1. Use Excel to calculate the SI of gypsum, amorphous SiO_2, and quartz for the Mississippi River water analysis given in Faure, table 10.2 (below).

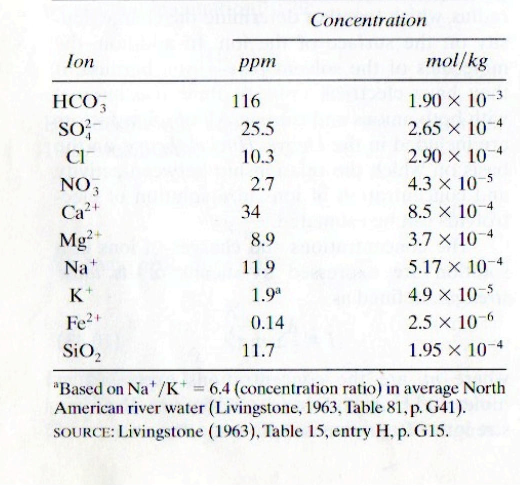

Table 10.2 Chemical Composition of Water of the Mississippi River at New Orleans

Ion	*Concentration* *ppm*	 *mol/kg*
HCO_3^-	116	1.90×10^{-3}
SO_4^{2-}	25.5	2.65×10^{-4}
Cl^-	10.3	2.90×10^{-4}
NO_3^-	2.7	4.3×10^{-5}
Ca^{2+}	34	8.5×10^{-4}
Mg^{2+}	8.9	3.7×10^{-4}
Na^+	11.9	5.17×10^{-4}
K^+	1.9[a]	4.9×10^{-5}
Fe^{2+}	0.14	2.5×10^{-6}
SiO_2	11.7	1.95×10^{-4}

[a] Based on $Na^+/K^+ = 6.4$ (concentration ratio) in average North American river water (Livingstone, 1963, Table 81, p. G41).

SOURCE: Livingstone (1963), Table 15, entry H, p. G15.

2. Use Excel to create an iterative calculation of the solubility of gypsum, following the method described in Drever (1982) (attached). Use the Debye-Hückel parameters as shown, at 25 °C.

When ready, submit your file through Blackboard.

3. Consider a beaker of pure H_2O that is in equilibrium with CO_2 gas at different pressures. What is the pH in equilibrium with CO_2 gas at a pressure of

a. 1 atmosphere
b. 0.01 atmospheres (approximately the value in soils)
c. 3 x 10^{-4} atmospheres (approximately the value in air).

Show your calculations.

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + Ba_0\sqrt{I}} \qquad (2\text{–}6)$$

Table 2-1 Parameters for the Debye–Hückel equation at 1 atmosphere pressure (adapted from Manov et al. 1943; Klotz 1950).

T(°C)	A	B(×10⁻⁸)	a_0(×10⁸)	Ion
0	0.4883	0.3241	2.5	NH_4^+
5	0.4921	0.3249	3.0	K^+, Cl^-, NO_3^-
10	0.4960	0.3258	3.5	OH^-, HS^-, F^-
15	0.5000	0.3262	4.0	SO_4^{2-}, PO_4^{3-}, HPO_4^{2-}
20	0.5042	0.3273	4.0–4.5	Na^+, HCO_3^-, $H_2PO_4^-$
25	0.5085	0.3281	4.5	CO_3^{2-}
30	0.5130	0.3290	5	Sr^{2+}, Ba^{2+}, S^{2-}
40	0.5221	0.3305	6	Ca^{2+}, Fe^{2+}, Mn^{2+}
50	0.5319	0.3321	8	Mg^{2+}
60	0.5425	0.3338	9	H^+, Al^{3+}, Fe^{3+}

On the basis of Eq. (2–6), what are the activity coefficients of Ca^{2+} and SO_4^{2-} in a solution in equilibrium with gypsum at 25°C in the system $CaSO_4$–H_2O? What is the solubility of gypsum in water assuming these activity coefficients? How does it differ from the value calculated on the assumption that activities equal concentrations?

The solubility product of gypsum (previous examples) is $10^{-4.61}$. As a first approximation, let us assume that $m_{Ca^{2+}} = m_{SO_4^{2-}} = (10^{-4.61})^{1/2} = 4.95 \times 10^{-3}$.

$$I = \tfrac{1}{2}(4.95 \times 10^{-3} \times 4 + 4.95 \times 10^{-3} \times 4)$$
$$= 1.98 \times 10^{-2}$$

From Table 2-1,

$$A = 0.5085$$
$$B = 0.3281 \times 10^8$$
$$a_0 = 6 \times 10^{-8} \quad \text{for } Ca^{2+}$$
$$= 4 \times 10^{-8} \quad \text{for } SO_4^{2-}$$

Substituting these numbers in Eq. (2–6) gives

$$\log \gamma_{Ca^{2+}} = -0.224$$
$$\gamma_{Ca^{2+}} = 0.597$$
$$\log \gamma_{SO_4^{2-}} = -0.242$$
$$\gamma_{SO_4^{2-}} = 0.573$$

from
Drever (1982). The geochemistry
of natural waters

With these provisional values we can compute more accurate calcium and sulfate concentrations, and hence a more accurate ionic strength.

$$(m_{Ca^{2+}} \times 0.597)(m_{SO_4^{2-}} \times 0.573) = 10^{-4.61}$$

Since $m_{Ca^{2+}}$ must equal $m_{SO_4^{2-}}$ when gypsum dissolves,

$$m_{Ca^{2+}} = m_{SO_4^{2-}} = \left(\frac{10^{-4.61}}{0.597 \times 0.573}\right)^{1/2} = 0.847 \times 10^{-2}$$

On the basis of this number, the ionic strength is

$$I = 3.39 \times 10^{-2}$$

and

$$\gamma_{Ca^{2+}} = 0.531$$
$$\gamma_{SO_4^{2-}} = 0.499$$

These values will be more accurate than the provisional estimate, and they can be used to calculate a more accurate ionic strength, and hence more accurate activity coefficients. The iteration procedure can be repeated any number of times to give values of any desired mathematical accuracy. Doing this, we obtain the final answer,

$$I = 4.02 \times 10^{-2}$$
$$\gamma_{Ca^{2+}} = 0.510$$
$$\gamma_{SO_4^{2-}} = 0.475$$

The solubility of gypsum in water will then be

$$\left(\frac{10^{-4.61}}{0.510 \times 0.475}\right)^{1/2} = 10.1 \times 10^{-3} \text{ mol/kg}$$
$$= 1.37 \text{ g/}\ell \; CaSO_4$$
$$= 1.74 \text{ g/}\ell \; CaSO_4 \cdot 2H_2O$$

If we had assumed activities were equal to concentrations, the solubility of gypsum would have been

$$(10^{-4.61})^{1/2} = 4.95 \times 10^{-3} \text{ mol/kg}$$

This value is almost exactly half the value calculated with activity corrections, so, in this example, neglecting activity coefficients would have resulted in an error of a factor of 2.