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The effect of pressure on the thermodynamic properties of seawater

by Frank J. Millero¹ and Donald R. Schreiber¹

For many thermodynamic calculations in oceanography it is necessary to know the effect of pressure (or depth) on various thermodynamic properties. For example, to determine the adiabatic temperature gradient one needs to know the effect of pressure on the heat capacity (cp) which can be calculated from

$$cp^P = cp^0 - T \int_0^P (\partial^2 v / \partial T^2) dP \quad (1)$$

where P is the applied pressure, v is the specific volume and T is the absolute temperature. The differentials needed for this and other calculations can be derived from the equation of state of seawater. Recently, a new equation of state for seawater (Millero *et al.*, 1980; Millero and Poisson, 1981) has been adopted by the UNESCO/ICES/IAPSO joint panel on oceanographic tables and standards. By appropriate differentiation of this equation of state, it is possible to determine the pressure derivatives for the specific volume of seawater solutions.

To estimate the effect of pressure on the partial molal thermochemical properties (Millero and Leung, 1976), it is necessary to know the partial molal volumes of "sea salt" and water as a function of pressure. This can be accomplished by fitting the apparent molal volumes (ϕ_v) of seawater solutions to a function of pressure. The values of ϕ_v are defined by

$$\phi_v = \frac{10^3(\rho_0 - \rho)}{\rho_0 \rho m} + \frac{M_T}{\rho} \quad (2)$$

where ρ_0 is the density of water, ρ is the density of seawater, m is the molality and M_T is the molecular weight of "sea salt" (Millero and Leung, 1976). The partial molal volumes of sea salt and water are related to ϕ_v by

$$V_2 = \phi_v + m(\partial\phi_v/\partial m)_{T,P} \quad (3)$$

$$V_1 = V_1^0 - (m^2 M_1 / 1000) (\partial\phi_v/\partial m)_{T,P} \quad (4)$$

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Table 1. Coefficients for the equation $\phi_v = \phi_v^* + AI^{1/2} + BI$ for "sea salt"**.

Term	Coefficients
For ϕ_v^* , $\phi_v^*(0^\circ\text{C})$	11.224
t	2.5893(E-1)
t^2	-5.0642(E-3)
t^3	5.4345(E-5)
t^4	-3.636(E-7)
P	8.3479(E-3)
Pt	-2.3294(E-4)
Pt^2	5.5830(E-6)
Pt^3	-6.4740(E-8)
Pt^4	3.370(E-10)
P^2	-2.3834(E-6)
P^2t	7.0171(E-8)
P^2t^2	-1.5533(E-9)
P^2t^3	1.171(E-11)
P^2	2.210(E-10)
For A , $I^{1/2}$	2.7839
$I^{1/2}t$	-5.5030(E-2)
$I^{1/2}t^2$	9.1918(E-4)
$PI^{1/2}$	-5.6947(E-4)
$PI^{1/2}t$	5.2892(E-5)
$PI^{1/2}t^2$	-1.4151(E-6)
$PI^{1/2}t^3$	6.170(E-9)
$P^2I^{1/2}$	4.158(E-7)
$P^2I^{1/2}t$	-1.974(E-8)
$P^2I^{1/2}t^2$	3.272(E-10)
For B , I	1.6777(E-1)
It	-4.375(E-3)
PI	-9.007(E-4)
PII	1.059(E-5)
P^2I	1.326(E-7)

* The standard error of the fit is $0.0016 \text{ cm}^3 \text{ mol}^{-1}$. A check value for $\phi_v = 20.619127$ at $I = 0.723$, $t = 25^\circ\text{C}$ and $P = 1000\text{b}$. The densities calculated from the ϕ_v equation agree with the equation of state to $\pm 5 \times 10^{-6} \text{ g cm}^{-3}$ over the entire temperature, salinity and pressure range.

where the molar volume of water at infinite dilution $\bar{V}_1^0 = M_1/\rho_0$, $M_1 = 18.0154$ is the molecular weight of water.

We have calculated values of the ϕ_v of seawater solutions from 0 to 40°C ($t = 5^\circ$ intervals), 0 to 40 salinity ($S = 5$ intervals) and 0 to 1000 b ($P = 100$ b intervals) from densities obtained from the new international equation of state (Millero *et al.*, 1980; Millero and Poisson, 1981). These values have been fit to polynomial functions of temperature ($t^\circ\text{C}$), applied pressure (P , bar) and ionic strength (I , mol kg H_2O^{-1}). The equation is of the form

Table 2. Values of the partial molal properties of water and "sea salt" at 0 and 25°C and $S = 35$.

P	0°(C)				25°(C)			
	\bar{V}_1	\bar{V}_2	$\bar{\kappa}_2 \times 10^4$	E_2	\bar{V}_1	\bar{V}_2	$\bar{\kappa}_2 \times 10^4$	E_2
0 b	18.005	15.016	-63.20	0.1824	18.059	17.852	-41.70	0.0670
200	17.829	16.216	-56.82	0.1542	17.902	18.645	-37.71	0.0580
400	17.664	17.293	-50.97	0.1296	17.753	19.364	-34.25	0.0499
600	17.509	18.258	-45.65	0.1085	17.612	20.018	-31.32	0.0426
800	17.364	19.122	-40.86	0.0911	17.478	20.620	-28.92	0.0360
1000	17.227	19.896	-36.60	0.0772	17.352	21.179	-27.06	0.0303

$$\phi_v = \phi_v^0 + AI^{1/2} + BI \quad (5)$$

where ϕ_v^0 , A and B are polynomial functions of t and P . The coefficients for Eq. (5), determined by the method of least squares, are given in Table 1. Although seawater is composed of a number of components, it is convenient to treat thermodynamics as if it was composed of one component, "sea salt." This convention is valid for average seawater diluted or evaporated and of a fixed relative composition (Millero and Leung, 1976). By appropriate differentiation of Eq. (5), it is possible to determine the partial molal volume of "sea salt" and water

$$\bar{V}_2 = \phi_v + I(\partial\phi_v/\partial I)_{T,P} \quad (6)$$

$$\bar{V}_1 = \bar{V}_1^0 - (mI/55.508) (\partial\phi_v/\partial I)_{T,P} \quad (7)$$

It is also possible to determine the partial molal expansibility of "sea salt"

$$E_2 = (\partial\bar{V}_2/\partial T)_P \quad (8)$$

and the partial molal compressibility of "sea salt"

$$\bar{\kappa}_2 = -(\partial\bar{V}_2/\partial P)_T \quad (9)$$

Values of \bar{V}_1 , \bar{V}_2 , $\bar{\kappa}_2$ and E_2 for seawater solutions with $S = 35$ and $t = 0^\circ\text{C}$ and 25°C are given in Table 2. The ionic strength and molality are related to the salinity by (Millero and Leung, 1976)

$$I = \frac{19.9201S}{1000 - 1.00488S} \quad (10)$$

$$m = \frac{16.0030S}{1000 - 1.00488S} \quad (11)$$

By appropriate integration of the \bar{V}_2 as a function of pressure, it is possible to determine the effect of pressure on the activity (a_2)

$$\ln a_2^P = \ln a_2^0 - \int_0^P (\bar{V}_2/RT) dP \quad (12)$$

the partial molal enthalpy (\bar{H}_2),

$$\bar{H}_2^P = \bar{H}_2^0 + \int_0^P [\bar{V}_2 - T(\partial\bar{V}_2/\partial T)] dP \quad (13)$$

and the partial molal entropy (\bar{S}_2) of "sea salt"

$$\bar{S}_2^P = \bar{S}_2^0 + \int_0^P (\partial\bar{V}_2/\partial T) dP . \quad (14)$$

For many oceanographic calculations the pressure in bars can be equated to the depth in meters divided by 10 m. For more careful work the pressure in bars is given by

$$P = 10^{-2} g z/\nu \quad (15)$$

where g is the gravitational constant (m sec^{-2}), z is the depth (m) and ν is the specific volume (g cm^{-3}). An empirical relation for this conversion has recently been given by Saunders (1981).

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