CALCULATION OF THE EFFECT OF PRESSURE UPON IONIC EQUILIBRIA IN PURE WATER AND IN SALT SOLUTIONS[1]

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Received March 14, 1941

Tables of standard partial molal and ionic volumes, and their pressure coefficients, are given for aqueous solutions at 25°C. These are used to estimate the effect of pressure upon the ionization constants of water and weak acids, and the solubility constants of several minerals. A pressure of 1000 bars causes a two- to eight-fold increase in these quantities at 25°C. The increase at other temperatures is briefly discussed, and rough values of ΔH^0 and ΔS^0 for the ionization of water are recorded as a function of pressure.

To give the results oceanographic interest, similar tables and calculations are presented for "salt water" (0.725 molal sodium chloride) of the same ionic strength as sea water. The calculations feature a shift of the standard states to "salt water," and the use of empirical methods of estimating standard volumes and their pressure coefficients in this medium. The effect of pressure upon ionic equilibria in "salt water" is less than in pure water.

The general thermodynamic relation which describes the effect of pressure upon the equilibrium constant is well known, but is rarely applied to condensed systems involving ions. This neglect of the important variable, pressure, is largely due to the scarcity of reliable values of the partial molal volumes and compressibilities of ionic solutes, especially in solutions containing several electrolytes. The present review is concerned with compiling preliminary tables of these quantities, and describing methods by which they may be evaluated from existing data. Their use will be illustrated by calculating the effect of pressure upon several ionic equilibria of interest to geologists and oceanographers.

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[1] Presented at the Symposium on Reactions and Equilibria in Chemical Systems under High Pressure, which was held under the auspices of the Division of Physical and Inorganic Chemistry at the One-hundredth Meeting of the American Chemical Society, Detroit, Michigan, September 9–13, 1940.

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I. THE SOLVENT MEDIUM IS PURE WATER

The variation of the thermodynamic equilibrium constant with pressure is given by

$$RT\left(\frac{\partial \ln K}{\partial P}\right)_{T,m} = -\Delta\bar{V}^0 = -\left[\sum^{p}\bar{V}_2^0 - \sum^{r}\bar{V}_2^0\right] \tag{1}$$

$\Delta\bar{V}^0$ is the algebraic difference between the partial molal volumes of the products and the reactants in their standard states. A component which takes part in the reaction as a pure phase is in its standard state by convention. The standard state of a solute is the hypothetical 1 molal solution in which its activity coefficient is unity. The partial molal volume of such a component is equal to its value at infinite dilution of all solute species. These conventions permit variations of pressure at constant composition, as required by equation 1.

For any solute, $\bar{V}_2^0$ can be obtained by extrapolating the apparent molal volume,

$$\phi_v = \frac{M_2}{d_0} - \frac{1000}{d_0}\left(\frac{d - d_0}{c}\right) \tag{2}$$

or other (12, 17) suitable function of the density, to infinite dilution. M_2 is the molecular weight of the solute, and c its concentration in moles per liter of solution. The densities of the solution and of the pure solvent are represented by d and d_0, respectively. By definition

$$\phi_v^0 \equiv \bar{V}_2^0 \tag{2a}$$

For ionic solutes the extrapolation is based upon the observation (34, 36) that ϕ_v varies linearly with $\sqrt{c}$ in dilute solutions, or

$$\phi_v = \phi_v^0 + S_v\sqrt{c} \tag{3}$$

For non-electrolytes (19, 35) and weak electrolytes (9, 21), ϕ_v varies linearly with c and the degree of dissociation, respectively. Table 1 contains values of $\bar{V}_2^0 (= \phi_v^0)$ for representative electrolytes at 25°C. and 1 atmosphere. The discordance between independently determined values for most of these salts is largely due to uncertainties in extrapolation, since an error of 0.001 per cent in density produces an error of $0.01/c$ cc. in ϕ_v. Independent extrapolations (8, 37) of the same data (6) often disagree by ±0.1 cc. The figures printed in bold face are the most self-consistent values we could obtain by imposing the condition of additivity of partial molal ionic volumes at infinite dilution, and are probably accurate to ±0.2 cc., unless rounded off to the nearest cubic centimeter.

Before equation 1 can be used over any considerable range, $\Delta\bar{V}^0$ must be expressed as a function of P. If the partial molal compressibility (18),

TABLE 1

Partial molal volumes of electrolytes at infinite dilution in water at 25°C. and 1 atmosphere

ELECTROLYTE	S_v	$\bar{V}_2^0$	REFERENCE	ELECTROLYTE	S_v	$\bar{V}_2^0$	REFERENCE
HCl	0.95	18.07	(42)	KI	1.56	45.36	(37)
18.1		17.98	(5)	**45.3**		45.23	(8)
		18.20	(8)			45.28	(12)
LiCl	1.49	17.00	(37)			45.34	(33)
17.1		17.06	(8)	KOH	4.35	2.9	(18)
LiBr	1.16	24.08	(37)	**3.4**		4.06	(3)
24.0		24.07	(8)	KNO_3	2.30	38.18	(15)
LiI	0.85	35.50	(37)	**38.0**		37.6	(30)
35.6		35.60	(8)			37.98	(33)
LiOH	3.00	−6.0	(18)	$KClO_3$		**46**	(30)
−6.3				$KBrO_3$		**44**	(30)
NaCl	2.15	16.40	(8)	$KHCO_3$	2.6	**32.7**	*
16.6		16.28	(37)	K_2CrO_4	11.7	**37.1**	(24)
		16.61	(31)	K_2SO_4	12.07	32.28	(43)
		16.35	(12)	**31.9**		32.36	(27)
		16.67	(42)			32.30	(1)
		16.62	(23)			31.96	(24)
		16.44	(15a)	RbCl	2.22	31.87	(37)
NaBr	1.76	23.51	(37)	**31.8**		31.71	(8)
23.5		23.45	(8)	RbBr	2.04	38.71	(37)
		23.48	(9)	**38.7**		38.70	(8)
		23.45	(15a)	RbI	1.62	50.31	(37)
NaI	1.35	35.10	(37)	**50.3**		50.40	(8)
35.1		35.00	(8)	CsCl	2.17	39.15	(37)
		35.09	(15)	**39.2**		39.02	(8)
NaOH	4.18	−6.7	(18)	CsBr	1.90	46.19	(37)
−6.8		−5.94	(4)	**46.1**		46.20	(8)
NaO_2CCH_3	1.9	40.1	*	CsI	1.58	57.74	(37)
40.0		39.72	(33)	**57.7**		57.90	(8)
$NaHSO_4$	1.8	**27**	*			57.54	(26)
Na_2SO_4	12.16	11.52	(9)	NH_4Cl	1.45	35.98	(30)
11.5		11.10	(12)	**36.0**		36.26	(33)
		11.39	(33)	NH_4NO_3	0.97	47.56	(20)
Na_2CO_3	11.30	**−6.74**	(9)	**47.2**		47.24	(9)
KF	3.35	**6.60**	(8)			47.49	(2)
KCl	2.33	26.52	(37)	$AgNO_3$	2.61	28.01	(24)
26.8		26.36	(8)	**28.3**		28.76	(33)
		26.57	(27)	$MgCl_2$	4.26	**15.3**	(38)
		26.87	(30)	$CaCl_2$	6.00	18.25	(18)
		26.74	(43)	**18.5**		18.54	(33)
		26.65	(33)			18.6	(38)
		26.81	(9)	$SrCl_2$	?	17.94	(31)
KBr	1.94	33.73	(37)	**18.0**		18.6	(38)
33.7		33.54	(8)	$BaCl_2$	4.83	23.60	(18)
		33.97	(43)	**23.9**		24.1	(25)
		33.56	(22)	$CdCl_2$	5.9	**23.2**	(33)
		33.88	(33)	$LaCl_3$	11.87	**16.0**	(28)
		33.77	(29)	CH_3CO_2H		50.7	*
$KMnO_4$		**51.7**	(26)				

* *International Critical Tables.*

$$\bar{K}_2^0 \equiv -\left(\frac{\partial \bar{V}_2^0}{\partial P}\right)_{T,m} \tag{4}$$

of each component is known at the standard pressure, 1 atmosphere,[3] it is satisfactory for many purposes to consider $\bar{K}_2^0$ constant over a moderate pressure range.[4] In this case the partial molal volume at any pressure (P) is given by

$$\bar{V}_2^{0(\mathrm{P})} = \bar{V}_2^0 - \bar{K}_2^0(P - 1) \tag{5}$$

and substitution in equation 1 leads to

$$RT \ln (K^{(\mathrm{P})}/K) = -\Delta\bar{V}^0(P - 1) + \frac{1}{2}\Delta\bar{K}^0(P - 1)^2 \tag{6}$$

upon integration.

A more complete expression, applicable at higher pressures, may be derived from the relation,

$$\bar{V}_2^{(\mathrm{P})} - V_2^{(\mathrm{P})} = \frac{-A}{B + P_e + P} \cdot \frac{\mathrm{d}P_e}{\mathrm{d}m} \tag{7}$$

obtained by Gibson (11). This relation is an extension of the Tait (39) equation, and is based upon Tammann's (40) hypothesis that, in the presence of an ionized solute, the solvent behaves as though it were subjected to a constant effective pressure, P_e, in addition to the external pressure, P. P_e is a property of the solution and a function of the concentration. The constants A and B are characteristic of the pure solvent.[5] A, B, and P_e are independent of P. V_2 represents the molal volume of the pure solute in the liquid state.

At any given concentration and temperature, differentiation of equation 7 yields

$$\bar{K}_2^{(\mathrm{P})} - K_2^{(\mathrm{P})} = \frac{-A}{(B + P_e + P)^2} \cdot \frac{\mathrm{d}P_e}{\mathrm{d}m} \tag{8}$$

at the pressure P. Since K_2, the molal compressibility of the pure liquid electrolyte, should not differ greatly from that of the solid, we shall assume that K_2 is negligible compared to $\bar{K}_2$ at all concentrations and pressures with which we are concerned. Therefore elimination of $A\ \mathrm{d}P_e/\mathrm{d}m$ between equation 8, and itself rewritten for $P = 1$, leads to

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[3] For condensed systems *at ordinary atmospheric pressures* it will be unnecessary to distinguish between 1 bar and 1 atmosphere.

[4] It can be shown by equation 10 that an increase of 100 bars decreases $\bar{K}_2^0$ less than 7 per cent in aqueous solution at 25°C.

[5] For aqueous solutions at 25°C., $B = 2996$ bars and $A = 434.3 \times 0.3150$ cc. per kilo of water (10); see reference 11.

$$\bar{K}_2^{(P)} = \bar{K}_2\left[\frac{B + P_e + 1}{B + P_e + P}\right]^2 \tag{9}$$

at any concentration, or

$$\bar{K}_2^{0(P)} = \bar{K}_2^0\left[\frac{B + 1}{B + P}\right]^2 \tag{10}$$

at infinite dilution. This equation relates $\bar{K}_2^{0(P)}$ to $\bar{K}_2^0$ in a very simple manner, and its integration results in the expression

TABLE 2

Partial molal compressibilities of electrolytes at infinite dilution in water at 25°C. and 1 atmosphere

ELECTROLYTE	$10^4\bar{K}_2^0$	REFERENCE	ELECTROLYTE	$10^4\bar{K}_2^0$	REFERENCE
HCl	−8	(20)	Na_2CO_3	−171	(13)
LiCl	−42	(20)	K_2CrO_4	−139	(13)
NaCl	−52	(20)	Li_2SO_4	−146	(14)
KCl	−45	(20)	Na_2SO_4	−154	(14)
LiOH	−78	(20)	K_2SO_4	−139	(14)
NaOH	−89	(20)	Cs_2SO_4	−119	(14)
KOH	−81	(32)	$(NH_4)_2SO_4$	−91	(14)
KO_2CCH_3	−47	(32)	$BaCl_2$	−115	(13)
LiCl	−41	(13)	$CaCl_2$	−87†	(18)
NaCl	−48	(13)	$MgSO_4$	−153	(14)
KCl	−44	(13)	$CdSO_4$	−127	(14)
NaBr	−42	(13)	$CuSO_4$	−132	(14)
KBr	−34	(13)	$ZnSO_4$	−140	(14)
CsBr	−25	(13)	$BeSO_4$	−93	(14)
LiI	−17	(13)	$CeCl_3$	−176	(13)
KI	−18	(13)			
KCNS	−22	(13)			
KNO_3	−30	(13)	HO_2CCH_3	+7	(13)
$KHCO_3$	−35	*	H_2O	+8.22	(13)

* *International Critical Tables.*

† At 30°C. and 100 bars.

$$\bar{V}_2^{0(P)} = \bar{V}_2^0 - \bar{K}_2^0\left[\frac{(B + 1)(P - 1)}{B + P}\right] \quad . \tag{11}$$

for $\bar{V}_2^{0(P)}$ as a function of the pressure. By combining this expression with equation 1 and integrating, we obtain the desired relation,

$$RT \ln (K^{(P)}/K) = -\Delta\bar{V}^0(P - 1) + \Delta\bar{K}^0\left[(B + 1)(P - 1) - (B + 1)^2 \ln\left(\frac{B + P}{B + 1}\right)\right] \tag{12}$$

by which $K^{(P)}$ is calculable at pressures as high as 1000 atmospheres, or more.

The individual values of $\bar{K}_2^0$ can be obtained in a manner (18) analogous to that used in determining $\bar{V}_2^0$, but it is more convenient to employ the expression

$$\bar{K}_2^0 = -\left[\frac{\bar{V}_2^{0(P_2)} - \bar{V}_2^{0(P_1)}}{P_2 - P_1}\right]\frac{(B + P_2)(B + P_1)}{(B + 1)^2} \tag{13}$$

derived from equation 10 by integration over any pressure interval, P_1 to P_2. Since P_1 may be assigned the value unity, equation 13 permits the calculation of $\bar{K}_2^0$ from density measurements at a single high pressure, P_2. Table 2 contains values of $\bar{K}_2^0$ at 25°C. and 1 atmosphere. Those values which have not been previously reported were calculated by equation 13.

TABLE 3

Partial molal ionic volumes and compressibilities at infinite dilution in water at 25°C. and 1 atmosphere

(Relative to H^+)

CATION	$\bar{V}_i^0$	$10^4\bar{K}_i^0$	ANION	$\bar{V}_i^0$	$10^4\bar{K}_i^0$
H^+	0	0	OH^-	−5.3	−44
Li^+	−1.0	−34	F^-	−2.1	
Na^+	−1.5	−42	Cl^-	+18.1	−8
K^+	+8.7	−37	Br^-	+25.0	+2
Rb^+	+13.7		I^-	+36.6	+18
Cs^+	+21.1	−27	$CH_3CO_2^-$	+41.5	−10
NH_4^+	+17.9	−11	NO_3^-	+29.3	+7
Ag^+	−1.0		CNS^-		+15
Mg^{++}	−20.9	−83	HCO_3^-	+24	+2
Ca^{++}	−17.7	−71	MnO_4^-	+43	
Sr^{++}	−18.2		ClO_3^-	+46	
Ba^{++}	−12.3	−99	BrO_3^-	+44	
Be^{++}		−23	CrO_4^{--}	+19.7	
Cd^{++}	−13	−57	CO_3^{--}	−3.7	−85
Cu^{++}		−62	SO_4^{--}	+14.5	−70
Zn^{++}		−70			
La^{+++}	−38.3				
Ce^{+++}		−152			

Values of the partial molal ionic volumes, $\bar{V}_i^0$, and partial molal ionic compressibilities, $\bar{K}_i^0$, are given in table 3. These properties of the individual ions are relative, and are obtained by setting the partial molal volume and compressibility of the hydrogen ion equal to zero. This convention is analogous to that used in tabulating ionic entropies, and is very convenient for numerical calculations. The value, $\bar{V}_2^0 = 18.1$ cc., for hydrochloric acid, which is the average of three closely agreeing determinations, yields the secondary reference value, $\bar{V}_i^0 = 18.1$ cc., for the chloride ion. All other ionic volumes were obtained by suitable combinations of this value with the partial molal volumes of salts at infinite dilution. The calculation of $\bar{K}_i^0$ was similar, but only one value of $\bar{K}_2^0$ for hydrochloric acid was available. Since $\bar{V}_i^0$ and $\bar{K}_i^0$ for a particular ion can often be calculated by several combinations of independent data, the evaluation of these individual ionic properties permits an averaging process which decreases the probable error in the estimation of $\Delta\bar{V}^0$ and $\Delta\bar{K}^0$.

TABLE 4

The effect of pressure upon the equilibrium constant of the reaction, $H_2O \rightleftarrows H^+ + OH^-$, *in pure water**

P IN BARS	$K^{(P)}/K$					$\Delta\bar{H}^0$ 25°C.	$\Delta\bar{S}^0$ 25°C.
	5°C.	15°C.	25°C.	35°C.	45°C.		
1	1	1	1	1	1	13.5†	−18.7‡
200	1.24_6	1.225	1.202	1.180	1.16_3	13.2	−19.4
400	1.54_3	1.490	1.435	1.384	1.34_5	12.9	−20.1
600	1.8_{96}	1.80_0	1.703	1.61_2	1.5_{45}	12.6	−20.8
800	2.3_{17}	2.16_3	2.009	1.86_8	1.7_{66}	12.2	−21.8
1000	2.8_{16}	2.58_5	2.358	2.15_4	2.0_{09}	11.8	−22.8
$\Delta\bar{V}^0$.......	−26.1	−24.9	−23.4	−21.8	−20.6		

* $\Delta\bar{K}^0 = -52 \times 10^{-4}$ (at 25°C.) used at all temperatures.

† Kilocalories.

‡ Calories.

In illustrating the use of table 3, we have estimated $\Delta\bar{V}^0$ for several ionic equilibria, and calculated log $K^{(P)}/K$ by equation 12. The results for the important reaction

$$H_2O \rightleftarrows H^+ + OH^-$$

are shown in table 4 and figure 1. The ionization constant increases with pressure, and the relative increase is the greater the lower the temperature. In fresh water at 0°C. and at a depth corresponding to a pressure of 1000 bars, the ionization constant of water would be about three times its value at the surface. For pure liquid water, the molal volume and its variation with pressure were calculated from density and compressibility data given in the *International Critical Tables.* From table 3, $\bar{V}^0_{H^+} + \bar{V}^0_{OH^-} = -5.3$ cc. at 25°C. The temperature coefficient of this quantity was estimated by subtracting the temperature coefficient of $\bar{V}_2^0$ for sodium chloride (8, 16) from the sum of the corresponding values for hydrochloric acid (5) and sodium hydroxide (4). Since the magnitude of $\Delta\bar{V}^0$ could hardly be in error by more than 1 cc. at the extreme temperatures, its decrease with temperature is unmistakable. On the other hand, the value of $\Delta\bar{K}^0$ could be estimated at 25°C. only, and had to be used at all temperatures. Without attempting to estimate the accuracy of the results, the inadequacy of the data is indicated by limiting the decimal places recorded in table 4.

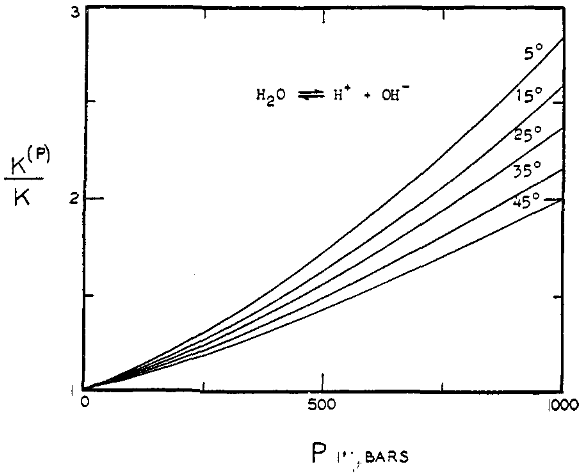

FIG. 1. The effect of pressure upon the ionization of pure water

TABLE 5

The effect of pressure upon ionic equilibria in pure water at 25°C.

REACTION	$\Delta\bar{V}^0$ P = 1*	$10^4\Delta\bar{K}^0$ P = 1*	$K^{(P)}/K$				
			P = 200*	P = 400*	P = 600*	P = 800*	P = 1000*
$CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^-$......	−9.2	−17	1.075	1.154	1.235	1.32	1.41
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$...........	−29	0†	1.26	1.60	2.02	2.6	3.2
$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$............	−27.8	−87	1.241	1.522	1.85	2.22	2.65
Anhydrite $\rightleftharpoons Ca^{++} + SO_4^{--}$......	−49.3	−142	1.47	2.12	3.00	4.20	5.80
Calcite $\rightleftharpoons Ca^{++} + CO_3^{--}$.........	−58.3	−157	1.58	2.44	3.69	5.52	8.10
Aragonite $\rightleftharpoons Ca^{++} + CO_3^{--}$......	−55.3	−157	1.54	2.32	3.44	5.01	7.18
Magnesite $\rightleftharpoons Mg^{++} + CO_3^{--}$.....	−52.3	−169	1.50	2.21	3.18	4.49	6.24
Witherite $\rightleftharpoons Ba^{++} + CO_3^{--}$......	−61	−185	1.61	2.53	3.88	5.84	8.60

* Total pressure in bars.

† $\Delta\bar{K}^0$ assumed negligible.

The values of $\Delta\bar{H}^0$ and $\Delta\bar{S}^0$ given in table 4 are rough estimates which may be considerably in error at the higher pressures. Nevertheless, it seems safe to conclude that these thermochemical quantities become more negative, the higher the pressure.

Table 5 shows the effect of pressure upon other important ionization and solubility constants at 25°C. For the solids, the molal volumes and their pressure coefficients were calculated from densities and compressibilities given in the *International Critical Tables.* $\bar{V}_2^0$ and $\bar{K}_2^0$ for unionized acetic acid are given in tables 1 and 2. $\bar{V}_2^0$ is known (7) to be 35 cc. for dissolved carbon dioxide at 25°C., and, assuming that $\bar{K}_2^0$ for this solute is not much greater than the value for acetic acid, $-\Delta\bar{K}^0 < 10$ for the first step in the ionization of carbonic acid and is neglected.

Note that $\Delta\bar{V}^0$ is negative for all of the reactions in table 5. Rough calculations indicate that $\Delta\bar{V}^0$ for the ionization of acetic acid becomes more positive with increasing temperature. This was also the case with water. Therefore, pressure will presumably decrease the ionization constants of these weak electrolytes at very high temperatures. At 25°C., $\Delta\bar{V}^0$ for the process of solution of sparingly soluble salts is usually large, and negative. It is small and negative for the silver halides; and for some very soluble salts, such as lithium iodide and ammonium nitrate, $\Delta\bar{V}^0$ is small and positive at 25°C. Water of crystallization seldom alters $\Delta\bar{V}^0$ by more than 5 cc. at this temperature.

II. THE SOLVENT MEDIUM IS "SALT WATER" (0.725 MOLAL SODIUM CHLORIDE)

The calculation of the effect of pressure upon ionic equilibria in salt solutions is important because of its bearing upon problems in oceanography. Since the ionic strength of normal sea water (41) is about 0.725,[6] we shall illustrate the calculation for reactions taking place in a 0.725 molal sodium chloride solution (0.713 normal at 25°C.), hereafter referred to as "salt water".

The first step is to shift the standard state from pure water to salt water so that the activity coefficients of all added solutes become unity at infinite dilution in salt water. The activity of water and the activity coefficient of sodium chloride are also unity in 0.725 *m* sodium chloride solution. As a result of this convention, the thermodynamic constant for a reaction in salt water is equal to the mass action "constant" for the reaction at infinite dilution in this medium. The latter may be determined for the ionization of weak electrolytes by electromotive-force measurements. The thermodynamic constant for the solution of a sparingly soluble electrolyte in salt water is practically equal to the solubility product in salt water, just as in this case the thermodynamic constant and solubility product are nearly identical in pure water. For a more soluble electrolyte, its activity coefficient would have to be considered in pure water, but in salt water the

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[6] This would correspond to a chlorinity of 19.430 ‰, according to the recent calculations of J. Lyman and R. H. Fleming (Sears Foundation: J. Marine Research **3**, 134 (1940)).

thermodynamic constant would still be approximately equal to the solubility product, because activity coefficients vary only slightly with concentration at ionic strengths of the order 0.725. In any case, the effect of pressure upon an equilibrium in salt water is given by

$$RT\left(\frac{\partial \ln K^*}{\partial P}\right)_{T,m} = -\Delta\bar{V}^{0*} = -\left[\sum^{p} \bar{V}_2^{0*} - \sum^{r} \bar{V}_2^{0*}\right] \qquad (14)$$

if we let an asterisk indicate the use of this medium in defining the standard state.

The second step is the evaluation of partial molal volumes ($\bar{V}_2^{0*}$) at infinite dilution in salt water. Wirth's (42, 43) studies of mixed electrolyte solutions yield results from which these values may be directly evaluated for hydrochloric acid and for potassium chloride, potassium bromide, and potassium sulfate. In the absence of further suitable data of the same nature, all other values of $\bar{V}_2^{0*}$ must be estimated from results obtained in simple binary solutions. For such systems, equation 3 leads to the relation,

$$\bar{V}_2 = \bar{V}_2^0 + A_v\sqrt{\Gamma} \qquad (15)$$

in which Γ is the ional concentration ($\Sigma c_i z_i^2$), and

$$A_v = \frac{(3000 - c\bar{V}_2^0)\,S_v}{(2000 + c^{3/2}S_v)(\nu z_+ z_-)^{1/2}} \simeq \frac{3/2\ S_v}{(\nu z_+ z_-)^{1/2}} \qquad (16)$$

The approximate expression for A_v may be used at 0.725 m without introducing an error greater than 0.1 cc. Wirth (43) observed that, below $\Gamma \simeq 1.5$, the presence of sodium chloride in a solution of any one of the three potassium salts affects the partial molal volume of the latter only by its contribution to Γ, the numerical value of A_v remaining unchanged. Upon the *assumption* that this behavior is characteristic of all salts in the presence of sodium chloride, we obtain

$$\bar{V}_2^{0*} = \bar{V}_2^0 + A_v\sqrt{2 \times 0.713} \qquad (17)$$

by substituting the value of Γ corresponding to the 0.725 m solution of sodium chloride. This equation will serve as a good approximation, but it is not likely to be strictly valid, even for salts. For hydrochloric acid in sodium chloride solutions it yields a value of $\bar{V}_2^{0*}$ some 0.3 cc. lower than the direct experimental (42) value, 19.6, which is used to evaluate $\bar{V}_{\text{Cl}}^{0*}$, the secondary reference upon which the other ionic volumes in table 6 are based. In the estimation of the latter quantities, A_v was derived from the approximate form of equation 16 and the values of S_v given in table 1.

The third and last step is the representation of $\bar{V}_2^{0*}$ as a function of the pressure, and the integration of equation 14. There appear to be no measurements of compressibilities in solutions of mixed electrolytes which permit the calculation of $\bar{K}_2^{0*}$ directly. In the preceding paragraphs, two assumptions were introduced which should enable us to approximate this quantity. Thus, the equation

$$\bar{K}_2 = \bar{K}_2^0 + A_K\sqrt{\Gamma} \tag{18}$$

in which the parameter A_K is characteristic of a given electrolyte (18), may be assumed applicable in mixtures containing sodium chloride without changing the value of A_K. Accordingly

$$\bar{K}_2^{0*} \simeq \bar{K}_2^0 + A_K\sqrt{2 \times 0.713} \tag{19}$$

in salt water at 25°C. On the other hand, if it be assumed that the effect of 0.725 m sodium chloride upon the compressibility of another electrolyte at infinite dilution in this medium is the same as that of an external pressure equal to the effective pressure (P_e = 207 bars) due to the sodium chloride, then

$$\bar{K}_2^{0*} \simeq \bar{K}_2^0\left[\frac{B+1}{B+P_e}\right]^2 = \bar{K}_2^0\left[\frac{B+1}{B^*}\right]^2 \tag{20}$$

In the new medium, salt water, B^* (= $B + P_e$) plays a similar rôle to that of B in pure water. For a 0.725 m sodium chloride solution, P_e = 207

TABLE 6

Partial molal volumes and compressibilities at infinite dilution in "salt water" (0.725 m sodium chloride) at 25°C. and 1 atmosphere

COMPOUNDS	$\bar{V}_2^{0*}$	$10^4\bar{K}_2^{0*}$	IONS†	$\bar{V}_i^{0*}$	$10^4\bar{K}_i^{0*}$
H_2O	18.86‡	+6.89‡	H^+	0	0
HCl	19.6‡	−7	Na^+	−0.6	−37
NaCl	19.0‡	−45	K^+	9.7	−32
KCl	29.3‡	−39	NH_4^+	19.6	
KBr	36.2‡	−30	Mg^{++}	−21	−73
KI	47.3	−16	Ca^{++}	−16.6	−62
KNO_3	41.1	−26	Ba^{++}	−12.1	−86
KOH	8.4	−71	Cl^-	19.6	−7
$KHCO_3$	36	−30	Br^-	26.4	+2
K_2SO_4	41.4‡	−122	I^-	37.5	+16
Na_2CO_3	1.5	−150	OH^-	−1	−38
$CaCl_2$	22.6	−76	NO_3^-	31	+6
$BaCl_2$	27.1	−100	HCO_3^-	26	+2
$MgCl_2$	18.4		CO_3^{--}	2.7	−74
$MgSO_4$		−133	SO_4^{--}	22	−60

† Some of the ionic quantities are averages obtained from several combinations of data in addition to those given in this table.

‡ These quantities were evaluated directly from experimental data.

bars at 25°C., and $B = 2996$ bars at this temperature (10). The right-hand member of equation 20 is therefore $0.87\bar{K}_2^0$.

Equations 19 and 20 involve assumptions analogous to those upon which equations 17 and 7 are based, but, unlike the latter equations, are not yet subject to experimental verification. Fortunately, $\bar{K}_2^{0*}$ need not be accurately known for most calculations, and alternative values estimated by equations 19 and 20 differ only by 10 to 20 per cent. The provisional estimates of $\bar{K}_2^{0*}$ recorded in table 6 are based upon equation 20.

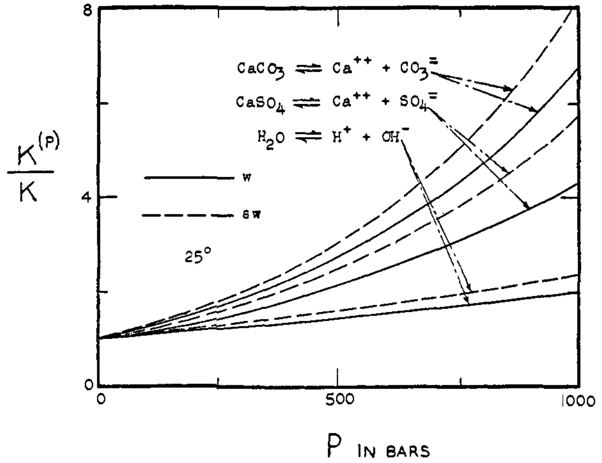

FIG. 2. Comparison of the effects of pressure upon ionic equilibria in pure water (———) and in salt water (- - - - -) at 25°C.

According to equation 7, $\bar{K}_2^{0*(P)}$ is given at any pressure by

$$\bar{K}_2^{0*(P)} = \bar{K}_2^{0*}\left[\frac{B^* + 1}{B^* + P}\right]^2 \tag{21}$$

from which we obtain

$$\bar{V}_2^{0*(P)} = \bar{V}_2^{0*} - \bar{K}_2^{0*}\left[\frac{(B^* + 1)(P - 1)}{B^* + P}\right] \tag{22}$$

Combination of this expression with equation 14 leads to

$$RT \ln (K^{*(P)}/K^*) = -\Delta\bar{V}^{0*}(P - 1)$$
$$+ \Delta\bar{K}^{0*}\left[(B^* + 1)(P - 1) - (B^* + 1)^2 \ln\left(\frac{B^* + P}{B^* + 1}\right)\right] \tag{23}$$

Equations 21, 22, and 23 are formally identical with equations 10, 11, and 12 and are presumably valid over the same range of pressures, but, in view of the assumptions involved in the numerical evaluation of $\bar{V}_2^{0*}$ and $\bar{K}_2^{0*}$ in the absence of adequate experimental data, the accuracy with which pressure effects may now be calculated in salt water is undoubtedly inferior to that of similar calculations in pure water. The effect of pressure upon several ionic equilibria in salt water is shown in figure 2. The results are compared with those previously given for pure water. It is noteworthy that, in every case so far examined, the effect of pressure and the presence of sodium chloride alter the rate of change of the equilibrium constant with pressure in the same direction, a result which may be shown to be in accord with Tammann's hypothesis.

In conclusion, we note that the relatively large factor, RT, which appears in equations 12 and 23, makes it unnecessary to know the volume and compressibility terms with high accuracy if the pressure is less than 1000 atmospheres. Furthermore, this factor is usually more important than changes of $\Delta\bar{V}^0$ with temperature, when comparisons are made at several temperatures.

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