

Table IV. Comparison of Sublimation Enthalpies

Reference	Temp, ° K	ΔH_T , cal/mole	$\Delta H_{\text{sub}}^{\circ}$ (2nd), ^a cal/mole	$\Delta H_{\text{sub}}^{\circ}$ (3rd), cal/mole
Dysprosium				
This work	1239-1534	69,880 ± 320	72,420	69,600 ± 140
Habermann (7)	1257-1690	69,050 ± 240	71,920	69,390 ± 130
Kovtun (10)	1125-1346	72,400	74,510	67,490 ± 230
Savage (16)	1080-1400	69,300 ± 600	71,420	...
White (22)	1278-1566	60,100 ± 300	62,740	...
Erbium				
This work	1352-1587	73,640 ± 680	76,580	75,510 ± 130
Habermann (7)	1392-1790	79,280 ± 270	82,660	75,820 ± 350
Kruglykh (11)	1188-1453	60,530	63,030	72,350 ± 430
Savitskii (17)	1373-1573	64,750 ± 2150	67,620	80,280 ± 670
Trulson (20)	1208	73,180 ± 340	75,350	...
White (22)	1349-1743	64,500 ± 600	67,660	...

^a Calculated at the average temperature from ΔH_T and thermal functions.

studied by Pethe et al. (13) but not at low oxygen pressures. The residue weights correspond to those estimated to occur from a specimen reaction with dissolved oxygen in the tantalum cell. The accuracy of the measured vapor pressures suggests the formation of oxide residue from sources within the cell and not to a "getter" type reaction. If the oxide sources were external to the cell, the dysprosium and erbium vapor pressures would only be in error by approximately 1.0% and 6.0%, respectively. The significant differences between this work and that of Habermann and Daane occur at the lower temperatures where pyrometric temperature measurement is most subject to error.

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Correlation Equation for Solubility of Carbon Dioxide in Water, Seawater, and Seawater Concentrates

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The solubility of carbon dioxide in pure water, synthetic seawater, and synthetic seawater concentrates with three- and five-times normal salts content, in the temperature range of -5° to 25°C, and from 1 to 45 atm pressure

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has been determined experimentally and reported elsewhere in tabular and graphical form (7-9).

The gas solubility is a function of temperature, pressure, and solvent composition, as is to be expected. Since both phases are nonideal, this functional relationship is not a simple one. The solubility isobars for pure water, Figure 4 in ref. 9 and for synthetic seawater and its concentrates, Figure 1 in this paper, lead one to suspect that empirical

An equation expressing the solubility of CO₂ in pure water, synthetic seawater, and synthetic seawater concentrates from 1 to 45 atm pressure and -5° to 25° C has been developed. The solubility is expressed as a function of pressure, temperature, and the salts concentration of the solvent.

curve fitting methods are probably limited to one isobar in one solvent. The use of the pressure-dependent form of the Bunsen absorption coefficient, recommended by other workers (1), also did not prove to be satisfactory. Therefore, recourse to chemical thermodynamics and certain empirical correlations in the literature was made to develop the desired equations; this work is reported in more detail elsewhere (7, 8), and in much abridged form in the following paragraphs.

The thermodynamic fundamentals used as starting points were the equality of the fugacity or activity for each component in all phases, and the Gibbs-Duhem equation relating activities and concentrations in the liquid phase. The thermodynamic variables then had to be expressed in terms of the experimental variables.

The reference or standard state fugacities chosen were, for the solvent, f_1^0 (the fugacity of the pure liquid at the same temperature as the solution and at a specified pressure), and for the solute, f_2^0 (the dilute solution defined in terms of Henry's law):

$$f_2^0 = x_2 \lim_{x_2 \rightarrow 0} (f_2/x_2) = H \quad (1)$$

Also, for the solute in the liquid phase, its activity, ν_2 , can be expressed in terms of its partial molar volume, \bar{V}_2 , and other terms as

$$\nu_2 = \frac{f_2^V}{x_2 f_2^0} = \exp \left(\int_{p_1^s}^p \frac{\bar{V}_2 dp}{RT} \right) \quad (2)$$

Even in extremely dilute solutions, the CO₂-H₂O system is nonideal. Therefore, Equation 1 is modified in terms of an apparent activity coefficient of CO₂, ν_2^* , to give

$$f_2^0 = \nu_2^* H \quad (3)$$

The relationship 3, taking as a reference pressure the saturation pressure of the solvent, p_1^s (where $\nu_2 = 0$), transforms Equation 2 into

$$\frac{f_2^V}{x_2} = \nu_2^* H \exp \left(\int_{p_1^s}^p \frac{\bar{V}_2 dp}{RT} \right) \quad (4)$$

Then, assuming that $\bar{V}_2 = \bar{V}_2^\infty$ is the partial molar volume at infinite dilution, and that \bar{V}_2 is pressure independent, Equation 4 becomes

$$\ln \frac{f_2^V}{x_2} = \ln H + \ln \nu_2^* + \frac{\bar{V}_2^\infty (p - p_1^s)}{RT} \quad (5)$$

The activity coefficient of the solvent, ν_1 , is a function of its composition and is therefore frequently given as a power series of solute mole fractions, such as

$$\ln \nu_1 = \frac{A_2}{RT} (x_2)^2 + \frac{A_3}{RT} (x_2)^3 + \frac{A_4}{RT} (x_2)^4 + \dots = \sum_{n=2}^n \frac{A_n}{RT} (x_2)^{n-1} \quad (6)$$

where the A terms are empirical coefficients which, at constant composition, are functions of temperature only.

The Gibbs-Duhem equation and Equation 6 enable one to evaluate the apparent activity coefficient for CO₂:

$$\ln \nu_2^* = \sum_{n=2}^n \frac{A_n}{RT} (1 - x_1)^{n-1} \left(\frac{1}{n-1} + x_1 \right) \quad (7)$$

When x_2 is very small the fugacities are proportional to mole fractions. Applying Equation 7 to 5 and omitting negligible higher order terms lead to

$$\ln \frac{f_2^V}{x_2} = \ln H + \left[\bar{V}_2^\infty - \frac{2 A_2}{H} \right] \frac{p - p_1^s}{RT} \quad (8)$$

Michels and Michels (6) and McCormack and Schneider (4, 5) have determined the empirical constants in the virial equations of state for CO₂ which permit the calculation of its fugacity, f_2^V , as a function of pressure and temperature. An alternate method of computing the fugacity of CO₂ is to employ tabulated thermodynamic properties data (2, 3) and the relationship

$$f_2^V = p^{id} \exp \left[\left(\frac{h - E_0^0}{RT_0} \right) \left(\frac{T_0}{T} \right) - \frac{s}{R} - \left(\frac{F^0 - E_0^0}{RT} \right) \right] \quad (9)$$

By use of Equation 9 or the virial equation to compute f_2^V and the experimental data to compute x_2 , the ratios f_2^V/x_2 were calculated for each solvent and plotted as constant temperature lines against the pressure. Figure 2, the plot for pure water, is typical of these graphs. For each solvent the graph is a family of straight, parallel lines, the slope of which is different in each case. The slope of each family of curves, determined from the graphs, is then plotted against the dimensionless salt concentration factor, S , the ratio of the weight of total salts per unit weight of water in the solvent, divided by the salts concentration in normal seawater expressed in the same units; the equation for the slope of this curve is

$$m = 0.00395 [1 + e^{-2S - 0.390}] \quad (10)$$

where m is a nonideality factor.

The values of the Henry's law constants for the various solvents as functions of temperature are calculated from the plots of f_2^V/x_2 vs. p by locating the points where both x_2 and p are zero. Plotting the log of the Henry's law constant against the reciprocal of the absolute temperature gives a family of straight lines as is expected from the van't Hoff equation

$$\partial \ln H / (\partial 1/T) = - \frac{\Delta \bar{h}_2^*}{R} \quad (11)$$

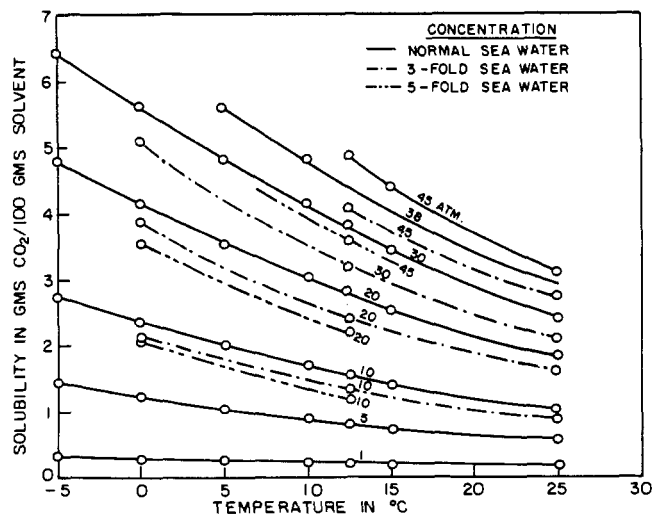


Figure 1. Solubility of CO₂ in synthetic seawater and synthetic seawater concentrates

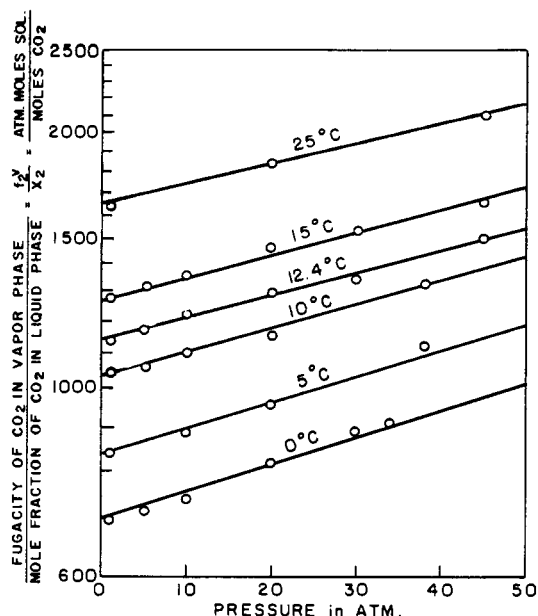


Figure 2. Calculation graph of liquid-gas equilibrium as a function of pressure

From this plot, the slopes and intercepts for the various solvents give $-\Delta\bar{h}_2^\circ/R$ and $\Delta\bar{s}_2^\circ/R$, respectively, according to the equation

$$RT \ln f_2^\circ = RT \ln H = -\Delta\bar{F}_2^\circ = -\Delta\bar{h}_2^\circ + T\Delta\bar{s}_2^\circ \quad (12)$$

Plots of $\Delta\bar{h}_2^\circ/R$ against S , the dimensionless salt concentration ratio, and of $\Delta\bar{s}_2^\circ/R$ against S were then made, and the equations of these lines determined numerically. The equations are:

$$\Delta\bar{h}_2^\circ/R = 2698 + 368S \quad (13)$$

$$\Delta\bar{s}_2^\circ/R = 16.43 + 0.40S^{0.595} \quad (14)$$

Equation 5, with the appropriate quantities substituted into it, becomes

$$\ln x_2 = \ln p - \left[\left(\frac{-\Delta\bar{h}_2^\circ}{RT} + \frac{\Delta\bar{s}_2^\circ}{R} \right) - \frac{p}{R} \left(\frac{a_1}{T} + \frac{b_1}{T^2} - Rm \right) - \left(\frac{p}{R} \right)^2 \left(\frac{b_2}{T} + \frac{a_2 - a_1}{T^2} - \frac{2a_1b_1}{T^3} - \frac{b_1^2}{T^4} \right) \right] \quad (15)$$

and with the numerical values for the $\text{CO}_2\text{-H}_2\text{O}$ system substituted therein

$$\ln x_2 = \ln p - \left[(16.43 + 0.40S^{0.595}) - 1/T(2698 + 368S) \right] - \frac{p}{R} \left[\frac{203.14}{T} - \frac{9.756 \times 10^4}{T^2} - 0.00395R \left(1 + e^{-[2S + 0.390]} \right) \right] + \left(\frac{p}{R} \right)^2 \left(\frac{119.76}{T} + \frac{552.22}{T^2} - \frac{3.964 \times 10^7}{T^3} + \frac{9.517 \times 10^8}{T^4} \right) \quad (16)$$

For the limiting case of S being zero, pure water as the solvent, Equation 16 becomes

$$\ln x_2 = \ln p - \left[\left(16.43 - \frac{2698}{T} \right) - \frac{p}{R} \left(\frac{203.14}{T} - \frac{9.756 \times 10^4}{T^2} - 0.00662R \right) + \left(\frac{p}{R} \right)^2 \left(\frac{119.76}{T} + \frac{552.22}{T^2} - \frac{3.964 \times 10^7}{T^3} + \frac{9.517 \times 10^8}{T^4} \right) \right] \quad (17)$$

Equations 16 and 17 reproduce the experimental results within experimental accuracy, which is $\frac{1}{2}$ of 1% at the worst, and generally only a few tenths of 1%. Rather than use statistical methods, we determined the accuracy of both the experimental data and the correlation equations by numerical comparison with the values of other workers (where possible) and graphically.

NOMENCLATURE

- A_1, A_2 = empirical coefficients, Equation 6
 B = coefficient in virial equation of state, $\text{cm}^3/\text{g-mole}$
 C = coefficient in virial equation of state, $(\text{cm}^3/\text{g-mole})^2$
 E = total energy, cal/g-mole
 F = Gibbs function (free energy), cal/g-mole
 H = Henry's law constant, dimensionless
 R = universal gas constant = $82.0053 \text{ cm}^3\text{-atm/g-mole}^\circ\text{K}$; and $\text{cal/g-mole}^\circ\text{K}$
 S = salt content ratio (dimensionless) = wt of total salts per unit weight of water in solution divided by same ratio for normal seawater
 T = temperature, $^\circ\text{K}$
 V = molar volume, $\text{cm}^3/\text{g-mole}$
 a, b = empirical coefficients
 f = fugacity, atm
 h = enthalpy, cal/g-mole
 m = nonideality factor, dimensionless
 p = pressure, atm
 s = entropy, $\text{cal/g-mole}^\circ\text{K}$
 x = mole fraction, liquid phase
 ϕ = fugacity coefficient, dimensionless
 ν = activity coefficient, dimensionless
 ν^* = apparent activity coefficient, dimensionless

Superscripts

- id = ideal
 L, V = liquid and gas states, respectively
 s = saturation value
0 (zero) = standard or reference state
 \cdot = partial molar quantity
 ∞ = at infinite dilution-ideal state

Subscripts

- s = saturation value
1, 2 = solvent and solute, respectively
0 (zero) = reference state

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