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INFLUENCE OF PRESSURE ON CHEMICAL EQUILIBRIA IN AQUEOUS SYSTEMS—WITH PARTICULAR REFERENCE TO SEAWATER

(Technical Report)

Prepared for publication by

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Influence of pressure on chemical equilibria in aqueous systems – with particular reference to seawater (Technical Report)

Abstract: The influence of pressure on chemical equilibria in aqueous solutions and the parameters that influence such equilibria are reviewed in this work. Particular emphasis is given to equilibria in seawater, including mineral dissolution, weak acid dissociation and metal ion complexation. Intended perspectives include the capabilities of predictive models to describe chemical equilibria in low temperature geochemical systems and the extent to which predictive models are constrained by direct observations. In context of the importance of pressure as a key variable controlling the pathways and fate of environmental chemicals, a need for further direct observations of chemical equilibria at high pressure, under conditions which are often challenging to the experimentalist, is evident.

INTRODUCTION

Understanding the effect of pressure on chemical reactions and properties is important in a wide variety of disciplines, ranging from industrial properties to environmental reactions. In the seas pressures range to more than 1000 bars [1]. Such pressures can have a profound influence on equilibrium reactions in seawater, including weak acid ionization, complexation of metal ions and mineral dissolution. Since animals and bacteria are found at all ocean depths, pressure is also a major influence on the oceanic biosphere. The influence of pressure on physiological processes in seawater includes controls on enzymatic activities, transmembrane flux properties and the behavior of ionic equilibria [2]. Since the seas account for 70% of the earth's surface, thereby a major fraction of the earth's biosphere, and are a sink for industrial, domestic and nuclear wastes, it is important that we understand all the parameters that control chemical speciation and behaviour in the seas.

This review focuses on what is known about the influence of pressure on the thermodynamic aspects of chemical equilibria and the parameters that influence such equilibria in aqueous solutions—with a particular emphasis on such reactions in seawater, including mineral dissolution (solid $\rightleftharpoons$ solution equilibria). There have been many more studies on the influence of temperature on equilibrium processes but these are only mentioned here when they have been done in conjunction with pressure studies. Also not covered, but not irrelevant, are the many studies on the influence of pressure on the rates of chemical reactions, including rates of metal–ligand bond formation, and on redox processes. For these the reader is referred, in particular, to the works of van Eldik [3,4] and Swaddle [5,6]. Gas phase $\rightleftharpoons$ aqueous phase equilibria are not considered in this review because pressure is not a primary variable controlling the behaviour of such equilibria in most natural systems. Although the adsorption of highly charged metal ions on particulate matter in natural waters and seawaters is an important fundamental process in controlling environmental element distributions [7], adsorptive processes are not considered due to an extreme paucity of data relative to pressure dependencies.

Equilibria and equilibrium constants

Equilibrium constants can be expressed in a number of ways. The current accepted practice [8] is to express these in terms of formation constants (sometimes referred to as stability constants), i.e. for the general equilibrium reaction (1):



(charges omitted), the equilibrium constant, β , is given by (2):

$$\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r \quad (2)$$

Where brackets $[\]$ denote the concentrations of equilibrium species under a given set of conditions (i.e. temperature, pressure and ionic strength). H in the above equations represents the H^+ ion. In many cases $[H]$, taken from measured pH values, is used to represent ion concentration ($pH = -\log \{ [H^+]/\text{mol/dm}^3 \}$) while in other cases pH is reported in terms of H^+ activity ($pH = -\log(a_{H^+})$, a = activity of the ion [9]). In chemical oceanographic investigations involving complexation by organic ligands (L), metal concentrations ($[M]$) are conveniently taken as the total inorganic concentration, rather than as the free concentration of the metal ion (i.e. the sum of the concentrations of the species M , MCl_x , $M(CO_3)_y$, $M(OH)_z$, etc.). Likewise, for some equilibria the ligand concentration term is taken as its total concentration (e.g. in determining the acidity constant, K_{a1} for carbonate in seawater, the term $[L] = [CO_3^{2-}] + \sum [MCO_3]$). In these cases the constant so obtained is referred to as a *conditional* constant. *Stepwise* constants refer to the general equilibrium (3):



and hence $K_n = [ML_n]/[ML_{n-1}][L]$. Note, that $\beta_{101} = K_1$ and $\beta_{10n} = K_1.K_2.K_3 \dots K_n$.

For acid or base reactions it is more common for the equilibria to be expressed as stepwise acidity (dissociation) constants, as in (4):

$$K_{an} = [H][H_{n-1}L]/[H_nL] \quad (4)$$

hence, $K_{an} = \beta_{0,n-1,1}/\beta_{0,n,1}$ and $K_{a1} = 1/\beta_{0,1,1}$

All the above are concentration constants. *Thermodynamic* constants are expressed in terms of the activities (a_i) of the equilibrium species. In this case eqn 2 becomes

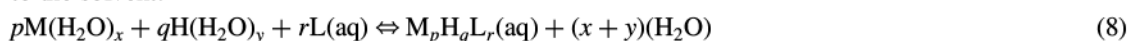
$$\beta_{pqr}^\circ = a_{M_p H_q L_r} / a_M^p \cdot a_H^q \cdot a_L^r \quad (5)$$

$$= [M_p H_q L_r] f_{MHL} / [M]^p f_M^p [H]^q f_H^q [L]^r f_L^r \quad (6)$$

$$= \beta_{pqr} \cdot \{ f_{MHL} / f_M^p f_H^q f_L^r \} \quad (7)$$

where, f_i is the activity coefficient of the ionic species i , and can be calculated as a function of the ionic strength of the medium. At infinite dilution $f_i \rightarrow 1.0$, so that $\beta_{pqr}^\circ = \beta_{pqr}$.

Omitted in the above equilibria, but of relevance to the effect of pressure, is the role of ion hydration. Equation 1, for example, is more correctly written by explicitly showing the release of waters of hydration to the solvent:



Here $(x+y)$ is the maximum number of water molecules released, charges are omitted for simplicity and the hydration of the ligand is assumed to be negligible compared to that of the (smaller) cations. Since the release of $x+y$ moles of water generally makes little difference to the total water concentration (water is also the solvent) this is usually ignored. In reality what this means is that the activity of water is taken as being unity. This is not a valid assumption over a large range of pressures.

Pressure dependence of equilibrium constants

At this point it is worth recalling LeChatelier's principle, enunciated in 1885 in relation to a reaction at equilibrium, that is: if a change occurs in one of the factors, e.g. concentration, temperature or pressure, that influence a system's equilibrium (or to be more correct the associated Gibbs free energy change) the system will readjust itself so as to annul, as far as possible, the effect of that change. In the case of pressure (and temperature) changes the new equilibrium position will establish a new equilibrium constant. For pressure changes this was expressed by Planck as:

$$RT \left(\frac{\partial \ln K}{\partial P} \right)_T = -\Delta V \quad (9)$$

ΔV is the difference between the partial molal volumes [10] of products and reactants, and (9) can equally be written with β or K_a instead of K . For molar values a density term for water needs to be added, as this varies with pressure.

Experimental measurements show that ΔV can also vary with pressure. This variation $[(\partial \Delta V / \partial P)_T]$ is given by the difference in the partial molal isothermal compressibilities between products and reactants, normally expressed as Δk .

Taking this into account and integrating eqn 9 gives:

$$RT \ln(\beta_P/\beta_0) = -\Delta V^\circ(P - 1 \text{ atm}) + 0.5\Delta k^\circ(P - 1 \text{ atm})^2 \quad (10)$$

where, ΔV° is the molal volume difference at atmospheric pressure ($P = 1 \text{ atm}$), Δk° is the partial molal (isothermal) compressibility difference at $P = 1$, and β_P and β_0 are the stability constants at pressures P and $P = 1 \text{ atm}$, respectively. This equation is claimed to give a good fit to experimental equilibrium data up to 2 kbar [11]. There have been many extensions to this equation. Above 2 kbar Δk° itself becomes pressure dependent.

As pointed out by North [12], eqn 10 is derived solely from classical thermodynamics and provides no insight into the molecular basis of ΔV° and Δk° . It is important at this stage to explore the relevant molecular features, particularly those of the solvent. As succinctly stated by Monnin [13], 'before studying the properties of solutions, one must know the thermodynamic properties of the solvent, for use in the expressions of the molal volumes and compressibilities.' This point has recently been emphasised by Swaddle [5] in terms of the intermolecular interactions between solutes and solvents.

Equation 8 reveals that association of either metal ions or hydrogen ions with a ligand involves bond-breaking ($M^{n+}-OH_2$, H^+-OH_2) and bond-making processes so that, in fairly simplistic terms, the accompanying free energy change can be broken down into covalent and ionic terms:

$$\Delta G = \Delta G(\text{ionic}) + \Delta G(\text{covalent}) \quad (11)$$

The covalent term is of importance in coordination compound formation involving, in particular, transition metal ions. The ionic contribution in (11) will be present in all systems involving a charged ligand and is a function of the medium separating the charged ions (dielectric constant and concentrations of other ions). In both terms of eqn 11, the role of water, as solvent and ligand, needs to be considered. Equilibrium processes are affected by the medium, whereby the influence of pressure on the medium itself contributes to the thermodynamic terms in (9) and (10).

Solvent and solution parameters [14,15]

A general effect of increasing pressure is to raise the melting and boiling points of liquids (above $\approx 5 \text{ GPa}$ it is impossible to prevent solidification of a liquid phase at room temperature). The raising of the melting point means that some common organic solvents have a limited liquid range under high pressures. Water, fortunately, differs in that it is more dense than ice at 0°C and hence its freezing point is actually lowered by increasing pressure—until at $\approx 300 \text{ MPa}$ where this trend is reversed. Pressure influence on the solubilities of gases and solids is apparently closely related to the melting and boiling points of the solvent. Such effects are particularly pronounced for solutions which, at room temperature, are saturated or near-saturated.

Dissolution of electrolytes in water results in a volume decrease. This is attributed to ion solvation effectively 'tying-down' some of the water molecules in the solvation shells of the ions. This phenomenon is known as *electrostriction*.

Viscosity is particularly pressure sensitive, increasing exponentially with pressure. Conductivity, a property often used in studying pressure effects, depends on the mobility of ions in solution which in turn is pressure sensitive. It was recognised sometime ago that the viscosity of an electrolyte solution (η) is related to that of pure water (η_0) by the relationship:

$$\eta = \eta_0(1 + A\sqrt{C} + BC) \quad (12)$$

where, C is the electrolyte concentration and A and B are constants of the electrolyte. The ion-solvent constant B has been shown to be divisible into intrinsic, void and electrostriction contributions. The chief value of the viscosity B coefficients (values for single ions are available) appears to lie in their indication of qualitative solvation trends and the effects of ions on solvent structural properties [16]. Note, that both single ion B -values and ionic conductances are determined by the ease of movement of solvated ions through the solution, and hence both are intimately dependent on the solvent's viscosity. In fact, the well known Stokes' law relates the effective radius, r , of a solvated ion to its mobility in solution, μ , and the solvent's viscosity, η :

$$r = 1/6\pi\eta\mu \quad (13)$$

The density (D) of liquids increases with pressure and can be described by the so-called Tait equation: ($D_0 - D_p/D_0 = C \log(1 + B/P)$) (14)

where B and C are constants characteristic of the solvent. With its low compressibility, water shows only a limited change in density ($\approx 20\%$ increase up to 1 GPa pressure) compared with other solvents. Even so, the density of water is commonly expressed as a function of pressure.

Dielectric constant is an important parameter which increases with pressure in a manner similar to the increase of density in (14). Changes in dielectric constant exert significant influences on interion electrostatic attraction and consequently the degree of formation of ion-pairs. The temperature-dependence of the dielectric constant is much larger than for pressure. For example, the dielectric constant of water at 2 kbar varies from 9.6 at 600 °C to 5.6 at 800 °C [17], whereas it only changes by a factor of ≈ 1.1 on going from 1 bar to 2 kbar. Such conditions of temperature and pressure are within the geothermal range. The low dielectric constants of geothermal fluids at such temperatures means that ion-pairing is very strong even at ligand concentrations as low as 10^{-2} molar. It should also be recalled that the dielectric constant appears as a multiplicative factor in the Debye–Hückel eqn 15, and the many extensions of this equation that relate the activity coefficient (f) of an ion to the ionic strength (I) of a solution:

$$-\log f_i = A z_i^2 \sqrt{I} \quad (15)$$

where, z_i is the charge on the ion. The A term in (15) contains the dielectric constant to the power $-3/2$.

In translating equilibrium data from zero concentration (thermodynamic constants) to higher concentrations (e.g. that of seawater) knowledge of activity coefficients and their pressure dependencies are needed. From eqn 9, and using the concentration constant β_{pqr} from (7), we get:

$$-RT(\partial \ln \beta_{pqr} / \partial P)_T = \Delta V^\circ + RT(\partial \ln \gamma / \partial P)_T \quad (16)$$

where γ is the quotient $f_{\text{MHL}}/f_{\text{M}}^p f_{\text{H}}^q f_{\text{L}}^r$ from eqn 7. Hamann [18] has pointed out that this dependence arises for two reasons: first, because the activity coefficient is intrinsically pressure dependent at constant composition (as given in the last term in eqn 16), and second, it is also solution composition dependent—as intimated above. In many cases stability constants (concentration values) are determined in media with a high inert salt concentration (e.g. 0.7 M NaClO₄ or 0.7 M NaCl to mimic seawater) but, where this is not the case, as in conductimetric measurements, the dependence of solution composition on pressure needs to be taken into account in the calculation of activity effects. There have been a number of correlations of activity coefficients with pressure and temperature changes. For a comprehensive coverage of earlier work see Millero [19]. The relation between activity coefficients and pressure at a constant temperature is most simply given by the expression:

$$\ln(f^P/f^\circ) = (V - V^\circ)P/\nu RT - 0.5(k - k^\circ)P^2/\nu RT \quad (17)$$

where ν = the number of ions formed by one molecule of the electrolyte, V and k are the partial molal volume and compressibility of the electrolyte at the ionic strength of the solution, and V° and k° are corresponding values at infinite dilution. Using partial molal volume and compressibility data (17) appears to give reasonable values up to a pressure of 1 kbar. Some representative values for f^P/f° are given in Table 1.

Table 1 Calculated influence of pressure on the activity coefficients of NaCl solutions at 25 °C {Ratio f^P/f° }*

Ionic strength (mol/dm ³)	Pressure (bars)				
	200	400	600	800	1000
0.1	1.003	1.006	1.009	1.012	1.014
0.5	1.008	1.015	1.021	1.027	1.032
1.0	1.011	1.021	1.030	1.038	1.045
2.0	1.016	1.030	1.043	1.055	1.065

* Data from [19]

The effect on the activity coefficients from Table 1 is seen to be relatively small even at 1 kbar. Omission of the compressibility term in (17) has only a minor effect. More recently Monnin [13] has used a combination of experimental data (densities and compressibilities) and Pitzer's ion interaction approach to determine activity coefficients at both high temperatures and pressures for binary and multicomponent systems. For binary systems, the activity coefficient was found to follow the relationship:

$$f = 0.5\nu|z^+z^-|A_k/b \cdot \{\ln(1 + b\sqrt{I})\} \quad (18)$$

where $A_k = (\partial A/\partial P)_T$, A is the Debye–Hückel slope and b is a constant.

Ionization of water

Owen & Brinkley [20] computed the effect of pressure on this all-important property of pure water. Some of their results are given in Table 2. Hamann [21] reports water ionization constants at pressure P (K_w^P) over a larger pressure range. At 2 kbar and 25 °C Hamann found a K_w^P/K_w° ratio equal to 4. The computed results of Owen & Brinkley for a 0.725-M NaCl solution were not greatly different from those of pure water (e.g. at 25 °C and 1000 atm K_w^P/K_w° was 2.1 compared to 2.358 for pure water).

Table 2 Calculated effect of pressure on the ionization constant for pure water*

Pressure (bars)	K_w^P/K_w°		
	5 °C	25 °C	45 °C
1	1	1	1
200	1.24	1.202	1.16
1000	2.8	2.36	2.0

* Data from [20]; K_w° = value at 1 atm.

This increase in the ionization of water with pressure will of course be reflected in all acid–base equilibria.

Acid–base (weak electrolyte) equilibria

Table 3 gives some ionization volumes for weak electrolytes. The negative and relatively large volume changes associated with ionization reactions reflect the strong solvation (and hence electrostriction) of the ions formed. For other weak electrolytes the volume changes can be calculated by an additive process, e.g. that for acetic acid (HOAc) can be obtained from other known partial molal volumes as in (19),

$$\Delta V^\circ = V^\circ(\text{NaOAc}) + V^\circ(\text{HCl}) - V^\circ(\text{NaCl}) - V^\circ(\text{HOAc}) \quad (19)$$

from which the pressure dependence of the ionization constant of acetic acid can be calculated. A number of these dependencies have also been determined experimentally (mainly by spectroscopic and conductimetric methods). There are extensive compilations of ionization volumes by Hamann [22], Asano and LeNoble [23], Isaacs [15] and Millero [24] [25].

Table 3 Ionization volumes of some weak electrolytes, at 25 °C and 1 atm*

	$\Delta V^\circ/\text{cm}^3/\text{mol}$
H ₂ O	–22.07
H ₂ S	–16.3
CH ₃ CO ₂ H	–11.5
H ₃ PO ₄	–16.5 (1st ionization) –24.0 (2nd ionization)
H ₂ CO ₃	–27.0 (1st ionization) –28.1 (2nd ionization)

* Data from [15]

Because of electrostriction accompanying ionization, the degree of ionization invariably increases with increasing pressure, i.e. weak electrolytes become stronger. Experimental measurements indicate that for carboxylic acids dissociation constants increase by a factor of about 3 when the pressure is raised to 3 kbar (at 25 °C). The corresponding increase for amines is ≈ 10 . North [12] derived an expression for the pressure dependence of weak electrolyte ion association in which the solutes are considered to be hydrated and incompressible. The expression for a partial molal volume change on this basis was taken as:

$$\Delta V_P = \Sigma V(\text{hydrated products}) - nV_w^P - \Sigma V(\text{hydrated reactants}) \quad (20)$$

where V_w^P is the partial molal volume of water at pressure P and n is the change in the number of solvated water molecules. In combination with Planck's eqn 9, he derived the expression:

$$RT/(P - 1 \text{ atm}).\ln(K_P/K_1) = -\Delta V^\circ + n[AV_w^\circ[1 - (B + P)/(P - 1 \text{ atm}).\ln((B + P)/(B + 1 \text{ atm}))]] \quad (21)$$

A and B are constants derived from literature experimental values. By plotting the left-hand side against the expression in brackets ($[\]$) a straight line was obtained for a number of electrolytes in water. The slope of the plot equals n and the intercept $-\Delta V^\circ$. The values obtained in this way for ΔV° were found to be in good agreement with experimental values. Selected ΔV° results are given in Table 4. The pressure dependence of the volume change for the investigated equilibria was shown to be a function of the number of solvated water molecules released in the course of the reactions.

Table 4 Calculated and experimental molal volumes (ΔV°) and solvation numbers (n) at 25 °C

	$\Delta V^\circ/\text{cm}^3/\text{mol}$		
	calc*	experimental	n^*
H ₂ O	-20.8	-22.1	5.2
CH ₃ CO ₂ H	-11.2	-11.5	2.3
NH ₃	-29.4	-29.4	8.0

* Calculated using eqn 21, data from [12]

Ion-pair formation

Ion-pairing is a consequence of the electrostatic attraction between ions of opposite charge to form distinct pairs $M^{x+}A^{y-}$. Their formation is reversible and hence can be described by an equilibrium constant. Significant ion-pairing occurs in solvents of low dielectric constant and in water when both charges are ≥ 2 . The amount of ion-pairs formed may readily be measured by conductivity and by partial molal volume measurements—their formation generally results in a volume increase since solvation of the ion-pair is less favourable than for the separate ions. There are two recognised types of ion-pairs; those that retain some solvation and hence referred to as 'solvent separated', and those in which solvent molecules have been excluded and referred to as 'contact pairs' (also referred to as 'outer sphere' and 'inner sphere' complexes, respectively). Both formation constants and volume changes are larger for the contact pairs (these may also have some covalent contribution to their formation). Some representative values are given in Table 5 (note that in this table *formation* of ion pairs is described and hence ΔV° refers to *association* reactions).

Recently Mesmer and his group [27] have carried out conductivity measurements on dilute aqueous sodium chloride solutions up to 600 °C and 300 MPa with results very similar to those reported earlier [28]. In keeping with the results shown in Table 4, ion association decreased with increasing pressure (but increased with increasing temperature). These authors also found a good correlation between the ion association constant (K_m) and solution density (D):

$$\log K_m/(\text{mol}/\text{dm}^3)^{-1}] = 0.997 - 650.07\text{K}/T - (10.420 - 2600.5\text{K}/T) \log D/\text{kg}/\text{dm}^3 \quad (22)$$

and indicated that this gives a better fit over the temperature and pressure range studied than did previous equations.

The occurrence of ion-pair formation in natural waters has been proposed from considerations of

Table 5 Estimated molar volume changes for ion-pair formation (25 °C and 1 atm)

M^{x+}	A^{y-}	K/mol/kg	I	$\Delta V^\circ/\text{cm}^3/\text{mol}$	Ref.
Li^+	F^-	2.2	1	6.37	[79]
Na^+	F^-	1.7	1	2.97	[79]
K^+	F^-	1.3	1	1.35	[79]
Rb^+	F^-	0.85	1	2.43	[79]
Cs^+	F^-	0.69	1	2.65	[79]
Mg^{2+}	SO_4^{2-}	212	0	8.0	[15]
Ca^{2+}	SO_4^{2-}	204	0	11.0	[15]
Cr^{3+}	OH^-	7.1×10^9	0	13	[15]
Fe^{3+}	OH^-	6.3×10^{11}	0	24	[15]
Li^+	$\text{B}(\text{OH})_4^-$	5.3	1	9.1	[80]
Na^+	$\text{B}(\text{OH})_4^-$	3.0	1	8.4	[80]
K^+	$\text{B}(\text{OH})_4^-$	2.8	1	6.5	[80]
Rb^+	$\text{B}(\text{OH})_4^-$	3.7	1	7.6	[80]
Cs^+	$\text{B}(\text{OH})_4^-$	2.8	1	6.9	[80]

activity coefficients in these media and from studies of pressure effects [29]. Although there have been very few studies made on a seawater medium, Millero and co-workers ([24], and references therein) have calculated ΔV° and Δk° values for numerous ion-pairs in aqueous solutions from molal volumes and compressibilities. The basis of this approach is the subdivision of the observed molal volumes, as in (23):

$$V(\text{observation}) = (1 - \alpha)V\{\text{MA}\} + \alpha V\{M^{x+}, A^{y-}\} \quad (23)$$

in which, α = fraction of free ions, $V\{M^{x+}, A^{y-}\}$ is the sum of the apparent molal volumes of the free ions at the ionic strength of the medium and $V\{\text{MA}\}$ is the molal volume of the ion-pair. The calculations give results in good agreement with experimental values up to 1 kbar pressure. However, as Millero points out, there is a lack of such data for seawater, mainly due to experimental difficulties. (As an example, solubility limitations for many of the salts of anions known to form ion-pairs with Mg^{2+} and Ca^{2+} make direct volume and compressibility measurements impossible).

Solid-solution equilibria

As burial rates in the deep ocean are very slow, minerals on the seafloor have long contact times with seawater. While the molar volumes of many minerals are quite large (positive), the partial molar volumes of their constituent ions in solution are negative. Consequently, partial molar volume changes for mineral dissolution are large and pressure is seen to exert strong controls on mineral solubility at high pressure.

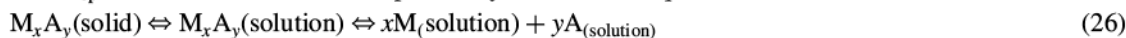
As with other equilibria, the variation of the (equilibrium) solubility product, K_{sp} , is given by:

$$(\partial \ln K_{\text{sp}}^\circ / \partial P)_T = -\Delta V_r^\circ / RT \quad (24)$$

where, ΔV_r° is the standard partial molal volume of the reaction for dissolution of the mineral, i.e.:

$$\Delta V_r^\circ = V^\circ(\text{solution}) - V^\circ(\text{solid}) \quad (25)$$

and, K_{sp} refers, in the case of a simple binary solid, to the equilibrium:



assuming total ionization of the dissolved solid, in which case, K_{sp}° is expressed in terms of activities as:

$$K_{\text{sp}}^\circ = a_M^x \cdot a_A^y = f_M^x [M]^x f_A^y [A]^y = f_M^x f_A^y \cdot K_{\text{sp}} \quad (27)$$

As such, K_{sp} is dependent on temperature and pressure and, through the activity coefficients f_M and f_A , is dependent on the ionic medium. (Note that the activity of the solid is taken as unity.)

For dilute solutions, i.e. sparingly soluble salts in water, activity coefficients approach unity and $K_{\text{sp}}^\circ = K_{\text{sp}}$. In seawater the departure of activity coefficients from unity can be large due to both ion atmosphere effects and the ion pairing or complexation of M and A in solution. Most studies of mineral solubility have focused on the influence of temperature. The small number of studies of pressure effects have found that, in general, solubilities increase with increasing pressure and that these increases can be

substantial. Linear dependencies of $\ln K_{sp}$ on pressure up to 1 kbar, indicate a generally negligible compressibility influence under such conditions. However, Millero in a very comprehensive and thoughtful review [24] concluded that the best fits to experimental data are obtained by including the effects of aqueous compressibilities in descriptions of solubility equilibria when such data are available.

Millero [24] noted differences between calculated and measured molal reaction volumes measured for seawater. These differences were attributed to deficiencies in the molal volume values or discrepancies in experimental measurements. It should also be remembered that in a multicomponent ionic system, such as seawater, there will be a number of species whose extent of formation will be correlated—a relevant example of this is the hydroxy metal species. Such correlations are more often than not ignored in calculations involving multicomponent media. One exception to this is the report by Aggarwal *et al.* [30] which includes changes in solution composition in their solubility calculations. They point out that the increased activity of free ions with increased pressure means that the influence of pressure on the saturation state of minerals will be lessened. To illustrate this they calculated the effect of pressure on the saturation states of three minerals—anhydrite, calcite and albite (an aluminosilicate)—in water, using the computer program SOLMINEQ 88. Their calculations showed a substantial difference, in pressure effects when aqueous species activities were considered in the calculations. Unfortunately, there are no direct experimental data with which to check their predictions.

INFLUENCE OF PRESSURE ON CHEMICAL EQUILIBRIA IN SEAWATER

Direct observations

Descriptions of the influence of pressure on chemical processes in seawater have included acid-base equilibria, ion-pairing equilibria and the solubility of minerals. In many cases, characterisations of equilibria in seawater are based upon models and observations of the behaviour of dilute solutions rather than direct observations of seawater. A partial summary of previous experimental investigations of equilibrium pressure dependencies relevant to seawater is shown in Table 6. The best characterised reactions shown in this table are those for the reactions of H^+ with $B(OH)_4^-$, CO_3^{2-} and HCO_3^- . This emphasis was undoubtedly given in response to the dominant controls exerted by these reactions on the acid-base behaviour of seawater. A second substantial focus, seen in Table 7, is the ion pairing behaviour of SO_4^{2-} . Observations of the influence of pressure on sulfate ion pairs with monovalent, divalent and trivalent cations account for nearly all direct measurements of the partial molal volume changes which accompany ion pairing reactions. An assessment of the magnitudes of the partial molal volumes of reaction in Table 7 shows that ΔV° (25 °C) for SO_4^{2-} ion pairs generally follows the trend which would be expected from increasing extents of hydration for monovalent, divalent and trivalent cations. For monovalent cations, ΔV° (25 °C) ranges between 3.3 and 7.8 cm³/mol, for divalent cations ΔV° (25 °C) ranges between 7.3 and 10.1 cm³/mol, and ΔV° (25 °C) for trivalent lanthanides is of the order of 25 cm³/mol. Partial molal volume changes for reactions of H^+ with SO_4^{2-} , CO_3^{2-} , HCO_3^- , $B(OH)_4^-$, and OH^- range between 22 cm³/mole and 33 cm³/mole. The large ΔV° (25 °C) values in these cases also follow from the much larger change in H^+ hydration state during ion pairing than is the case for ion pairing of larger monovalent cations.

In addition to studies of the influence of pressure on solution equilibria (Tables 6 and 7), the influence of pressure on mineral solubility has been studied in both aqueous electrolytes and seawater. The variety of minerals which have been investigated includes CaF_2 [31], $SrSO_4$ [31,32], $Si(OH)_4$ [33,34] and $CaCO_3$ [35–39]. Seawater is undersaturated at all depths with respect to formation of CaF_2 , $SrSO_4$, and hydrated silica. In contrast, with respect to both major oceanic polymorphs of $CaCO_3$ (calcite and aragonite) seawater is undersaturated at great depth and supersaturated in the upper ocean. The molar volumes of calcite and aragonite are 36.93 cm³/mol and 34.15 cm³/mol. The corresponding molar volume changes for calcite and aragonite dissolution in seawater are approximately –36.5 cm³/mol at 5 °C [40].

The significance of pressure on oceanic equilibria

Based upon direct observations of the effect of pressure on equilibria relevant to seawater it is known that pressure substantially influences the distributions of a variety of important chemical species in seawater.

Table 6 Experimental observations (25 °C) of the influence of pressure on ionization equilibria relevant to seawater ($HX = H^+ + X$)

HX	$\Delta V^\circ/\text{cm}^3/\text{mol}$	Dilute solutions	Seawater	$\Delta V^\circ/\text{cm}^3/\text{mol}$
H_2O	-22.05	[21,81]	—	—
$\text{B}(\text{OH})_3^\circ$	-32.5 ± 2.7	[82–85]	[105]	-25.7
H_2CO_3	-27.4	[82,86,87]	[105]	-22.6
HCO_3^-	-28.1	[82]	[105]	-14.6
HSO_4^-	-21.6	[88]	—	—
H_2S	-15.0	[89,90]	—	—
HF	-13.7	[15]	—	—
NH_4^+	+6.9	[91,92]	—	—
H_3PO_4	-16.3	[90,93]	—	—
H_2PO_4^-	-24.0	[15]	—	—
HPO_4^{2-}	—	—	—	—

Table 7 Experimental observations (25 °C) of the influence of pressure on ion pairing equilibria relevant to seawater ($M + X = \text{MX}$)

MX	$\Delta V^\circ/\text{cm}^3/\text{mol}$	Dilute solutions	Seawater
LiSO_4^-	5.8	[94]	—
NaSO_4^-	7.8 ± 0.5	[94,95]	[50]
KSO_4^-	5.9	[94,96]	—
RbSO_4^-	3.3	[94]	—
CsSO_4^-	6.2	[94]	—
$\text{NH}_4^+ \text{SO}_4^-$	3.4	[94]	—
CaSO_4°	11.0	[15]	—
MgSO_4°	7.3	[49,97]	—
MnSO_4°	8.2 ± 0.3	[98–100]	[98,99]
CoSO_4°	9.3 ± 2.3	[100]	—
NiSO_4°	10.1 ± 1.5	[98–100]	—
CuSO_4°	9.6 ± 1.6	[98,99,101]	—
ZnSO_4°	9.2 ± 1.1	[101]	—
$\text{NaB}(\text{OH})_4^\circ$	8.4 ± 0.4	[102]	—
LaSO_4^+	23.7 ± 2.5	[103]	—
EuSO_4^+	25.6	[104]	—
GdCO_3^+	54	—	[44]
FeOH^{2+}	26.9	[65]	—

The magnitudes of the partial molal volume changes for protonation of $\text{B}(\text{OH})_4^-$, CO_3^{2-} and HCO_3^- in seawater (Table 6) are sufficient to decrease the pH of seawater by about 0.15 units between the surface and the average depth of the seafloor (4000 m). The solubility product of calcite and aragonite over this depth range increases by approximately a factor of two. Figure 1 shows the predicted solubility product (K_{sp}') of calcite relative to the surface ocean K_{sp}' , for temperature and salinity conditions encountered in the Pacific Ocean at $9^\circ 37.1'\text{S}$ and $103^\circ 34.0'\text{W}$ [41]. Temperature and salinity exert only a small influence on the CaCO_3 solubility product over the range of temperature $26.18^\circ\text{C} \geq t \geq 1.81^\circ\text{C}$ and salinity $36.16 \geq S \geq 34.52$ at this station. The solubility product of calcite (and aragonite) in the open ocean is principally controlled by pressure. In the context of transitions from $\text{CaCO}_{3(\text{s})}$ supersaturation to undersaturation at mid-depths in the oceans [42] and the high order dependence of $\text{CaCO}_{3(\text{s})}$ dissolution rates on saturation state [40,43], pressure is seen to exert a major control on global CO_2 cycling behaviour on both long and short time scales. Although the reaction volumes for marine phosphorites such as fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) have not been directly measured, the large

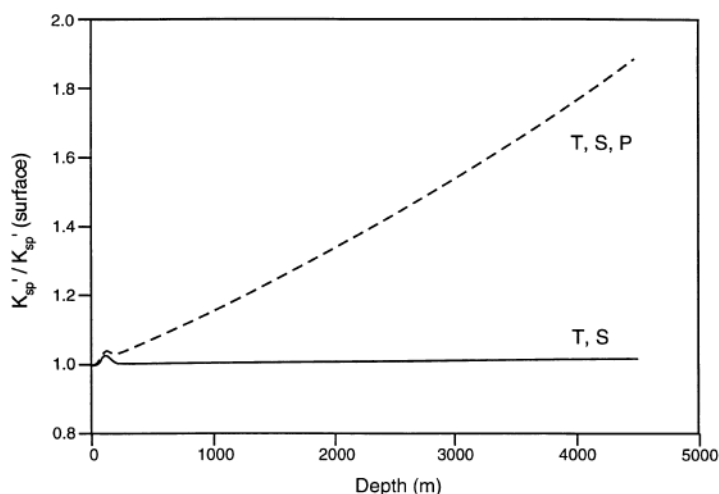


Fig. 1 The influence of temperature, salinity and pressure on the solubility product of calcite is shown for conditions typical of the equatorial Pacific ocean. An inflection point in calculated $K_{sp}'/K_{sp}'(\text{surface})$ is observed due to a lens of high salinity seawater centered at approximately 100 m. Calculated curves are shown which include the effects of temperature, salinity and pressure (T, S, P) and which include only the effects of temperature and salinity (T, S).

molal volumes of these minerals ($V \approx 160 \text{ cm}^3/\text{mol}$) strongly suggest that hydrostatic pressure exerts a significant influence on the persistence of phosphorite deposits in marine sediments. From the increasing trend in the ΔV values for complexation of monovalent, divalent and trivalent cations by SO_4^{2-} , it should be expected that pressure will exert much larger controls on the chemical behaviour of trivalent and tetravalent metals in seawater than is the case for divalent metals. While the partial molal volume changes for lanthanide complexation by SO_4^{2-} is comparatively large ($\Delta V \approx 25 \text{ cm}^3/\text{mol}$), direct observations [44] of lanthanide complexation by CO_3^{2-} in synthetic seawater produced ΔV estimates for GdCO_3^+ formation of the order of $54 \text{ cm}^3/\text{mol}$ or larger. In view of the importance of higher order lanthanide complexes ($\text{Ln}(\text{CO}_3)_2^-$) in seawater [45,46], presumably with larger ΔV values than those for LnCO_3^+ formation, the influence of pressure on the equilibria of these metals in seawater should be considerably larger than is the case for the protonation of $\text{B}(\text{OH})_4^-$, CO_3^{2-} , and HCO_3^- . The substantial importance of higher order hydrolysis products ($\text{M}(\text{OH})_3$ and $\text{M}(\text{OH})_4$ for trivalent and tetravalent cations in seawater [47] suggests that pressure may exert a much larger influence on the free ion concentrations of these metals (M^{3+} and M^{4+}) than is the case for the influence of pressure on $[\text{H}^+]$ in seawater.

Questions of the significance of pressure in controlling oceanic processes are not limited to those surrounding the absolute magnitudes of ΔV for chemical equilibria. In the case of sulfate ion pairing in seawater, it is known that interactions with Na^+ , Mg^{2+} and Ca^{2+} partitions sulfate between NaSO_4^+ , MgSO_4° , CaSO_4° and free SO_4^{2-} . The fraction of the total sulfate, which is present as MgSO_4° is of special interest in this case because magnesium sulfate ion pairs exist in several forms (MgSO_4 , $\text{Mg}(\text{H}_2\text{O})\text{SO}_4$ and $\text{Mg}(\text{H}_2\text{O})_2\text{SO}_4$) and interconversion of these chemical forms causes attenuation of acoustical energy in seawater [48,49]. The dependence of sound attenuation on depth in the oceans is influenced by the relative magnitudes of the molal volume changes for NaSO_4^- , MgSO_4° and CaSO_4° formation in seawater. If ΔV for NaSO_4^- is sufficiently large compared to ΔV for MgSO_4° in seawater, SO_4^{2-} liberated from NaSO_4^- dissociation with increasing pressure results in increasing MgSO_4° concentrations in spite of decreasing MgSO_4° formation constants with increasing pressure. Due to an absence of direct measurements of ΔV for MgSO_4° and CaSO_4° under conditions relevant to seawater, predictions of increasing [50] or nearly constant [51] sound attenuation with increasing depth in seawater are model dependent.

Predictions of equilibrium pressure dependencies

Predictions of the dependence of seawater equilibria on hydrostatic pressure are based on both direct

observations and modelled behaviour. Millero [24] has provided an extensive summary of observations and procedures that can be used to assess the partial molal volume behaviour of a variety of ions and complexes in seawater. Millero's partial molal volume assessment [24] principally covers the major constituents of seawater (concentrations $\geq 1 \times 10^{-4}$ molal) and the protonation behaviour of important interactive anions such as OH^- , HS^- and phosphate. In the absence of direct observations, partial molal volume estimations can involve application of specific interaction models [52,53], Young's rule [54–56] and semiempirical methods and correlations [19,57,58]. A partial summary of Millero's [24] partial molal volume predictions at 25 °C for freshwater and seawater is shown in Table 8. The V° (water) values shown in column 2 show correlations with both ionic radius and ionic charge. Comparisons of V° values for Na^+ and K^+ , as well as F^- and Cl^- , demonstrates the influence of ionic radius on V° values. Comparisons of V° values for $\text{HCO}_3^-/\text{CO}_3^{2-}$ and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ show the substantial reductions in V° values (i.e. increasingly negative V°) attributable to strong hydration of highly charged ions.

Table 8 Conventional* partial molal volumes, $V^\circ/(\text{cm}^3/\text{mol})$ at 25 °C†

Species	Water	Seawater
H_2O	18.07	18.05
$\text{B}(\text{OH})_3^\circ$	39.22	40.46
H_3PO_4	47.71	–
H^+	0	0
Na^+	–1.21	–0.72
K^+	9.03	9.61
Mg^{2+}	–21.15	–19.67
Ca^{2+}	–17.83	–16.00
Sr^{2+}	–17.86	–15.67
F^-	–1.16	1.91
Cl^-	17.82	19.64
OH^-	–3.98	–0.05
$\text{B}(\text{OH})_4^-$	21.84	32.78
HCO_3^-	24.29	27.76
H_2PO_4^-	31.42	–
SO_4^{2-}	13.98	22.38
CO_3^{2-}	–3.78	13.2
HPO_4^{2-}	5.53	–
PO_4^{3-}	–30.46	–

* Data from [39].

† 'conventional' values are defined as relative to $V^\circ(\text{H}^+) = 0$ at 25 °C.

Differences between V° (water) and V° (seawater) are generally small for neutral and singly charged ions. Differences between V° (water) and V° (seawater) are also small for doubly charged cations but not for doubly and triply charged anions. This apparent divergence in the behaviour of cations and anions in pure water and seawater is dominantly attributable to the different conventions used in describing the V° behavior of cations and anions in seawater. In Table 6, ΔV° (seawater) values for the species CO_3^{2-} , HCO_3^- and $\text{B}(\text{OH})_4^-$ are defined, conventionally, in terms of the V° properties of those ions summed over their free and ion-paired forms. As an example, CO_3^{2-} in seawater is comprised of both free ions and ion pairs with Na^+ , Mg^{2+} and Ca^{2+} . Approximately 85% of the carbonate ions in seawater are ion paired as NaCO_3^- , MgCO_3° and CaCO_3° . These ion pairs, with low ionic charge, have much larger V° values than free hydrated CO_3^{2-} and thereby contribute to the substantial observed increase in V° for carbonate ions between water (where all CO_3^{2-} is free) and seawater (where CO_3^{2-} is dominantly complexed). This conventional description of the V° (seawater) behavior of CO_3^{2-} and HCO_3^- allows quantitative descriptions of CO_3^{2-} and HCO_3^- protonation in seawater without auxiliary characterizations of ΔV° for CO_3^{2-} and HCO_3^- ion pairing reactions with Na^+ , Mg^{2+} and Ca^{2+} .

The influence of ion pairing on phosphate partial molal volume behaviour is expected to be much

larger than is the case for carbonate. As is the case for CO_3^{2-} , due to the constancy of seawater composition and the low concentrations of PO_4^{3-} and HPO_4^{2-} compared to Na^+ , Mg^{2+} and Ca^{2+} , the partial molal volumes of PO_4^{3-} and HPO_4^{2-} in seawater can be expressed in terms of a summation over free and ion paired forms of phosphate. The association constants for formation of CaPO_4^- and MgPO_4^- in seawater are on the order of 3×10^4 and 6×10^3 , whereupon the dissociation of free HPO_4^{2-} in seawater leads predominantly to the formation of the species CaPO_4^- and MgPO_4^- , which should have substantially larger partial molal volumes than free PO_4^{3-} . Due to the insolubility of phosphate salts under neutral to weakly alkaline conditions in seawater, the molar volume properties of these ion pairs are, at present, unknown. Lo Surdo *et al.* [59] assessed the influence of pressure on phosphate equilibria through measurements of the apparent molal volumes of aqueous sodium and potassium phosphate solutions. In the absence of direct observations of molal volume changes for PO_4^{3-} ion pairing with Ca^{2+} and Mg^{2+} or direct observations of H_2PO_4^- and HPO_4^{2-} dissociation in seawater at high pressure, capabilities for describing the physical chemistry of phosphate in the deep ocean will remain limited.

Solubility limitations, which are an inherent problem in descriptions of phosphate equilibria in seawater, are also the central cause of a nearly complete absence of direct observations of the influence of pressure on trace metal equilibria in seawater. As a result of challenging experimental constraints, partial molal volume characterisations for the more abundant, less reactive, constituents in seawater have only recently been extended to include the more highly reactive trace constituents of seawater. Shock and co-workers [60–64] have examined correlations among the standard molal thermodynamic properties of aqueous ions and complexes (molal entropies, enthalpies, volumes, etc.) which allow calculation of the physico-chemical properties of a wide variety of geochemically important equilibria at high temperatures and pressures. With respect to the partial molal volume characteristics of equilibria, the correlations of Shock and co-workers are based upon very few direct observations. Although the characterizations of Shock and co-workers are primarily intended for predictions at high temperatures, they also provide useful interim predictions of the behaviour of important chemical equilibria at high pressure and low temperatures.

Table 9 summarises predicted [5,63,64] molal volumes and volume changes (1 atm and zero ionic strength) for geochemically important equilibria in seawater. Three types of equilibria are considered in Table 9: (i) Cations whose complexation behaviour in seawater is strongly dominated by chloride complexation are represented by Ag^+ , Au^+ , Hg^{2+} and Au^{3+} ions; (ii) Trivalent lanthanide and actinide ions whose seawater speciation is strongly dominated by carbonate complexation are represented by Gd^{3+} ; (iii) Tetravalent and small trivalent cations, whose equilibria in seawater are strongly dominated by hydrolysis are represented by Al^{3+} , Fe^{3+} and Hf^{4+} .

Examination of the cumulative molal volume changes ($\Sigma \Delta V_n$) for chloride complexation ($\text{M} + n\text{Cl}^- = \text{MCl}_n$) of Ag^+ , Au^+ , Cu^+ and Hg^{2+} shows similar and consistent molal volume changes with increasing chloride concentration. Increasing pressure uniformly favours species of higher positive charge (lower extent of complexation). Since the dominant complex of Ag^+ , Au^+ and Cu^+ in seawater is expected to be MCl_3^{2-} [47], with ΔV values on the order of $34 \text{ cm}^3/\text{mol}$, the degree of complexation (ratio of total metal to free metal) is predicted to decrease by approximately a factor of four in response to pressure changes between the surface ocean and 10 000 m depths. Since the dominant species of Hg^{2+} in seawater is HgCl_4^{2-} , the cumulative molal volume change ($\Sigma \Delta V = 42.6 \text{ cm}^3/\text{mole}$) given in Table 9 indicates that the total metal to free metal concentration ratio between the surface ocean and 10 000 m will decrease by approximately a factor of six. In response to a decrease in temperature between 25°C and 5°C the overall extent of Ag^+ and Cu^+ complexation increases by a factor smaller than three, and the extent of Hg^{2+} complexation increases by a factor of approximately five [47]. These comparisons indicate that the influences of temperature and pressure on the complexation of these ions by Cl^- are in opposition, and are of comparable magnitudes. Figure 2 shows the calculated influence of salinity and temperature on the ratio of Ag^+ and AgCl_3^{2-} concentrations in the Pacific Ocean at $9^\circ 37.1'\text{S}$ and $103^\circ 34.0'\text{W}$. The enthalpy data for these calculations were taken from [47] and the partial molal volume change for complexation of Ag^+ by Cl^- is given in Table 9. Figure 2 shows that the $[\text{Ag}^+]/[\text{AgCl}_3^{2-}]$ ratio decreases rapidly between the surface and 1000 meters in response to a decrease in temperature of about 22.6°C . Over the next 3 km the temperature at this station [41] changes by only 2.8°C and pressure exerts a dominant influence on Ag^+ speciation. In sharp contrast to this result, the cumulative volume change for the complexation

Table 9 Estimated partial molal volume behaviour [62–64] for selected trace metal equilibria at 25 °C and infinite dilution

Species	$V^\circ/\text{cm}^3/\text{mol}$	$\Delta V_n^\circ/\text{cm}^3/\text{mol}$	$\Sigma\Delta V_n^\circ/\text{cm}^3/\text{mol}^\dagger$
H^+	0	–	–
Cl^-	17.8	–	–
CO_3^{2-}	–5.0	–	–
H_2O	18.1	–	–
Ag^+	–0.8	–	–
AgCl°	25.2	8.2	8.2
AgCl_2^-	54.4	11.4	19.6
AgCl_3^{2-}	86.8	14.6	34.2
AgCl_4^{3-}	123.0	18.4	52.6
Cu^+	–8.0	–	–
CuCl°	17.2	7.4	7.4
CuCl_2^-	45.4	10.4	17.8
CuCl_3^-	76.9	13.7	31.5
Au^+	12.5	–	–
AuCl°	38.6	8.3	8.3
AuCl_2^-	69.3	12.9	21.2
AuCl_3^{2-}	103.4	16.3	37.5
Hg^{2+}	–19.6	–	–
HgCl^+	4.4	6.2	6.2
HgCl_2°	31.2	9.0	15.2
HgCl_3^-	61.0	12.0	27.2
HgCl_4^{2-}	94.2	15.4	42.6
Au^{3+}	–31.4	–	–
AuCl_4^-	–20.7	–	–60.5
Al^{3+}	–44.4	–	–
AlOH^{2+}	–2.2	24.1	24.1
Al(OH)_2^+	18.7	2.8	26.9
Al(OH)_3°	31.1	–5.7	21.2
Al(OH)_4^-	46.2	–3.0	18.2
Fe^{3+}	–37.0	–	–
FeOH^{2+}	–24.9	–6.0	–6.0
Fe(OH)_2^+	–23.7	–16.9	–22.9
Fe(OH)_3°	25.3	30.9	8.0
Fe(OH)_4^-	37.1	–6.3	1.7
Hf^{4+}	–54.4	–	–
Hf(OH)^{3+}	–12.9	23.4	23.4
Hf(OH)_2^{2+}	15.6	10.4	33.8
Hf(OH)_3^+	35.1	1.4	35.2
Hf(OH)_4°	36.3	–16.9	18.3
Hf(OH)_5^-	61.6	7.2	25.5
Gd^{3+}	–40.4	–	–
GdCO_3^+	–23.1	22.3	22.3

$^\dagger \Sigma\Delta V_n^\circ = \Delta V_1^\circ + \Delta V_2^\circ + \dots \Delta V_n^\circ$

equilibrium $\text{Au}^{3+} + 4\text{Cl}^- = \text{AuCl}_4^-$ is negative, whereby increasing pressure favours complexation. Since substantial charge neutralisation is generally expected to produce positive molal volume changes for ionic equilibria, this surprising prediction deserves further scrutiny.

In contrast to the generally regular pattern of molal volume changes for reactions involving chloride, the ΔV patterns for stepwise hydrolysis of Al^{3+} , Fe^{3+} and Hf^{4+} are irregular and dissimilar. While ΔV for formation of AlOH^{2+} and HfOH^{3+} are highly positive, ΔV for FeOH^{2+} formation is negative. Formation of the uncharged species Fe(OH)_3° from Fe(OH)_2^+ is accompanied by a very large positive

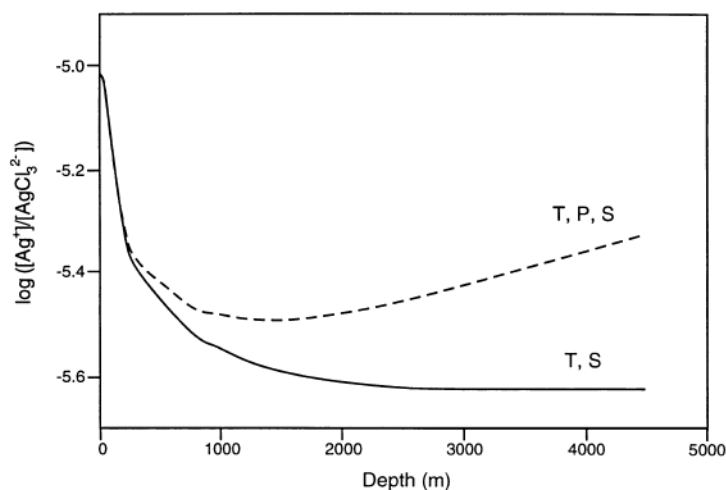


Fig. 2 The influence of temperature, salinity and pressure on the calculated ratio of Ag^+ and AgCl_3^{2-} concentrations is shown for the same hydrographic conditions depicted in Fig. 1. In response to salinity variations between approximately 36.16 and 34.52 at this station, the chloride ion concentration varies between approximately 0.587 mol/kg(H_2O) and 0.561 mol/kg(H_2O).

molal volume change while molal volume changes for formation of neutral species from $\text{Al}(\text{OH})_2^+$ and $\text{Hf}(\text{OH})_3^+$ are negative. It is difficult to rationalise the predicted ΔV behaviour for FeOH^{2+} , whereby increasing pressure favours the formation of FeOH^{2+} from Fe^{3+} ($\Delta V_1 = -6 \text{ cm}^3/\text{mol}$) and formation of $\text{Fe}(\text{OH})_2^+$ from FeOH^{2+} ($\Delta V_2 = -16.9 \text{ cm}^3/\text{mol}$), followed by a dramatic reversal of this trend in the form of a positive ΔV_3 for $\text{Fe}(\text{OH})_3^\circ$ formation ($\Delta V_3 = +30.9 \text{ cm}^3/\text{mol}$).

Prediction of a negative ΔV value for FeOH^{2+} formation is important because this equilibrium is one of the few trace metal reactions which has been relatively well-studied. The direct spectrophotometric observations of Martinez *et al.* [65] indicate that ΔV for the reaction $\text{Fe}^{3+} + \text{H}_2\text{O} = \text{FeOH}^{2+} + \text{H}^+$ at infinite dilution is positive ($\Delta V = +4.8 \pm 0.3 \text{ cm}^3/\text{mol}$). The nearly $11 \text{ cm}^3/\text{mol}$ difference between this observation [65] and predictions (Table 9) is of special significance because of the use of FeOH^{2+} molal volume properties by Sverjensky *et al.* [63] for general predictions of MOH^{2+} molal volume behaviour for first hydroxide complexes of trivalent metals.

A decrease in temperature between 25°C and 5°C is expected [47] to decrease the overall extent of Al^{3+} , Fe^{3+} and Hf^{4+} complexation in seawater by factors of ≈ 30 – 50 . The positive $\Sigma\Delta V$ values for aluminium and hafnium hydrolysis indicate that increasing pressure will further reduce the extent of these metal's complexation in seawater. The unusual behaviour of molal volume changes for Fe^{3+} hydrolysis (Table 9) makes the reliability of predicted $\text{Fe}(\text{III})$ speciation in the deep ocean uncertain. In general, ΔV predictions for hydrolysis equilibria are very data-limited and have complex and unusual behaviours. Further experimental investigation is prerequisite to reliable predictions of the influence of pressure on hydrolysis equilibria.

The molal volume change predicted for GdCO_3^+ formation in Table 9 is approximately equal to the observed (Table 7) molal volume changes for complexation of La^{3+} and Eu^{3+} by SO_4^{2-} . Formation constants for lanthanide complexation by carbonate [45] are larger than those for sulphate complexation [66] by more than three orders of magnitude. It is reasonable to expect that the stronger complexation of lanthanides by carbonate ions would prove more effective in liberating a portion of the eight to nine lanthanide waters of hydration than is the case for sulfate ions. If so, it would be expected that ΔV values for carbonate complexation should be larger than the ΔV values for LaSO_4^+ and EuSO_4^+ formation shown in Table 7. Some support for this contention is provided in a study in synthetic seawater [44] which indicated $\Delta V > 54 \text{ cm}^3/\text{mol}$ for the reaction $\text{Gd}^{3+} + \text{CO}_3^{2-} = \text{GdCO}_3^+$.

Lanthanide complexation in seawater involves both MCO_3^+ and $\text{M}(\text{CO}_3)_2^-$ formation. No ΔV predictions for $\text{M}(\text{CO}_3)_2^-$ formation are currently available. However, since ΔV values for $\text{M}(\text{CO}_3)_2^-$ formation should be larger than those for MCO_3^+ formation, it seems clear that pressure will exert

significant controls on lanthanide complexation in seawater. Since the reaction enthalpies for lanthanide complexation are very small [45], pressure is expected to exert a greater influence than temperature on lanthanide complexation behaviour in the oceans.

The importance of direct observations of equilibria at high pressure

Based on the limited evidence available it seems clear that, over the range of temperature extremes encountered in seawater (i.e. $\Delta t \cong 30^\circ\text{C}$), the influence of temperature on many chemical equilibria in seawater is substantially larger than the influence of pressure. Nevertheless, it is important to note that temperatures within approximately 80% of the ocean's volume are between 0°C and 5°C [67]. Since most of the ocean's volume is nearly isothermal, the oceanic environment provides an unusual emphasis on pressure as an important variable influencing chemical processes.

Published work on the influence of pressure on chemical equilibria at low temperature provides an incomplete and uncertain picture of the role of ocean depth (pressure) on chemical equilibria. A major emphasis in previous work on equilibrium pressure dependencies has been given to the ionic interactions of sulfate. The interactions of sulfate in seawater are important with respect to the major cationic constituents of seawater (Na^+ , Mg^{2+} , Ca^{2+} and Sr^{2+}) and significant issues with respect to the dependence of the concentration of MgSO_4° on pressure [51] remain unresolved. However, the importance of SO_4^{2-} interactions on the behaviour of reactive trace constituents of seawater is very limited. Only a very small fraction ($\leq 10\%$) of divalent trace metals (e.g. Fe^{2+} , Mn^{2+} , Zn^{2+}) is complexed with sulfate and the behaviour of trivalent and tetravalent metals in seawater is strongly dominated by hydrolysis equilibria and carbonate complexation. Furthermore, the very similar magnitudes of ΔV for sulfate ion pairing of divalent metals (Table 7) indicates that the influence of pressure on sulfate ion pairing will have little influence on the comparative chemistries of these elements. In the context of current models of seawater chemical speciation [47,68], and the comparative abundance of ΔV° characteristics for sulfate ion pairing, it is probable that further investigation of sulfate complexation will result in only minor improvements in understanding the influence of pressure on metal behaviour in seawater.

Although significant uncertainties remain in characterisations of the influence of pressure on acid-base equilibria in seawater, the greatest area of uncertainty in predicting the influence of pressure on oceanic equilibria is certainly that of the behaviour of reactive trace metals. Current predictive models for trace metal behaviour at high pressure [63,64] are based not only on a very limited database, but also on data of questionable quality. Sverjensky *et al.* [63] have highlighted the importance of critical experiments in order to confirm or refine thermodynamic predictions based on correlations among equations-of-state parameters and standard partial molal properties (25°C and 1 bar). In some cases it appears that critical experimental data are already available. The data of Martinez *et al.* [65] strongly suggest that the partial molal volume data selected for FeOH^{2+} and CrOH^{2+} [63], upon which molal volume estimates for all other MOH^{2+} species are based, are flawed. Clearly, there is a critical need for further experimental investigation of hydrolysis equilibria at high pressure.

Through the use of the computational procedures of Shock and co-workers [60–64] a relatively small base of high quality data may be used to provide wide-ranging characterisations of hydrolysis behaviour at high pressure. A strong case can also be made for the importance of a few high quality observations furthering an understanding of the influence of pressure on yttrium, lanthanide and trivalent actinide behaviour in seawater. The complexation behaviour of these elements is very highly correlated [69]. Measurements of the influence of pressure on MCO_3^+ and $\text{M}(\text{CO}_3)_2^-$ formation for even a few elements should provide reliable assessments of the comparative solution chemistries of approximately 16 elements throughout the range of conditions encountered in seawater.

Although all of the preceding discussion of complexation phenomena in seawater has been devoted to inorganic species, it is well known that the solution chemistry of some metals in seawater is strongly influenced, if not dominated, by organic complexation [70–77]. The conditional formation constants for metal complexation by natural organic ligands [78], present in seawater at nanomolar concentrations, are of the order of 10^{13} and greater. At the present time no investigations of the role of pressure or temperature on complexation by this class of very strongly complexing ligands have been performed.

Although the importance of organic complexation on trace metals is largely confined to the shallow ocean where ligand concentrations exceed metal concentrations [78], investigations of the role of pressure on these organic complexation equilibria could provide important insights surrounding the coordinative properties and molecular architecture of these ligands. At present there is little known about the nature of organic ligands in seawater other than complexation capacity and comparative complexation behaviour. As a starting point, there is a definite need for experimental studies of metal complexation with well-defined organic ligands of relevance to seawater, at atmospheric pressure as well as at high pressures.

CONCLUSIONS

Hopefully, this review will stimulate both chemical oceanographers and 'bench' chemists to take a renewed interest in the influence of pressure on chemical speciation in seawater. As we have attempted to indicate—changes in speciation can have a profound influence on the behaviour of both inherent (biological) and extraneous (e.g. wastes) systems in the ocean depths. What is strikingly apparent is the dearth of experimental data, for both pure water and, particularly, seawater.

Interpretations of pressure effects have mostly been made on the basis of molal volume changes. There now appears to be good agreement for many simple systems between calculated and the limited number of experimental values of molal volume changes. As indicated here there are a number of other pressure-dependent physico-chemical factors that influence the behaviour of ion-solvent and ion-ion interactions. This raises the question as to whether interpretations based solely on molal volume changes of chemical equilibria adequately describe the behaviour of the system. What would be useful in this context would be studies, initially on well defined systems, to compare results from molal volume changes with those from other equilibrium-related measurements, e.g. spectroscopic determinations. In complex multiequilibrium systems, such as seawater, the interdependence (correlation) between systems at equilibrium needs to be taken into account.

Finally, there is an obvious urgent need to define the, all important, organic systems present in seawater and their role in metal binding—both homogeneously (aqueous phase) and heterogeneously (particulate adsorption).

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