

Some Quantitative Relationships for Ionization Reactions at High Pressures

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Abstract

A simple formula is proposed to describe the pressure dependence of the variable Φ in El'yanov and Gonikberg's linear free energy relationship for ionization reactions in solution at high pressure.

The expression, given in equations (10) and (12), provides a good description of the influence of pressure on ionization equilibria in aqueous solutions. It permits El'yanov's general linear relationships between Φ and ionization free energies, enthalpies and entropies, pH and Hammett's ρ parameter, to be expressed in terms of the pressure in convenient analytical forms.

The formula is shown to be consistent with the simple electrostatic theory of ion hydration, allowing for the effect of pressure on the dielectric constant of water. Combined with the theory, it provides a general means of predicting ionization constants over a wide range of pressures and temperatures simply from knowledge of the changes in molar volume, enthalpy and entropy which accompany the reactions at atmospheric pressure.

Introduction

The thermodynamic relationship¹ which expresses the influence of pressure P on the molal ionization constant K of a weak electrolyte in solution is

$$\partial RT \ln K / \partial P = -\Delta V \quad (1)$$

where ΔV denotes the molar volume change accompanying the reaction (if K is the 'thermodynamic' ionization constant expressed as a product of activities, ΔV is then the volume change at infinite dilution²), R is the gas constant and T is the absolute temperature. This relationship can be integrated to give

$$RT \ln(K_p/K_0) = -\Delta V_0 P + \frac{1}{2} \Delta \kappa_0 P^2 + \frac{1}{6} \Delta \lambda_0 P^3 + \dots \quad (2)$$

where the subscripts ₀ and _p denote values at atmospheric pressure and at a relative pressure P (the symbol P denotes the absolute pressure minus atmospheric pressure), and

$$\Delta \kappa = -\partial \Delta V / \partial P \quad (3)$$

$$\Delta \lambda = \partial \Delta \kappa / \partial P \quad (4)$$

¹ Planck, M., *Ann. Phys. Chem.*, 1887, **30**, 250.

² Hamann, S. D., in 'High Pressure Physics and Chemistry' (Ed. R. S. Bradley) Vol. 2, p. 132 (Academic Press: New York 1963); also in 'Modern Aspects of Electrochemistry' (Eds J. O'M. Bockris and B. E. Conway) Vol. 9, p. 78 (Plenum Press: New York 1974).

Although ΔV_0 can often be measured by density methods at atmospheric pressure, the values of $\Delta\kappa_0$, $\Delta\lambda_0$, ... can only be obtained from measurements made over a range of moderate or high pressures.

There have been several attempts to replace the series (2) by simpler, and general, expressions. They are summarized below in chronological order.

Owen and Brinkley³ assumed that the pressure dependence of $\Delta\kappa$ could be represented by the Tait equation of state, and on that basis derived the relationship

$$RT \ln(K_P/K_0) = -\Delta V_0 P + \Delta\kappa_0 [BP - B^2 \ln(1 + P/B)] \quad (5)$$

where B is a parameter characteristic of the solvent. To apply this equation at high pressures it is necessary to know both ΔV_0 and $\Delta\kappa_0$, which requires measurements of both the densities and the compressibilities of related solutions of strong electrolytes. Kearns⁴ applied it in that way to the self-ionization of water and obtained fair agreement with Hamann's⁵ measured values of K_P/K_0 to a maximum pressure of 2 kbar (1 kbar = 10^3 bar = 10^8 Pa \equiv 986.92 atm). However, the equation fails to fit the more recent results of Linov and Kryukov⁶ at higher pressures—it departs by a factor of 2 at 8 kbar (see the dotted curve of Fig. 2 below).

El'yanov and Gonikberg⁷ found that the ionization constants of weak acids and bases in water, over the pressure range 0–3 kbar, can be fitted closely by the relationship

$$\log(K_P/K_0) = -\Phi \Delta V_0 / T \quad (6)$$

where Φ is a function of P only and has almost the same value, within $\pm 5\%$, for seven different acids and bases. They tabulated average values of Φ at 1, 2 and 3 kbar, and later⁸ showed that these values give a good description of the behaviour of 24 other weak electrolytes at pressures up to 3 kbar. Using values of Φ calculated from the ionization constants of ammonium hydroxide in water and piperidine in methanol at pressures up to 12 kbar, they showed that (6) describes the self-ionization constant K_w of water very well over the pressure range 0–8 kbar. Recently, El'yanov⁹ has found that (6) also gives a good fit of the ionization constants of acetic and sulphanilic acids over the same pressure range. He pointed out⁹ that it is a 'linear free energy relationship' for the influence of pressure; he analysed its properties and showed that similar linear dependences upon Φ must hold for enthalpy changes ΔH , entropy changes ΔS , and Hammett's ρ parameter in ionization reactions, as well as for the pH of buffer solutions. He also showed that the coefficients in the linear relationships should be calculable from data measured at atmospheric pressure. These conclusions were checked and confirmed by comparison with experiment.⁹

Lown *et al.*¹⁰ truncated the series (2) to the terms in ΔV_0 and $\Delta\kappa_0$ and concluded that it then describes the experimental data well up to 2 kbar, but fails at higher

³ Owen, B. B., and Brinkley, S. R., *Chem. Rev.*, 1941, **29**, 461.

⁴ Kearns, E. R., Dissertation, Yale University, 1966.

⁵ Hamann, S. D., *J. Phys. Chem.*, 1963, **67**, 2233.

⁶ Linov, E. D., and Kryukov, P. A., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1972, **4**, 10.

⁷ El'yanov, B. S., and Gonikberg, M. G., *Izv. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1967, 1044; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1967, 1007.

⁸ El'yanov, B. S., and Gonikberg, M. G., *Zh. Fiz. Khim.*, 1972, **46**, 1494; *Russ. J. Phys. Chem.*, 1972, **46**, 856.

⁹ El'yanov, B. S., *Aust. J. Chem.*, 1975, **28**, 933.

¹⁰ Lown, D. A., Thirsk, H. R., and Lord Wynne-Jones, *Trans. Faraday Soc.*, 1968, **64**, 2073.

pressures (in fact there are signs that it is inadequate below 2 kbar). They also observed that there is a rough proportionality between $\Delta\kappa_0$ and ΔV_0 , represented by $\Delta\kappa_0 \approx (2.14 \times 10^{-4} \text{ bar}^{-1}) \times \Delta V_0$, so that the truncated formula can be written

$$RT \ln(K_P/K_0) = -\Delta V_0 P (1 - 1.07 \times 10^{-4} P) \quad (7)$$

where P is in bars.

From a highly simplified model of hydration, North¹¹ has derived a relationship of the form

$$RT \ln(K_P/K_0) = -\Delta V_0 P + C f(P, T) \quad (8)$$

where $f(P, T)$ is a function related to the compressibility of water and C is a coefficient proportional to the number n of 'hydrating' molecules. This formula fits the experimental results for a number of ionization reactions, including the ionization of ammonium hydroxide at pressures up to 12 kbar, but in its original form it lacks generality because n is quite different for different electrolytes and must be adjusted empirically.*

It is apparent that, of the formulae discussed above, El'yanov and Gonikberg's relationship (6) is the most general and accurate. It is the purpose of this paper to propose a simple analytical expression for Φ , in (6), which considerably simplifies its application at high pressures.

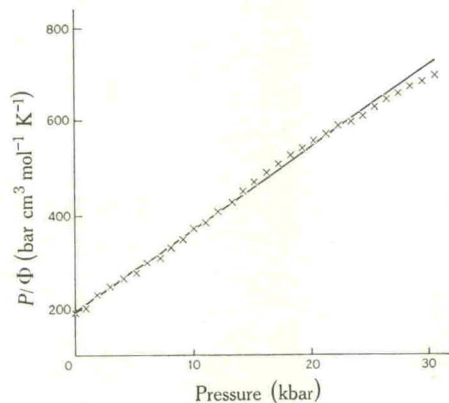


Fig. 1. Pressure dependence of the ratio P/Φ .

A Simple Expression for the Pressure Dependence of Φ

Fig. 1 shows a plot of the pressure dependence of the ratio P/Φ based on the values of Φ listed by El'yanov and Gonikberg.⁷ The points up to 12 kbar fall on a straight

* Dr North (personal communication) has more recently observed that there is an approximate proportionality between the parameters ΔV^0 and n in his treatment,¹¹ with $n \approx -\Delta V^0 / (4.7 \text{ cm}^3 \text{ mol}^{-1})$, and that if this value of n is substituted in his equation (10), it becomes

$$RT \ln(K_P/K_0) = -\Delta V^0 P \left[1 + \frac{\Delta V_w^0}{4.7 \text{ cm}^3 \text{ mol}^{-1}} \left(1 + \frac{B+P}{P} \ln \frac{B+P}{B} \right) \right]$$

which has the same general form as equation (6) of this paper. The factor in square brackets is within 2% of our factor $1/(1+bP)$ (equation (12)) between 0 and 10 kbar, but it deviates progressively at higher pressures, by about 90% at 30 kbar.

¹¹ North, N. A., *J. Phys. Chem.*, 1973, 77, 931.

line, very little scatter, but at higher pressures there are deviations which reach about 3% at 30 kbar. Since the values of Φ at pressures above 12 kbar were derived indirectly,⁷ these deviations can be ignored and we may assume that the following relationship holds with good accuracy

$$P/\Phi = a(1+bP) \quad (9)$$

The factor a is the limiting value of P/Φ as P tends to zero and so, from (2) and (6), is equal to $R \ln 10$. Equation (9) can therefore be rewritten

$$\Phi = P/(1+bP)R \ln 10 \quad (10)$$

and (6) becomes

$$\log(K_p/K_0) = -\Delta V_0 P/(1+bP)RT \ln 10 \quad (11)$$

or

$$RT \ln(K_p/K_0) = -\Delta V_0 P/(1+bP) \quad (12)$$

The value of b given by the slope of the line in Fig. 1 is $9.2 \times 10^{-5} \text{ bar}^{-1}$.

Table 1. Values of the functions Φ , W and X
 Φ from equation (10); W from equation (13); X from
 equation (14)

P (kbar)	Φ (mol cm ⁻³ K)	W	$10^5 X$ (bar ⁻¹)
0	0	1.000	18.4
1	4.78	0.839	14.1
2	8.82	0.713	11.1
3	12.3	0.614	8.85
4	15.3	0.534	7.18
5	17.9	0.469	5.91
6	20.2	0.415	4.92
7	22.2	0.392	4.14
8	24.1	0.332	3.52
9	25.7	0.299	3.01
10	27.2	0.271	2.60
11	28.6	0.247	2.26
12	29.8	0.226	1.97

Table 1 lists values of Φ calculated from formula (10), and Table 2 compares experimental values^{6,10,12,13*} of K_p/K_0 with those calculated from equation (12); the values of ΔV_0 were chosen to give the best fit of the data. The agreement is remarkably good except in the case of ammonium hydroxide, where the discrepancies are within the experimental errors. The results for water and ammonium hydroxide are shown in Fig. 2, where the crosses are experimental points; the continuous curves are from

* A correction has been applied because of high pressure phase transitions¹⁴⁻¹⁶ of Teflon.

¹² Hamann, S. D., and Strauss, W., *Trans. Faraday Soc.*, 1955, **51**, 1684.

¹³ Ellis, A. J., and Anderson, D. W., *J. Chem. Soc.*, 1961, 1765.

¹⁴ Weir, C. E., *J. Res. Nat. Bur. Stand.*, 1950, **45**, 465; 1953, **50**, 95; 1954, **53**, 245.

¹⁵ Pistorius, C. W. F. T., *Polymer*, 1964, **5**, 315.

¹⁶ Beecroft, R. I., and Swenson, C. A., *J. Appl. Phys.*, 1959, **30**, 1793.

equation (12); the dashed curves are based on the truncated equation of Lown *et al.*¹⁰ using their estimated values of ΔV_0 and $\Delta \kappa_0$, and the dotted curve for water is given by Owen and Brinkley's equation (5), using the value of $\Delta \kappa_0$ measured by Kearns.⁴

Table 2. Relative molal ionization constants at high pressures

Experimental values of K_P/K_0 are in ordinary type. Calculated values of K_P/K_0 were derived from equation (12) and are in *italics*

K_P/K_0 values at pressures P (kbar)											
1	2	3	4	5	6	7	8	9	10	11	12
Acetic Acid in Water at 25°C; $\Delta V_0 - 11.7 \text{ cm}^3 \text{ mol}^{-1}$											
1.546 ^A	2.201	3.047									
<i>1.541</i>	<i>2.219</i>	<i>3.033</i>									
Self-ionization of Water at 25°C; $\Delta V_0 - 21.4 \text{ cm}^3 \text{ mol}^{-1}$											
2.19 ^B	4.18	7.25	12.0	18.6	27.6	38.9	51.3				
<i>2.17</i>	<i>4.20</i>	<i>7.38</i>	<i>12.0</i>	<i>18.5</i>	<i>27.0</i>	<i>37.8</i>	<i>51.1</i>				
Ammonium Hydroxide in Water at 45°C; $\Delta V_0 - 29.0 \text{ cm}^3 \text{ mol}^{-1}$											
	6.02 ^C		26.2		75.2		174		320		494
	<i>6.38</i>		<i>24.8</i>		<i>69.6</i>		<i>157</i>		<i>304</i>		<i>522</i>

^A Mean values from the results of Hamann and Strauss,¹² Ellis and Anderson¹³ and Lown *et al.*¹⁰

^B From the measurements of Linov and Kryukov.⁶

^C From the measurements of Hamann and Strauss.¹² The values listed here differ slightly from those originally published. A correction has been applied for changes in the cell constant of the conductance cell caused by the high pressure phase transitions¹⁴⁻¹⁶ of Teflon.

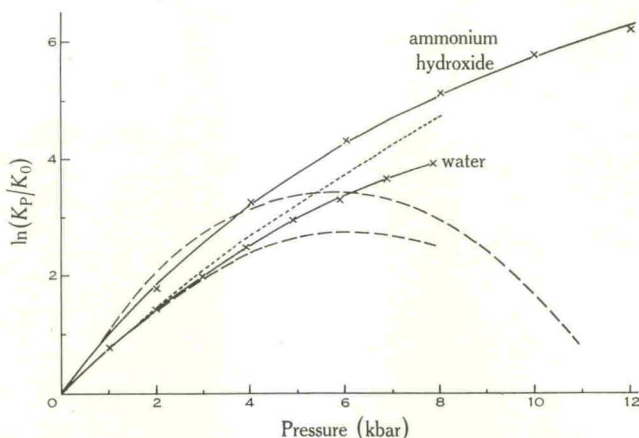


Fig. 2. A logarithmic plot of the ionization constant of ammonium hydroxide in water at high pressures, at 45°C, and of water at 25°C. The solid curves are given by equation (12), the dashed curves by the equation of Lown *et al.*¹⁷ and the dotted curve by Owen and Brinkley's equation (5).

El'yanov's analysis (see Tables 2 and 3 of ref.⁹) shows that the function Φ is effectively independent of the temperature for ionization reactions in water—at least between 18 and 75°C. It follows that it should be possible to apply equation (12)

over a range of temperatures using a constant value of $b = 9.2 \times 10^{-5} \text{ bar}^{-1}$. Table 3 and Fig. 3 show that it gives a good description of the ionization of acetic acid in water over the very wide range of temperatures from 25 to 225°C, at pressures between 0 and 3 kbar.¹⁷ At 225°C, water has a dielectric constant of only 30 to 40 in that range of pressures,¹⁸ so that it is quite a different medium from ordinary water at 25°C. Nevertheless, the formula still applies, with the same value of b .

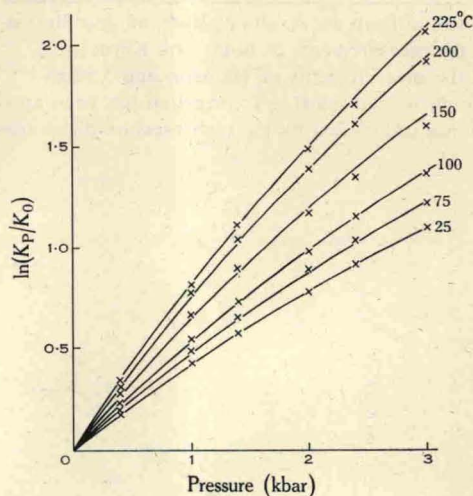
Table 3. Relative molal ionization constants of acetic acid in water at high pressures
Experimental values of K_p/K_0 are in ordinary type and calculated values are in *italics*

Temp. (°C)	ΔV_0 ($\text{cm}^3 \text{ mol}^{-1}$)	K_p/K_0 values at pressures P (kbar)					
		0.4	1.0	1.4	2.0	2.4	3.0
25	-11.3 _s	1.19 ^A	1.52	1.76	2.16	2.47	2.98
		<i>1.19^B</i>	<i>1.52</i>	<i>1.77</i>	<i>2.17</i>	<i>2.46</i>	<i>2.93</i>
225	-36.4 _s	1.41 ^A	2.29	3.00	4.34	5.43	7.76
		<i>1.40^B</i>	<i>2.24</i>	<i>2.98</i>	<i>4.43</i>	<i>5.64</i>	<i>7.92</i>

^A Experimental values of Lown, D. A., Thirsk, H. R., and Lord Wynne-Jones, *Trans. Faraday Soc.*, 1970, **66**, 51.

^B Values calculated from formula (12), with $b = 9.2 \times 10^{-5} \text{ bar}^{-1}$.

Fig. 3. A logarithmic plot of the ionization constant of acetic acid in water at high pressures and high temperatures. The curves are given by equation (12).



The Pressure Dependence of ΔV

Substitution of (12) into (1) and (3) gives the following relationships

$$\Delta V_p = \Delta V_0 / (1 + bP)^2 = W \Delta V_0 \quad (13)$$

$$\Delta \kappa_p = 2b \Delta V_0 / (1 + bP)^3 = X \Delta V_0 \quad (14)$$

which describe the pressure dependences of ΔV and $\Delta \kappa$. When $P = 0$, (14) reduces to $\Delta \kappa_0 = 2b \Delta V_0 = (1.84 \times 10^{-4} \text{ bar}^{-1}) \times \Delta V_0$, which is fairly close to the proportionality observed by Lown *et al.* (see the discussion of equation (7)).

¹⁷ Lown, D. A., Thirsk, H. R., and Lord Wynne-Jones, *Trans. Faraday Soc.*, 1970, **66**, 51.

¹⁸ Tödheide, K., in 'Water—A Comprehensive Treatise' (Ed. F. Franks) Vol. 1, p. 492 (Plenum Press: New York 1972).

Table 1 lists values of the functions W and X defined by (13) and (14). Table 4 compares 'experimental' values^{19,20} of ΔV_p (estimated graphically from the slopes of plots of $RT \ln K_p$ against P) for the ionization of 4-methoxybenzoic acid and ammonium hydroxide in water, with values calculated from equation (13). The maximum discrepancy is about 10% and is of the same order as the experimental errors.

Table 4. Molar volume changes (in $\text{cm}^3 \text{mol}^{-1}$) for ionization reactions at high pressures
Experimental values of ΔV_p are in ordinary type, calculated values in *italics*

ΔV_p at various pressures P (kbar)									
0	0.5	1.0	1.5	2.0	2.5	3.0	5.0	7.5	10.0
4-Methoxybenzoic Acid in Water at 25°C									
-11.32 ^A	-10.25	-9.35	-9.12	-8.22	-7.89	-7.66			
(-11.32) ^B	-10.35	-9.50	-8.74	-8.07	-7.48	-6.95			
Ammonium Hydroxide in Water at 45°C									
-28.5 ^C					-19.0		-14.0	-10.0	-7.0
(-28.5) ^B					-18.7		-13.3	-9.9	-7.7

^A Values from the work of Fischer, A., Mann, B. R., and Vaughan, J., *J. Chem. Soc.*, 1961, 1093.

^B Values from equation (13).

^C Values from Hamann, S. D., 'Physico-Chemical Effects of Pressure' p. 152 (Butterworths: London 1957).

The Electrostatic Theory of Ionization Reactions Under Pressure

It has been shown²⁰ that a semi-quantitative explanation of the influence of pressure on ionization equilibria in solution lies in its general effect in raising the dielectric constants of solvents, and so lowering the standard free energies of dissolved ions with respect to those of un-ionized molecules. Expressed in another way, the principal contributions to ΔV come from interactions between the ions and solvent (electrostriction).

The simplest theory of these interactions is given by Born's²¹ model of an ion as a conducting sphere of radius r immersed in a continuum of dielectric constant ϵ . The work needed to increase the charge of such an ion from zero to ze is $z^2e^2/2r\epsilon$ and the corresponding change in molar free energy in an ionization reaction is therefore

$$\Delta G_{e1} = Ne^2\theta/2\epsilon \quad (15)$$

where N is Avogadro's constant and θ denotes the sum

$$\theta = \sum_{\text{products}} z^2/r - \sum_{\text{reactants}} z^2/r \quad (16)$$

Formula (15) gives just the electrostatic part of the total Gibbs free energy change for reaction, ΔG , but for simplicity we shall assume that it is the only part which is significantly affected by pressure.²⁰

We shall also make the assumption that θ is independent of pressure, which is equivalent to supposing that the ions are effectively incompressible. That assumption

¹⁹ Fischer, A., Mann, B. R., and Vaughan, J., *J. Chem. Soc.*, 1961, 1093.

²⁰ Hamann, S. D., 'Physico-Chemical Effects of Pressure' p. 152 (Butterworths: London 1957).

²¹ Born, M., *Z. Phys.*, 1920, 1, 45.

is not always necessary, and some treatments have allowed for the compressibilities of the ions in specific cases.^{20,22} We make it here for the sake of generality.

With the above assumptions, the change of ΔG with pressure is

$$\Delta G_P - \Delta G_0 = \frac{1}{2} Ne^2 \theta (1/\epsilon_P - 1/\epsilon_0) \quad (17)$$

or, in a differential form

$$\partial \Delta G / \partial P = \Delta V = -(Ne^2 \theta / 2\epsilon) (\partial \ln \epsilon / \partial P) \quad (18)$$

In particular

$$\Delta V_0 = -(Ne^2 \theta / 2\epsilon_0) (\partial \ln \epsilon / \partial P)_0 \quad (19)$$

and substitution of this value in (17) gives

$$\Delta G_P - \Delta G_0 = -\Delta V_0 \epsilon_0 (\partial P / \partial \ln \epsilon)_0 (1/\epsilon_P - 1/\epsilon_0) \quad (20)$$

We have established empirically that the free energy change $\Delta G_P - \Delta G_0$ for ionization reactions is given, from (12), by

$$\Delta G_P - \Delta G_0 = \Delta V_0 P / (1 + bP) \quad (21)$$

so that, if (20) is also to apply, it is necessary that the pressure dependence of the dielectric constant be described by the relationship

$$\frac{1}{\epsilon_P} - \frac{1}{\epsilon_0} = -\frac{P}{1 + bP} \frac{1}{\epsilon_0} \left(\frac{\partial \ln \epsilon}{\partial P} \right)_0 \quad (22)$$

Inserting the experimental values of ϵ_0 and $(\partial \ln \epsilon / \partial P)_0$ for water at 25°C²³ and the value $b = 9.2 \times 10^{-5} \text{ bar}^{-1}$, we obtain

$$\epsilon_P = (1 + 9.2 \times 10^{-5} P) / (1.2757 \times 10^{-2} + 5.725 \times 10^{-7} P) \quad (23)$$

where P is in bars. Table 5 shows that values of ϵ_P calculated from this formula agree excellently with the experimental values of Lees²⁴ at pressures up to 10 kbar.

Table 5. The dielectric constant of water at 25°C
 P in kbar

P	$\epsilon_{\text{calc.}}^A$	$\epsilon_{\text{expt.}}^B$	P	$\epsilon_{\text{calc.}}$	$\epsilon_{\text{expt.}}$	P	$\epsilon_{\text{calc.}}$	$\epsilon_{\text{expt.}}$
0	(78.39)	78.39	4	90.91	90.57	8	100.13	100.22
1	81.92	81.87	5	93.47	93.13	9	102.07	102.41
2	85.17	85.00	6	95.85	95.58	10	103.88	104.55
3	88.16	87.88	7	98.06	97.94			

^A Calculated from equation (23).

^B From the measurements of Lees.¹⁴ A correction has been applied for an error of about 1% in the pressure scale, which Lees based on Bridgman's value of the freezing pressure of mercury at 0°C.

Dr M. Nakahara, of the Department of Chemistry, Kyoto University, Kyoto, Japan (personal communication), has examined our relationships (12) and (21) in a converse manner, observing that an empirical relationship which Dunn and

²² Whalley, E., *J. Chem. Phys.*, 1963, **38**, 1400.

²³ Owen, B. B., Miller, R. C., Milner, C. E., and Cogan, H. L., *J. Phys. Chem.*, 1961, **65**, 2065.

²⁴ Lees, W. L., Dissertation, Harvard University, 1949.

Stokes²⁵ used to fit their measured values of the dielectric constant of water under pressure

$$\epsilon_p = A + BP/(1 + CP) \quad (24)$$

can be recast as

$$\frac{1}{\epsilon_p} - \frac{1}{\epsilon_0} = -\frac{B}{A^2} \left[\frac{P}{1 + (C + B/A)P} \right] \quad (25)$$

This expression has the same form as our equations (12) and (22), with $b = C + B/A = 9.46 \times 10^{-5}$ bar²⁵ at 25°C. It follows that, with the same assumptions as we have made, the expression (25) leads directly to our general equation (21) for free energy changes, with only a slightly different value of b .

Some Linear Relationships in Φ^*

Finally, we can define a quantity Φ^* as

$$\Phi^* = P/(1 + bP) \quad (26)$$

and rewrite some of El'yanov's linear relationships⁹ in terms of this variable, so that they become analytical functions of the pressure. For this purpose we assume b to be independent of temperature. El'yanov's equation (2) then becomes

$$\Delta G_p - \Delta G_0 = \Delta V_0 \Phi^* \quad (27)$$

and his equations (4), (14), (15) and (16) become

$$\Delta V_p = \Delta V_0 \Phi^{*2}/P^2 \quad (28)$$

$$\Delta S_p = \Delta S_0 - m^* \Phi^* \quad (29)$$

$$\Delta H_p = \Delta H_0 - n^* \Phi^* \quad (30)$$

$$\gamma = n^*/m^* \quad (31)$$

where

$$m^* = \partial \Delta V_0 / \partial T \quad (32)$$

$$n^* = \Delta V_0 - T \partial \Delta V_0 / \partial T \quad (33)$$

The quantities with asterisks differ from the corresponding ones without them⁹ by the factor $R \ln 10$.

Within the approximations of the electrostatic treatment given in the last section, m^* and n^* should each be a simple product of ΔV_0 with a universal function of the temperature. From (19) we have

$$m^* = \frac{\partial \Delta V_0}{\partial T} = \frac{Ne^2 \theta}{2\epsilon_0} \left[\left(\frac{\partial \ln \epsilon}{\partial T} \right)_0 \left(\frac{\partial \ln \epsilon}{\partial P} \right)_0 - \frac{\partial}{\partial T} \left(\frac{\partial \ln \epsilon}{\partial P} \right)_0 \right] \quad (34)$$

$$= \Delta V_0 \left[- \left(\frac{\partial \ln \epsilon}{\partial T} \right)_0 + \frac{\partial}{\partial T} \left(\frac{\partial \ln \epsilon}{\partial P} \right)_0 \times \left(\frac{\partial P}{\partial \ln \epsilon} \right)_0 \right] \quad (35)$$

and

$$n^* = \Delta V_0 - m^* T \quad (36)$$

²⁵ Dunn, L. A., and Stokes, R. H., *Trans. Faraday Soc.*, 1969, **65**, 2906.

The ratio γ is theoretically independent of ΔV_0 . The term in square brackets in (35) is a universal function of T , only, and can be calculated from the derivatives measured by Owen *et al.*²³ Table 6 compares values of m^* , n^* and γ calculated from (35), (36) and (31) with the experimental values.⁹ The agreement is surprisingly good except in the case of n^* for acetic acid. The reasons for the difference in sign of ΔV_0 (and hence of m^* and n^*) for the two acids in Table 6 is discussed elsewhere.²⁶

Table 6. Experimental and theoretical effects of pressure on ΔH and ΔS for ionization reactions in water at 50°C

ΔV_0 and experimental values are from El'yanov,⁹ calculated values are from equations (34), (36) and (31)

Parameter (units)	Acetic acid	Sulphanilic acid
ΔV_0 (cm ³ mol ⁻¹)	-13.7	+2.15
$m^*_{\text{calc.}}$ (cm ³ mol ⁻¹ K ⁻¹)	-9.6×10^{-2}	$+1.51 \times 10^{-2}$
$m^*_{\text{expt.}}$ (cm ³ mol ⁻¹ K ⁻¹)	-6.4×10^{-2}	$+1.50 \times 10^{-2}$
$n^*_{\text{calc.}}$ (cm ³ mol ⁻¹)	17.3	-2.7
$n^*_{\text{expt.}}$ (cm ³ mol ⁻¹)	7.1	-2.7
$\gamma_{\text{calc.}}$ (K)	180	180
$\gamma_{\text{expt.}}$ (K)	109	180

To summarize, we have presented an empirical relationship which gives a good description of the influence of high pressures on ionization equilibria in aqueous solutions. It is consistent with the simple electrostatic theory of ionic hydration. Combined with the theory, it provides a means for predicting ionization constants over a wide range of pressures and temperatures, simply from the values at atmospheric pressure of K_0 , ΔV_0 and ΔH_0 .

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²⁶ Hamann, S. D., and Linton, M., *J. Chem. Soc., Faraday Trans. 1*, in press.