

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  $\Delta V_0$ , 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, North<sup>11</sup> 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  $\Phi$ , in (6), which considerably simplifies its application at high pressures.

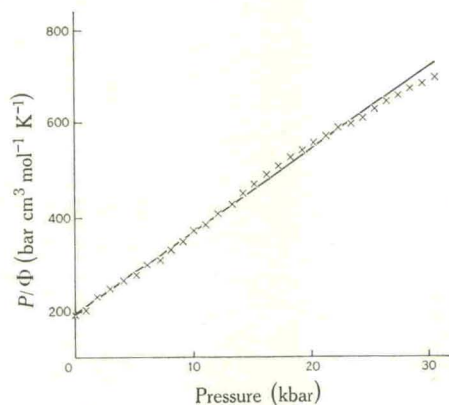


Fig. 1. Pressure dependence of the ratio  $P/\Phi$ .

### A Simple Expression for the Pressure Dependence of $\Phi$

Fig. 1 shows a plot of the pressure dependence of the ratio  $P/\Phi$  based on the values of  $\Phi$  listed by El'yanov and Gonikberg.<sup>7</sup> 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  $\Delta V^0$  and  $n$  in his treatment,<sup>11</sup> 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.

<sup>11</sup> 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  $\Phi$  at pressures above 12 kbar were derived indirectly,<sup>7</sup> 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  $P/\Phi$  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  $\Phi$ ,  $W$  and  $X$   
 $\Phi$  from equation (10);  $W$  from equation (13);  $X$  from  
 equation (14)

$P$ (kbar)	$\Phi$ (mol cm <sup>-3</sup> K)	$W$	$10^5 X$ (bar <sup>-1</sup> )
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  $\Phi$  calculated from formula (10), and Table 2 compares experimental values<sup>6,10,12,13\*</sup> of  $K_p/K_0$  with those calculated from equation (12); the values of  $\Delta V_0$  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 transitions<sup>14-16</sup> of Teflon.

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

<sup>13</sup> Ellis, A. J., and Anderson, D. W., *J. Chem. Soc.*, 1961, 1765.

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

<sup>15</sup> Pistorius, C. W. F. T., *Polymer*, 1964, **5**, 315.

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