

of individual elements. Applications of theoretical chemistry that have been described here and further research in these areas remain a challenge for present and future students of natural-water chemistry.

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TABLES 30–33

Table 30. Chemical thermodynamic data for carbon, oxygen, and sulfur species

[From Wagman and others (1968)]

Species	ΔG_f° (kcal/mol)
CH ₄ (g)	-12.13
CH ₄ (aq)	-8.22
CO ₂ (g)	-91.254
CO ₂ (aq)	-92.26
H ₂ CO ₃ (aq)	-148.94
HCO ₃ ⁻	-140.26
CO ₃ ²⁻	-126.17
O ₂ (aq)	3.9
OH ⁻	-37.594
H ₂ O(l)	-56.69
S ²⁻	20.5
HS ⁻	2.88
H ₂ S(g)	-8.02
H ₂ S(aq)	-6.66
HSO ₄ ⁻	-180.69
SO ₄ ²⁻	-177.97

Table 32. Chemical thermodynamic data for manganese species

Species	ΔG_f° (kcal/mol)	Source
Mn ²⁺ (aq)	-54.5	Wagman and others (1969).
MnOH ⁺ (aq)	-96.8	Do.
Mn(OH) ₃ ⁻ (aq)	-177.9	Do.
Mn(OH) ₂ (amorphous)	-147.0	Do.
MnCO ₃ (rhodochrosite)	-195.0	Robie and others (1978).
MnS (alabandite)	-52.14	Do.
Mn ₃ O ₄ (hausmannite)	-306.7	Wagman and others (1969).
β -MnOOH (feitknechtite)	-129.8	Hem and others (1982).
γ -MnOOH (manganite)	-133.3	Bricker (1965).
δ -MnO ₂ (birnessite)	-108.3	Do.
γ -MnO ₂ (nsutite)	-109.1	Do.

Table 31. Chemical thermodynamic data for iron species

[c, calculated]

Species	ΔG_f° (kcal/mol)	Source
Fe ²⁺ (aq)	-18.85	Robie and others (1978).
FeOH ⁺ (aq)	-62.58(c)	Baes and Mesmer (1976).
Fe(OH) ₃ ⁻ (aq)	-147	Wagman and others (1969).
FeO (stoichiometric)	-60.03	Robie and others (1978).
FeS ₂ (pyrite)	-38.3	Do.
FeS	-24.22	Do.
FeCO ₃ (siderite)	-159.35	Wagman and others (1969).
Fe ³⁺ (aq)	-1.1	Robie and others (1978).
FeOH ²⁺ (aq)	-54.83	Wagman and others (1969).
Fe(OH) ₂ ⁺ (aq)	-106.7(c)	Baes and Mesmer (1976).
Fe(OH) ₄ ⁻ (aq)	-198.4	Do.
Fe(OH) ₃ (amorphous)	-166	Feitknecht and Schindler (1963).
FeOOH (goethite)	-116.77	Robie and others (1978).
Fe ₂ O ₄ (magnetite)	-242.01	Do.

Table 33. Equilibrium constants for temperatures from 0° to 50°C for the system CaCO₃+H₂O+CO₂

[Ionic strength, 0.0]

T(°C)	Log K _{H₂O} ₁	Log K _h ₂	Log K ₁ ₃	Log K ₂ ₄	Log K _s ₅
0	-14.955	-1.114	-6.579	-10.625	2.274
10	-14.534	-1.270	-6.464	-10.490	2.131
20	-14.161	-1.406	-6.381	-10.377	1.983
30	-13.833	-1.521	-6.327	-10.290	1.837
40	-13.533	-1.620	-6.298	-10.220	1.685
50	-13.263	-1.705	-6.285	-10.172	1.537

1. Dissociation of water: $K_{H_2O} = [H^+][OH^-]$ (Ackerman, 1958).
2. Henry's law constant for solution of CO₂ in water: $K_h = [H_2CO_3]/P_{CO_2}$ (Harned and Davis, 1943).
3. First dissociation constant for carbonic acid: $K_1 = [HCO_3^-][H^+]/[H_2CO_3]$ (Harned and Davis, 1943).
4. Second dissociation constant for carbonic acid: $K_2 = [CO_3^{2-}][H^+]/[HCO_3^-]$ (Harned and Scholes, 1941).
5. Solubility constant for calcite: $K_s = [Ca^{2+}][HCO_3^-]/[H^+]$ (calculated from data of Jacobson and Langmuir, 1974).

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Explanatory Note to Plate 2

Nomograph for evaluating calcite equilibria $T=0^{\circ}\text{C}$ to 50°C , $I=0.0$ to 0.5

This nomograph provides a means of estimating the calcite saturation index (S.I.) for waters of known ionic strength (I) for temperatures (T) between 0° and 50°C . Besides the values for T and I it is necessary to know the concentrations (mg/L) of HCO_3 and Ca and the pH. Preferably pH and HCO_3 measurements should be made at the time samples are collected. Ionic strength can be computed using plate 1 if all major dissolved ion concentrations are known. For some waters an approximate value for I can be computed from the specific conductance of the water (Lind, 1970).

Instructions for use:

1. Place overlay (pl. 2B) on Ca vs HCO_3 grid (pl. 2A) so that match lines coincide.
2. While keeping the match lines exactly superimposed, move 2B until the determined value of I read on the ionic strength scale coincides with the temperature (measured at time of sample collection) value read on the temperature scale on 2A.
3. Locate in 2A the point of intersection of Ca and HCO_3 concentrations (in mg/L). The position of this point on the pH grid (2B) is the equilibrium pH for calcite saturation at these T and I values.
4. Compute calcite saturation index from the formula

$$\text{S.I.} = \text{pH}_{\text{measured}} - \text{pH}_{\text{equilib.}}$$

A positive value for S.I. indicates supersaturation. Importance of simplifying assumptions and related factors that may affect accuracy of S.I. values obtained with the nomograph are discussed under the topic headings "Calcium—Chemical Controls on Calcium Concentrations" in the text.