

per molecule. This equation assumes that the associated solvent molecules do not strongly influence one another and have but slight influence on the properties of the central molecule.

The terms of the last bracket of equation (4) are all independent of pressure and temperature and may be collected

$$(2/V_2 (B_{1,2} + nB_{2,2} - B_{1,2n})) = s_n/V_2 \quad (6)$$

The mole fraction  $x_1$  of unassociated solute molecules in the solution is due to the vapor pressure of the solid under the given temperature and pressure. This is approximately given by (Zwicker, 1954, p. 168).

$$\ln P^* = k - E/RT \quad (7)$$

where  $k$  is a constant, and  $E$  the molar heat of evaporation.  $E$  has a pressure dependence, but in view of the low compressibilities of solids, this will be small. Franck (1956, eq 15) suggests it should be of the form

$$E = E_0 + PV_f \quad (8)$$

where  $E_0$  is the value of  $E$  at zero pressure,  $P$  the pressure, and  $V_f$  the mole volume of the solid, assumed to be constant.

Now the number of molecules per unit volume of unassociated 1 is, at low  $P^*$  where  $V_1 = RT/P^*$ ,

$$q_1 = N^*/V_1 = (N^*/RT) (\exp \{k - (E_0 + PV_f/RT)\}) \quad (9)$$

where  $N^*$  is Avagadro's number. Noting that the number of molecules of 2 per unit volume is  $N^*/V_2$ ,

$$x_1 = q_1/q_1 + q_2 =$$

$$q_1/q_2 = V_2/V_1 = (V_2/RT (\exp \{k - (E_0 + PV_f/RT)\})) \quad (10)$$

Substituting equations (5), (6), and (10) in equation (4) gives

$$\ln x_{1,2n} = (k - nS_{21}/R) + s_n/V_2 - (n-1) \ln V_2 - \ln RT - (nH_{21} + E_0 + PV_f)/RT \quad (11)$$

Assuming that the bulk of 1 is present as the associated complex  $12_n$ ,  $x_{1,2n}$  may be identified with the analytically determined mole fraction of 1. Collecting constant terms in equation (11), the solubility of 1 under these conditions should obey an equation of the form

$$\log X_1 = (a + bP)/RT + c/V_2 + d \log V_2 + e \log T + f \quad (12)$$

where  $X_1$  is the analytically determined mole fraction of 1, and  $a, b, c, d, e, f$  are constants. This equation assumes that (a) the solubility of species 1 in solvent 2 is slight, (b) species 1 forms only one quantitatively important complex with solvent 2, and (c) the volume dependence of the free energy of complexing can be represented by terms linear in the volume, and (d) complex formation leaves the electronic configuration of the participating molecules unchanged, with the possible exception of slight changes in the configuration of the most loosely bound electrons. Equation (12) differs from that of Franck (1956) in that an explicit dependence of solubility on pressure, temperature, and mole volume is given, the log solubility depends on both  $1/V$  and  $\log V$ , and the dependence of log solubility on  $1/T$  is not linear.

Equation (12) is in a form suitable for regression analysis. The data in table 3 have been fitted to equation (12) by regression analysis using

TABLE 4A  
Solubility of albite in supercritical water calculated from solubility equations: silica

T (°A)	P (k bars)	V cm <sup>3</sup> /gm	-log X (calc)	ppm SiO <sub>2</sub> (calc)	ppm SiO <sub>2</sub> (observed)	T (°A)	P (k bars)	V cm <sup>3</sup> /gm	-log X (calc)	ppm SiO <sub>2</sub> (calc)	ppm SiO <sub>2</sub> (observed)
673	0.75	1.534	3.937	387	369	723	0.75	1.502	3.410	1297	1260
	1.00	1.444	3.829	467	485		1.00	1.444	3.333	1547	1605
	1.25	1.382	3.739	607	651		1.25	1.333	3.162	2293	2393
	1.50	1.333	3.663	723	752		1.50	1.305	3.112	2543	2550
	1.75	1.295	3.597	843	880		1.75	1.256	3.017	3203	3201
	2.00	1.264	3.539	963	1003		2.00	2.989	4.081	277	272
	2.50	1.213	3.435	1223	1223		2.50	2.248	3.798	530	481
	3.00	1.178	3.349	1493	1407		3.00	1.932	3.609	820	795
	3.50	1.146	3.267	1803	1805		3.50	1.751	3.469	1130	1150
								1.632	3.355	1473	1390
773	0.75	1.827	3.952	373	375	873	0.75	3.618	4.059	291	300
	1.00	1.631	3.782	550	572		1.00	2.669	3.807	520	550
	1.25	1.518	3.656	737	778		1.25	2.220	3.601	837	867
	1.50	1.447	3.565	907	945		1.50	1.953	3.451	1180	1140
	1.75	1.396	3.491	1080	1135		1.75	1.787	3.323	1583	1577
	2.00	1.354	3.429	1240	1300		2.00	1.676	3.224	1990	2082
	2.50	1.291	3.319	1600	1617		2.25	1.596	3.140	2413	2501
	3.00	1.243	3.224	1990	1967		2.50	1.407	3.074	2813	2815
	3.50	1.202	3.136	2437	2440						

Solubility equation

$$\log X \text{ SiO}_2 = \frac{2.478}{V} + \frac{30.089P - 2400.6}{T} - 2.0199$$