developed the 'activated complex' or 'transition state' theory. This provided, for the first time, a quasi-thermodynamic method of viewing reaction rates (the qualification 'quasi-' is important but is often forgotten). The theory supposes that, in a particular reaction, a state of chemical equilibrium exists between the initial reacting species and the transition state species and that the rate of reaction is governed by the difference in free energy between these two states.

In the present context, it is very interesting to find that Evans and Polanyi⁶¹⁾ began their first paper on the new theory with the sentence "One of the main objects of this discussion will be to consider the influence of pressure on the velocity of chemical reactions in solution". They then proceeded to derive the familiar relationship

$$\frac{\partial}{\partial P} RT \ln k = -\Delta V^\ddagger \quad (45)$$

where k denotes the reaction rate constant and ΔV^\ddagger is the molar volume change that occurs when the molecules pass from their initial state into the transition state. Evans and Polanyi⁶¹⁾ further suggested that this volume change is made up of two factors: $\Delta_1 V^\ddagger$, arising from

changes in the reacting molecules themselves, and J_2V^* , arising from interactions between the reacting molecules and the surrounding solvent. They clearly meant J_2V^* to include electrostrictive effects, because they referred to a possible contribution from the "process of desolvation of an ion reacting with an organic molecule". However, although they discussed the Menshutkin reaction of ethyl iodide with pyridine to form ethylpyridinium iodide



— a reaction which is considerably accelerated under pressure — they surprisingly made no mention of electrostriction as a factor contributing to the acceleration. Maybe this was because they seem to have thought the product to be covalent rather than ionic, for they wrote it as



A few years later, Stearn and Eyring⁶²⁾ also considered the influence of pressure on the rates of Menshutkin reactions in solution, but again they ignored electrostriction.

Perhaps the first clear evidence of the importance of electrostriction (and of the J_2V^* term) in determining the behaviour of reaction rates under pressure came from some experiments in 1953²⁹⁾ concerning the unimolecular, S_N1 , solvolysis of *tert*-butyl chloride in 80/20 ethanol/water solution at 25°C. This reaction proceeds through a slow step which involves the stretching, and ultimate heterolytic breaking, of the C-Cl bond to form a carbonium ion:

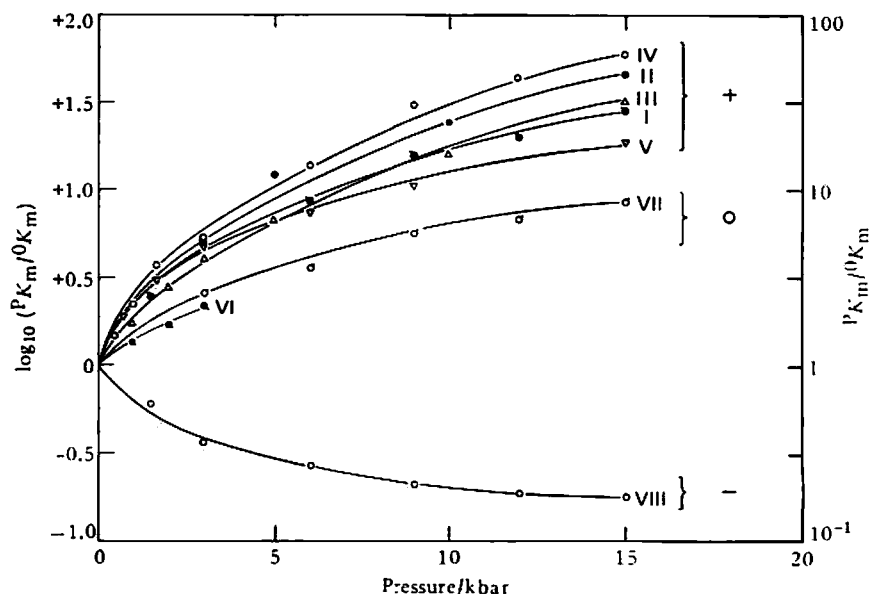
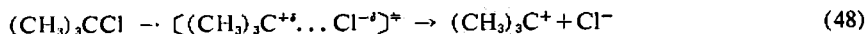


Fig. 6 The influence of pressure on some chemical reaction rates.⁶³⁾ The details of the reactions I-VIII are given in Table 2 of Ref. (63). The signs +, 0, and - indicate that they were accompanied by an increase, no change, and a decrease, respectively, in the number of ionic charges.



The bond-stretching that occurs in forming the transition state means that J_1V^* is positive (of the order of $+6 \text{ cm}^3 \text{ mol}^{-1,30})$ and if it were the only significant term in JV^* , the reaction would be retarded by an increase of pressure. The experiments showed that the reaction is actually accelerated to an extent that suggests that J_2V^* must be about $-25 \text{ cm}^3 \text{ mol}^{-1,30})$ which is of the same order as the electrostriction around free ions, and indicates that the charges may be almost fully developed in the transition state.

The clear predominance of the electrostrictive effect in the above reaction, and others, including Menshutkin reactions, led to a suggestion^{29,43)} that electrostriction might often be the determining factor in high-pressure reaction kinetics — at least for those reactions that involve the formation or removal of electrical charges. That view was soon supported by the experimental results that are shown in Fig. 6, where the signs +, 0 and — indicate that the reactions were accompanied by an increase, no change, and a decrease, respectively, in the number of ionic charges. Since that time, many hundreds of reaction rates have been measured under pressure⁴⁴⁾ and, although a few exceptions may have been found to this simple principle, it seems to remain a rather useful one.

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