

**SOLUTIONS MANUAL**



PRINCIPLES OF  
**ENVIRONMENTAL  
GEOCHEMISTRY**



© NELSON EBY

**PRINCIPLES OF ENVIRONMENTAL GEOCHEMISTRY**  
**SOLUTIONS MANUAL**  
**CHAPTER 2. THERMODYNAMICS AND KINETICS**

1. Why are herbivores more energy efficient than carnivores?

Herbivores are on the second trophic level. Carnivores are on the third trophic level or higher. Given a 10% efficiency for biological processes, herbivores are at least 10 times more energy efficient than carnivores.

2. What are *intensive variables*? What are *extensive variables*?

Intensive variables are independent of the magnitude of the system, i.e., they are the same everywhere. Examples are temperature and pressure. Extensive variables depend upon the magnitude of the system. Examples are volume and mass.

3. Distinguish between *open*, *closed*, and *isolated systems*.

An open system can exchange both energy and matter with the surrounding environment while a closed system can exchange only energy with the surrounding environment. An isolated system can exchange neither matter nor energy with the surrounding environment.

4. How can you tell if a reaction is *endothermic* or *exothermic*?

Endothermic reactions use heat energy and  $\Delta H$  for the reaction is negative. Exothermic reactions release heat energy and  $\Delta H$  for the reaction is positive.

5. Define *enthalpy* and *entropy*.

Enthalpy is a measure of the heat flow when processes occur at constant pressure and the only work done is pressure-volume work. Many students have a problem with the concept of entropy. I like to look at it in terms of statistical mechanics, in which case entropy is a measure of the disorder of a system. During any spontaneous reaction the entropy of the system increases, i.e, the disorder increases.

6. What is the *standard state*?

The standard state is in essence the reference conditions for thermodynamic calculations. For a solid it is a specified crystalline state at 1 atm and 25°C. For a liquid it is the pure liquid at 1 atm and 25°C. For a gas it is the ideal gas at 1 atm and 25°C.

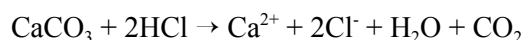
7. Define *heat capacity*.

Heat capacity is the amount of heat energy required to raise one gram of a substance 1°C. Heat capacity does vary as a function of temperature.

8. What is *Le Châtelier's principle* and how can it be used to predict changes in a reaction at equilibrium?

Le Châtelier's principle states that if a change, for example in concentration, temperature, or pressure, is imposed on a system at equilibrium, the equilibrium will shift in a direction that tends to reduce the change. For example, if we have a precipitation reaction that is at equilibrium, the addition of ions will result in the formation of more precipitate.

9. When you add HCl to CaCO<sub>3</sub>, the following reaction occurs:



This reaction will proceed differently if it is in a closed container (sealed from the atmosphere) versus open to the atmosphere (for example, on a desktop). How will the reaction differ under these two conditions?

If the container is open to the atmosphere the CO<sub>2</sub> will escape into the atmosphere. Since CO<sub>2</sub> is continually lost from the system the reaction moves to the right.

In the case of the closed system, the CO<sub>2</sub> concentration will increase. At some point, we will achieve equilibrium for this reaction and it will no longer run to the right.

10. What factors are responsible for the nonideal behavior of ions in solution?

The departure from ideal behavior is mainly caused by two factors: (1) electrostatic interactions between charged ions and (2) the formation of hydration shells around the ions. Hydration shells form because water is a dipolar molecule and will attach electrostatically to ions in solution.

11. What is an *aqueous complex*?

An aqueous complex is a dissolved species formed from two or more simpler species, each of which can exist in aqueous solution. For example, CaSO<sub>4(aq)</sub> which is the combination of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions.

12. NaCl dissolves in water to produce Na<sup>+</sup> and Cl<sup>-</sup>. Salt is added to a beaker of water until no more salt will dissolve and salt crystals are observed in the beaker.

- a. How many phases are present in this system?

Two. Solid NaCl and ions in solution.

- b. How many components are needed to completely describe the system, and what are the components?

Two. Na<sup>+</sup> and Cl<sup>-</sup>.

- c. What is the free energy of the system when it becomes saturated in NaCl, i.e., no more salt crystals dissolve in the solution?

At equilibrium the free energy of the system would be zero

13. What is the difference between activity and the measured concentrations of a species in solution?

Activity is the apparent or effective concentration of a species in solution and is the value used for thermodynamic calculations. Measured concentrations are the amount of the species actually present in solution.

14. Why and how does the formation of the aqueous complex  $\text{CaCO}_3(\text{aq})$  affect the solubility of calcite ( $\text{CaCO}_3$ )?

The complex increases the solubility of calcite because some of the  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  are used to form the aqueous complex. Hence, more calcite dissolves than would be predicted on the basis of the calcite solubility product.

15. Distinguish between *homogeneous* and *heterogeneous reactions*.

Homogeneous reactions only involve one phase while heterogeneous reactions involve two or more phases.

16. Why is an understanding of the kinetics of reactions important in dealing with environmental problems?

Thermodynamics tells us the direction in which a reaction will proceed, but kinetics tells us the rate at which a reaction will occur. The rate of a reaction is sensitive to temperature, and at low temperatures (i.e., surface temperatures) many reactions proceed very slowly. Thus, thermodynamics might predict that a particular compound would breakdown (decompose) in the natural environment but the reaction rate might be so slow that in actuality this decomposition does not occur.

17. How could you determine if a reaction was zeroth, first, or second order?

Based on the discussion in the textbook the anticipated answer is that one would graph the data and look at the resulting distribution. The log-log plot of reaction rate versus concentration would be most useful. With reference to Figure 2-3, for a zeroth-order reaction the rate is constant and the data plot as a horizontal straight line ( $n = 0$ ), for a first-order reaction the log-log plot gives a straight line with a slope of 1 ( $n = 1$ ), and for the second-order reaction the log-log plot gives a straight line with a slope of 2 ( $n = 2$ ).

18. What is an *inhibitor*?

An inhibitor is a foreign species adsorbed at points of high energy on the crystal surface that may inhibit crystal growth or dissolution.

19. For the reaction  $\text{Diamond} \rightarrow \text{Graphite}$ ,  $\Delta G_R^\circ = -2.9 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$  and 1 atm pressure. Thermodynamically, diamond should be the stable form of carbon at the earth's surface. Why don't diamonds invert to graphite at the earth's surface?

The reaction diamond to graphite has a large negative free energy so one would expect this reaction to occur spontaneously. However, the reaction requires a reordering of the crystal structure of diamond which necessitates the breaking of strong bonds. Hence, the reaction has a large activation

energy and does not occur at surface temperatures.

20. The rate-determining step in the growth of a particle can be either the rate at which species are added to the surface of the growing particle or the rate at which species diffuse to the surface of the growing particle. Figure 2-P20 schematically illustrates the variation in concentration of an ionic species in solution as a function of distance from the surface of a particle. For case A, what is the rate-controlling step, and why? For case B, what is the rate-controlling step, and why?

In case *A* the concentration of the ionic species is constant with distance from the particle surface indicating that the rate-controlling step is the addition of the ionic species to the surface of the growing particle, i.e., ions are abundant at the surface of the particle so their concentration doesn't limit the rate of particle growth. In case *B* there is a steep concentration gradient and the concentration of the species at the surface of the particle is zero. This indicates that the rate-controlling step is the rate at which the species diffuses through the solution to the surface of the growing particle, i.e., ions are added to the growing particle as soon as they reach the surface of the particle and their availability controls the rate of particle growth.

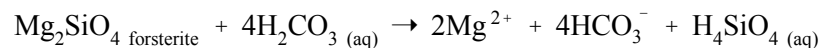
21. Refer to Case Study 2-2. What is meant by conservative behavior? Why did the authors conclude that barium would only behave conservatively in mixtures that contained less than 28% water from the contaminated aquifer while strontium would behave conservatively in all possible mixtures?

Conservative behavior occurs when there are no processes occurring in the system that affect the concentration of the species. In this case, the species concentration is controlled by simple mixing. Referring to the calculated saturation indices we see that for any water mixture, the water is undersaturated in both strontium containing phases (celestite and strontianite). When the contaminated alluvial aquifer water exceeds 28%, the water is saturated with respect to the barium containing phase (barite). Once the water is saturated with respect to barite, barium will be removed by precipitation and this species no longer behaves conservatively.

22. With reference to Case Study 2-3, what should happen to anorthite grains when acidified water passes through the soil horizon? Explain.

The groundwaters are strongly undersaturated with respect to anorthite (SI = -6.44). When acidified water passes through the soil horizon the anorthite grains should decompose. However, in terms of kinetics, this is a relatively slow reaction. Anorthite breaks down incongruently to ions in solution and a clay mineral.

23. During chemical weathering, forsterite is dissolved by the carbonic acid in rainwater. The weathering reaction is as follows:



Use the thermodynamic data from Appendix II, source 2, for the following calculations.

- a. Calculate the  $K_{\text{eq}}$  for this weathering reaction at 25°C.

Depending on how the student does the problem, there are two possible sets of answers.

(1) In part (d) we are going to need to calculate the equilibrium constant at 40°C. We can save some computational time by solving this part using enthalpy and free energy.

$$\Delta H_R^\circ = (2)(-467.0) + (4)(-689.93) + (-1457.3) - (-2175.7) - (4)(-699.09) = -178.96 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta S_R^\circ &= (2)(-137) + (4)(98.4) + (180) - (95.2) - (4)(189.31) = -552.84 \text{ J mol}^{-1} \\ &= -0.553 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta G_R^\circ = \Delta H_R^\circ - T\Delta S_R^\circ = (-178.96) - (298.15)(-0.553) = -14.08 \text{ kJ mol}^{-1}$$

$$\log K_{\text{eq}} = \frac{-(-14.08)}{5.708} = 2.47$$

$$K_{\text{eq}} = 10^{2.47} = 295$$

(2) Many students will solve this problem using the free energies at 25°C.

$$\Delta G_R^\circ = (2)(-455.4) + (4)(-586.8) + (-1307.9) - (-2056.7) - (4)(-623.14) = -16.64 \text{ kJ mol}^{-1}$$

The equilibrium constant in this case is,  $K_{\text{eq}} = 823$ . I use this discrepancy as a vehicle to discuss the issue of internal consistency and accuracy of thermodynamic data.

- b.** If the reaction is at equilibrium, using Le Châtelier's principle, predict what would happen if  $\text{Mg}^{2+}$  ions were added to the solution.

The addition of  $\text{Mg}^{2+}$  ions should cause the reaction to shift to the left, the direction that will minimize the increase in concentration of this species.

- c.** Using Le Châtelier's principle, predict what would happen to the equilibrium constant if the reaction occurred at a higher temperature.

The reaction is exothermic. Heat energy is consumed when the reaction moves to the left. Thus, we would expect the equilibrium constant to decrease with increasing temperature, i.e., the solubility of forsterite decreases.

- d.** Calculate the  $K_{\text{eq}}$  for this reaction at 40°C. Does the solubility of forsterite increase or decrease with increasing temperature? How does this result compare with your prediction in part (c).

(1) Using the results from solution (1) in part (a).

$$\ln K_{\text{eq}} = \frac{-\Delta H_R^\circ}{RT} + \frac{\Delta S_R^\circ}{R} = \frac{-(-178.96)}{(8.314 \times 10^{-3})(313.15)} + \frac{(-0.553)}{(8.314 \times 10^{-3})} = 68.74 - 66.51 = 2.23$$

$$K_{\text{eq}} = 10^{0.97} = 9.3 = K_{\text{sp}}$$

There has been a substantial decrease in the solubility of forsterite (from  $K_{sp} = 295$  to  $K_{sp} = 9.3$ ). The quantitative result is in agreement with our prediction from part (c).

(2) Using the results from solution (2) in part (a) and the van't Hoff equation

$$\ln K_t = \ln(10^{2.92}) + \frac{-178.96}{8.314 \times 10^{-3}} \left( \frac{1}{298.15} - \frac{1}{313.15} \right) = 3.27$$

$$\log K_{sp} = 1.42 \text{ and } K_{sp} = 26.3$$

Once again, there has been a substantial decrease in the solubility of forsterite (in this case from  $K_{sp} = 823$  to  $K_{sp} = 26.3$ ). The quantitative result is in agreement with our prediction from part (c).

24. a. Calculate the  $K_{sp}$  for magnesite ( $\text{MgCO}_3$ ) at 25°C. Use the thermodynamic data from Appendix II, source 2, for this calculation.



$$K_{eq} = \frac{[\text{Mg}^{2+}][\text{CO}_3^{2-}]}{[\text{MgCO}_3]} = [\text{Mg}^{2+}][\text{CO}_3^{2-}] = K_{sp}$$

$$\Delta G_R^\circ = (-455.4) + (-527.9) - (-1012.1) = 28.8 \text{ kJ mol}^{-1}$$

$$\log K_{sp} = \frac{-\Delta G_R^\circ}{5.708} = \frac{-28.8}{5.708} = -5.05$$

$$K_{sp} = 10^{-5.05} = 9.0 \times 10^{-6} = [\text{Mg}^{2+}][\text{CO}_3^{2-}]$$

- b. What is the solubility of magnesite in pure water? How much difference does it make if it is assumed that activity equals concentration versus activity calculated from the Debye-Hückel equation? (*Note:* In order to answer the latter part of the question, you will have to calculate the final solubility by successive approximations. Use the original ion concentrations to determine the ionic strength, then determine the activity coefficients. Use the coefficients to recalculate the ion concentrations. Repeat this process until there is no change in the activity coefficients.)

$$m_{\text{Mg}^{2+}} = m_{\text{CO}_3^{2-}} = (K_{sp})^{1/2} = (10^{-5.05})^{1/2} = 3.00 \times 10^{-3}$$

1<sup>st</sup> approximation:

$$I = \frac{1}{2} \sum m_i z_i^2 = \frac{1}{2} [(3.00 \times 10^{-3})(2)^2 + (3.00 \times 10^{-3})(2)^2] = 1.20 \times 10^{-2}$$

For  $\text{Mg}^{2+}$ :

$$\log \gamma_{\text{Mg}^{2+}} = \frac{-Az_i^2 \sqrt{I}}{1 + Ba_0 \sqrt{I}} = \frac{-(0.5094)(2)^2 (1.20 \times 10^{-2})^{1/2}}{1 + (0.3289 \times 10^8)(8.0 \times 10^{-8})(1.20 \times 10^{-2})^{1/2}} = -0.173$$

$$\gamma_{\text{Mg}^{2+}} = 0.67$$

For  $\text{CO}_3^{2-}$ :

$$\log \gamma_{\text{CO}_3^{2-}} = \frac{-(0.5094)(2)^2(1.20 \times 10^{-2})^{1/2}}{1 + (0.3289 \times 10^8)(4.5 \times 10^{-8})(1.20 \times 10^{-2})^{1/2}} = -0.192$$

$$\gamma_{\text{CO}_3^{2-}} = 0.64$$

2<sup>nd</sup> approximation:

Calculate new concentrations for the two ions taking into account activity. The concentrations of the two ions must be the same when magnesite dissolves

$$m_{\text{Mg}^{2+}} = m_{\text{CO}_3^{2-}} = \left( \frac{10^{-5.05}}{0.67 \times 0.64} \right)^{1/2} = 4.56 \times 10^{-3}$$

The new ionic strength =  $1.824 \times 10^{-2}$ . Using this new ionic strength to calculate the activity coefficients gives  $\gamma_{\text{Mg}^{2+}} = 0.63$  and  $\gamma_{\text{CO}_3^{2-}} = 0.59$ .

3<sup>rd</sup> approximation:

$$I = 1.959 \times 10^{-2} \quad \gamma_{\text{Mg}^{2+}} = 0.62 \quad \gamma_{\text{CO}_3^{2-}} = 0.58 \quad m_{\text{Mg}^{2+}} = m_{\text{CO}_3^{2-}} = 4.978 \times 10^{-3}$$

4<sup>th</sup> approximation:

$$I = 1.991 \times 10^{-2} \quad \gamma_{\text{Mg}^{2+}} = 0.62 \quad \gamma_{\text{CO}_3^{2-}} = 0.58 \quad m_{\text{Mg}^{2+}} = m_{\text{CO}_3^{2-}} = 4.978 \times 10^{-3}$$

There is no significant change between the 3<sup>rd</sup> and 4<sup>th</sup> approximation so the final solubility is  $4.978 \times 10^{-3}$ . Taking activity into account we find that the actual solubility of magnesite is 1.66X greater than that predicted by the simple assumption that activity equals concentration. Even in dilute solutions activity is important and should be taken into account when making thermodynamic calculations involving fresh water.

- c.  $\text{Mg}^{2+}$  and  $\text{CO}_3^{2-}$  form the complex  $\text{MgCO}_3(\text{aq})$ . For this complex,  $K_{\text{stab}} = 10^{2.98}$ . How does the existence of this complex affect the solubility of magnesite? A numerical answer is required.

$$[\text{MgCO}_3(\text{aq})] = K_{\text{stab}}[\text{Mg}^{2+}][\text{CO}_3^{2-}] = K_{\text{stab}}K_{\text{sp}}(\text{magnesite}) = (10^{2.98})(10^{-5.05}) = 10^{-2.07} = 8.5 \times 10^{-3}$$

From part (b) the solubility of magnesite is  $4.978 \times 10^{-3} \text{ mol L}^{-1}$ . The aqueous species has an activity coefficient of 1. Taking into account the aqueous species, the total solubility of magnesite is  $13.48 \times 10^{-3} \text{ mol L}^{-1}$ , and increase in solubility of 2.7X due to the formation of the aqueous complex.



25. The Hubbard Brook watershed in the White Mountain National Forest in New Hampshire, USA, has been the site of a long-term study on the effect of natural and anthropogenic processes on aquatic ecosystems. Water collected from the brook has the following chemical composition (Likens et al., 1977):

Concentration (mg L <sup>-1</sup> )			
Ca <sup>2+</sup>	1.7	SO <sub>4</sub> <sup>2-</sup>	6.3
Mg <sup>2+</sup>	0.4	HCO <sub>3</sub> <sup>-</sup>	0.9
Na <sup>+</sup>	0.9	SiO <sub>2(aq)</sub>	4.5
K <sup>+</sup>	0.3	pH	4.9
Cl <sup>-</sup>	0.55	TDS	19

Note that the pH for Hubbard Brook is much less than 5.7. This is a region in which acid rain is a problem, and the acid rain input is reflected in the water chemistry.

- a. Calculate the concentrations of the ionic species in mol L<sup>-1</sup>.

	mg L <sup>-1</sup>	At. wt.	mol L <sup>-1</sup> (x 10 <sup>-5</sup> )		mg L <sup>-1</sup>	At. wt.	mol L <sup>-1</sup> (x 10 <sup>-5</sup> )
Ca <sup>2+</sup>	1.7	40.078	4.24	Cl <sup>-</sup>	0.55	35.453	1.55
Mg <sup>2+</sup>	0.4	24.305	1.65	SO <sub>4</sub> <sup>2-</sup>	6.3	96.064	6.56
Na <sup>+</sup>	0.9	22.990	3.91	HCO <sub>3</sub> <sup>-</sup>	0.9	61.017	1.47
K <sup>+</sup>	0.3	39.098	0.77				

- b. Calculate the total negative and positive charge. Do the charges balance, i.e., does the total positive charge equal the total negative charge?

$$\text{Positive charge} = (2)(4.24 \times 10^{-5}) + (2)(1.65 \times 10^{-5}) + (1)(3.91 \times 10^{-5}) + (1)(0.77 \times 10^{-5}) = 1.65 \times 10^{-4}$$

$$\text{Negative charge} = (1)(1.55 \times 10^{-5}) + (2)(6.56 \times 10^{-5}) + (1)(1.47 \times 10^{-5}) = 1.61 \times 10^{-4}$$

The total negative and positive charges agree to within 2.5%. This is an acceptable result relative to the error involved in determining the water chemistry.

- c. Calculate the activity coefficients for Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> at 25°C using the Debye-Hückel equation.

$$I = \frac{1}{2} \sum m_i z_i^2 = \frac{1}{2} [(4.24 \times 10^{-5})(2)^2 + (1.65 \times 10^{-5})(2)^2 + (3.91 \times 10^{-5})(1)^2 + (0.77 \times 10^{-5})(1)^2 + (1.55 \times 10^{-5})(1)^2 + (6.56 \times 10^{-5})(2)^2 + (1.47 \times 10^{-5})(1)^2] = 2.88 \times 10^{-4}$$

A very common mistake made by students is to not include all the ions in calculating the ionic strength. No matter how many times you make the point, there seems to always be a subset of students who only use the ions involved in the reaction, in this case the dissolution of gypsum,

when calculating the ionic strength.

$$\log \gamma_{i_{Ca^{2+}}} = \frac{-Az_i^2\sqrt{I}}{1 + Ba_o\sqrt{I}} = \frac{-(0.5094)(2)^2(2.88 \times 10^{-4})^{1/2}}{1 + (0.3289 \times 10^8)(6.0 \times 10^{-8})(2.88 \times 10^{-4})^{1/2}} = -0.033$$

$$\gamma_{i_{Ca^{2+}}} = 0.93$$

$$\log \gamma_{i_{SO_4^{2-}}} = \frac{-Az_i^2\sqrt{I}}{1 + Ba_o\sqrt{I}} = \frac{-(0.5094)(2)^2(2.88 \times 10^{-4})^{1/2}}{1 + (0.3289 \times 10^8)(4.0 \times 10^{-8})(2.88 \times 10^{-4})^{1/2}} = -0.034$$

$$\gamma_{i_{SO_4^{2-}}} = 0.93$$

- d. At 25°C, gypsum has the following solubility product,  $K_{sp} = 10^{-4.60}$ . Is Hubbard Brook saturated or undersaturated with respect to gypsum. Calculate the IAP and the saturation index.

$$\frac{IAP}{K_{sp}} = \frac{(0.93)(4.24 \times 10^{-5})(0.93)(6.56 \times 10^{-5})}{10^{-4.60}} = 10^{-4.02}$$

Hubbard Brook is strongly undersaturated (by 4 orders of magnitude) with respect to gypsum.

26. The Rio Grande river at Laredo, Texas has the following water chemistry (Livingstone, 1963)

Concentration (mg L <sup>-1</sup> )			
Ca <sup>2+</sup>	109	SO <sub>4</sub> <sup>2-</sup>	238
Mg <sup>2+</sup>	24	HCO <sub>3</sub> <sup>-</sup>	183
Na <sup>+</sup>	117	SiO <sub>2(aq)</sub>	30
K <sup>+</sup>	6.7	TDS	881
Cl <sup>-</sup>	171		

The Rio Grande water chemistry is very different from that of Hubbard Brook (problem 25). Hubbard Brook is located in a forested watershed in the northeastern United States, a region of temperate climate and moderate rainfall; the Rio Grande is on the US-Mexico border, a warm region with low annual precipitation. The differences in climate are at least partly responsible for the differences in water chemistry. Use the thermodynamic data from Appendix II, source 2, for the following calculations.

- a. Calculate the concentrations of the ionic species in mol L<sup>-1</sup>.

	mg L <sup>-1</sup>	At. wt.	mol L <sup>-1</sup> (x 10 <sup>-3</sup> )		mg L <sup>-1</sup>	At. wt.	mol L <sup>-1</sup> (x 10 <sup>-3</sup> )
Ca <sup>2+</sup>	109	40.078	2.72	Cl <sup>-</sup>	171	35.453	4.82
Mg <sup>2+</sup>	24	24.305	0.99	SO <sub>4</sub> <sup>2-</sup>	238	96.064	2.48

	mg L <sup>-1</sup>	At. wt.	mol L <sup>-1</sup> (x 10 <sup>-3</sup> )		mg L <sup>-1</sup>	At. wt.	mol L <sup>-1</sup> (x 10 <sup>-3</sup> )
Na <sup>+</sup>	117	22.990	5.09	HCO <sub>3</sub> <sup>-</sup>	183	61.017	3.00
K <sup>+</sup>	67	39.098	1.71				

b. Calculate the solubility product (equilibrium constant) for gypsum given a water temperature of 30°C.

The solubility product for gypsum at 25°C ( $K_{sp} = 10^{-4.60}$ ) is given in problem 25b. Thus, the easiest way to answer this question is to use the van't Hoff equation (2-34).

$$\Delta H_R^0 = (-543.0) + (-909.34) + (2)(-285.83) - (-2022.92) = -1.08 \text{ kJ mol}^{-1}$$

$$\ln K_t = \ln(10^{-4.60}) + \frac{-1.08}{8.314 \times 10^{-3}} \left( \frac{1}{298.15} - \frac{1}{303.15} \right) = -10.60$$

$$\log K_t = -4.60$$

c. Calculate the activity coefficient for Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> at 30°C using the Debye-Hückel equation.

$$I = \frac{1}{2} \sum m_i z_i^2 = \frac{1}{2} [(2.72 \times 10^{-3})(2)^2 + (0.99 \times 10^{-3})(2)^2 + (5.09 \times 10^{-3})(1)^2 + (1.71 \times 10^{-3})(1)^2 + (4.82 \times 10^{-3})(1)^2 + (2.48 \times 10^{-3})(2)^2 + (3.00 \times 10^{-3})(1)^2] = 0.01969$$

$$\log \gamma_{i_{Ca^{2+}}} = \frac{-Az_i^2 \sqrt{I}}{1 + Ba_o \sqrt{I}} = \frac{-(0.5138)(2)^2(0.01969)^{1/2}}{1 + (0.3299 \times 10^8)(6.0 \times 10^{-8})(0.01969)^{1/2}} = -0.226$$

$$\gamma_{i_{Ca^{2+}}} = 0.59$$

$$\log \gamma_{i_{SO_4^{2-}}} = \frac{-Az_i^2 \sqrt{I}}{1 + Ba_o \sqrt{I}} = \frac{-(0.5138)(2)^2(0.01969)^{1/2}}{1 + (0.3299 \times 10^8)(4.0 \times 10^{-8})(0.01969)^{1/2}} = -0.243$$

$$\gamma_{i_{SO_4^{2-}}} = 0.57$$

d. By how much is the water supersaturated or undersaturated with respect to CaSO<sub>4</sub>·2H<sub>2</sub>O? Your answer should include a numerical estimate.

$$\frac{\text{IAP}}{K_{\text{sp}}} = \frac{(0.59)(2.72 \times 10^{-3})(0.57)(2.48 \times 10^{-3})}{10^{-4.60}} = 10^{-1.04}$$

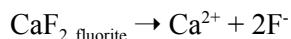
The Rio Grande river is undersaturated with respect to gypsum by about one order of magnitude, or it is only 9% saturated with respect to gypsum.

27. Fluoride is sometimes found in high concentrations in ground and surface waters. Fluoride, in low concentrations, is often added to drinking water to minimize dental carries, but in higher concentrations fluoride can pose a health risk. The following table gives the composition of relatively fluoride-rich waters from three locations: groundwaters drawn from the Bongo granite, Ghana, ground waters from Rajasthan, India and surface waters from Lake Abiata, Ethiopia. Use the thermodynamic data from Appendix II, Source 3, for the following calculations.

Ground and surface water chemistry (mg L <sup>-1</sup> )			
Species	Bongo granites, Ghana <sup>1</sup>	Rajasthan, India <sup>2</sup>	Lake Abiata, Ethiopia <sup>2</sup>
Ca <sup>2+</sup>	25.3	27.1	1.0
Mg <sup>2+</sup>	11.5	19.1	0.9
Na <sup>+</sup>	23.9	1101	4460
K <sup>+</sup>	2.0	5.9	192
Cl <sup>-</sup>	6.7	617	1911
F <sup>-</sup>	2.3	6.8	119
SO <sub>4</sub> <sup>2-</sup>	4.8	500	14.4
HCO <sub>3</sub> <sup>-</sup>	156	903	8420

- a. Two minerals that may control the concentration of fluoride ion in solution are fluorite (CaF<sub>2</sub>) and villiaumite (NaF). For each of the waters listed in the table, determine the saturation index at 25°C for these minerals. (*Note:* Activity is important and must be included in the calculations.) Would either of these minerals control the fluoride concentration of these waters?

For the dissolution of fluorite

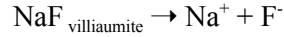


$$\Delta G_{\text{R}} = (-553.5) - (2)(-281.7) + (-1176.9) = 60.0 \text{ kJ mol}^{-1}$$

$$\log K_{\text{eq}} = \frac{-(60.0)}{5.708} = -10.51$$

$$K_{\text{sp}} = 10^{-10.51}$$

For the dissolution of villiaumite



$$\Delta G_{\text{R}} = (-261.9) - (-281.7) + (-546.3) = 2.7 \text{ kJ mol}^{-1}$$

$$\log K_{\text{eq}} = \frac{-(2.7)}{5.708} = -0.47$$

$$K_{\text{sp}} = 10^{-0.47}$$

The rest of the solution is found on spreadsheet **Problem 2-27.xls**.

	IAP/ $K_{\text{sp}}$		
	Ghana	India	Ethiopia
Fluorite	1416	1576	417
Villiaumite	$2.1 \times 10^{-7}$	$9.3 \times 10^{-6}$	$2.4 \times 10^{-4}$

Given that the solubility of fluorite is much less than that of villiaumite, fluorite is the mineral that could control the concentration of  $\text{F}^-$  in natural waters. All three waters are oversaturated with respect to fluorite and strongly undersaturated with respect to villiaumite. Fluorite should control the concentration of F ion in solution.

- b. What is a possible explanation for the very high concentrations of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , and  $\text{HCO}_3^-$  in the waters of Lake Abiata? The lake has a pH of 9.62.

This is an area with a very arid climate and thus a high rate of evaporation. This leads to a build-up of salts in residual waters and ultimately alkaline waters as indicated by the high pH value.

28. Knauss et al. (2000) determined various thermodynamic quantities for the aqueous solubilities of two organic liquids of environmental interest, trichloroethene (TCE) and tetrachloroethene (PCE). The thermodynamic data at 298 K are tabulated here. Note that the reaction is organic liquid  $\rightarrow$  organic liquid dissolved in water.

	$\Delta G_{\text{soln}}$ (kJ mol <sup>-1</sup> )	$\Delta H_{\text{soln}}$ (kJ mol <sup>-1</sup> )	$\Delta S_{\text{soln}}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta C_{\text{p, soln}}$ (J mol <sup>-1</sup> K <sup>-1</sup> )
TCE	11.282	-3.35	-49.07	385.2
PCE	15.80	-1.79	-59.00	354.6

- a. Calculate the equilibrium constants for both reactions.

$$\text{For TCE: } \log K_{\text{eq}} = \frac{-(11.282)}{5.708} = -1.977$$

$$\text{For PCE: } \log K_{\text{eq}} = \frac{-(15.80)}{5.708} = -2.77$$

- b.** If 1 kg of each organic liquid was spilled into 1000 kg of water, calculate the concentration of each organic liquid dissolved in the water.

The calculated equilibrium constants are for the following equilibrium relationship

$$K_{\text{eq}} = \frac{\text{Organic liquid dissolved}}{\text{Organic liquid}}$$

Thus,

$$\text{Organic liquid dissolved} = (K_{\text{eq}})(\text{Concentration of organic liquid})$$

$$\text{For TCE: Dissolved} = (10^{-1.97})(1 \text{ g kg}^{-1}) = 0.01 \text{ g kg}^{-1}$$

$$\text{For PCE: Dissolved} = (10^{-2.77})(1 \text{ g kg}^{-1}) = 1.7 \times 10^{-3} \text{ g kg}^{-1}$$

- c.** Using Le Châtelier's principle, predict what would happen to the solubility of each organic liquid in water with increasing temperature.

Enthalpy is negative for both reactions, i.e., the reactions are exothermic. Since the reactions are exothermic, with increasing temperature the reactions will shift to the left leading to a decrease in the equilibrium constant. This means that the solubility of the organic liquids in water will decrease with increasing temperature.

- d.** For each organic liquid calculate the equilibrium constant at 40°C. Were the predictions you made using Le Châtelier's principle, part (c), correct?

For TCE:

$$\ln K_t = \ln(10^{-1.977}) + \frac{-3.35}{8.314 \times 10^{-3}} \left( \frac{1}{298.15} - \frac{1}{313.15} \right) = -4.617$$

$$\log K_t = -2.005$$

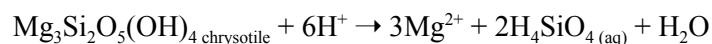
For PCE:

$$\ln K_t = \ln(10^{-2.77}) + \frac{-1.79}{8.314 \times 10^{-3}} \left( \frac{1}{298.15} - \frac{1}{313.15} \right) = -6.41$$

$$\log K_t = -2.79$$

In both cases the equilibrium constant decreases confirming the predictions based on Le Châtelier's principle

29. Asbestos minerals are considered to be a health hazard. The most common type of asbestos is chrysotile, and this mineral comprises about 95% of the asbestos in the United States. Small asbestos fibers can be taken into the lung, where they interact with the lining of the lung. This problem deals with the solubility of chrysotile asbestos in the lung. A later problem deals with the rate at which chrysotile fibers will break down in the lung. The dissolution reaction for chrysotile can be written



Use the thermodynamic data from Appendix II, source 3, for the following calculations.

- a. Calculate the equilibrium constant for this reaction at  $T = 37^\circ\text{C}$ , the average temperature of the human body.

The easiest way to do this problem is to use equation 2-33. We need to calculate both the change in enthalpy and the change in entropy for the reaction.

$$\Delta H_R^\circ = (3)(-466.8) + (2)(-1460.0) + (-285.8) - (-4361.7) - (6)(0) = -244.5 \text{ kJ mol}^{-1}$$

$$\Delta S_R^\circ = (3)(-138.0) + (2)(180.0) + (70.0) - (221.3) - (6)(0) = -205.3 \text{ J mol}^{-1}$$

$$\ln K_{\text{eq}} = \frac{-\Delta H_R^\circ}{RT} + \frac{\Delta S_R^\circ}{R} = \frac{-(-244.5)}{(8.314 \times 10^{-3})(310.15)} + \frac{-0.2053}{8.314 \times 10^{-3}} = 70.1$$

$$K_{\text{eq}} = 10^{30.4}$$

- b. For fluid in lung tissues,  $\text{pH} = 4$ ,  $\text{Mg}^{2+} = 8.7 \times 10^{-4} \text{ mol L}^{-1}$ , and  $\text{H}_4\text{SiO}_{4(\text{aq})} = 1.5 \times 10^{-6} \text{ mol L}^{-1}$ . Assume activity equals concentration. Are the lung fluids under- or oversaturated with respect to chrysotile? Give a numerical answer.

$$\text{AP} = \frac{[\text{Mg}^{2+}]^3[\text{H}_4\text{SiO}_{4(\text{aq})}]^2}{[\text{H}^+]^6} = \frac{[8.7 \times 10^{-4}]^3[1.5 \times 10^{-6}]^2}{[10^{-4}]^6} = 1482$$

Compared to the equilibrium constant calculated in part (a), the lung fluids are strongly undersaturated with respect to chrysotile.

- c. Redo the calculation in part (b) given an ionic strength for the lung fluids of 0.12.

For the uncharged species,  $\text{H}_4\text{SiO}_{4(\text{aq})}$ , the activity coefficient is (equation 2-44)

$$\gamma = 10^{0.11} = 10^{(0.1)(0.12)} = 1.028$$

For  $\text{Mg}^{2+}$

$$\log \gamma_{i_{\text{Mg}^{2+}}} = \frac{-Az_i^2 \sqrt{I}}{1 + Ba_o \sqrt{I}} = \frac{-(0.5205)(2)^2(0.12)^{1/2}}{1 + (0.3315 \times 10^8)(8.0 \times 10^{-8})(0.12)^{1/2}} = -0.376$$

$$\gamma_{i_{\text{Mg}^{2+}}} = 0.42$$

For  $\text{H}^+$

$$\log \gamma_{i_{\text{H}^+}} = \frac{-Az_i^2 \sqrt{I}}{1 + Ba_o \sqrt{I}} = \frac{-(0.5205)(1)^2(0.12)^{1/2}}{1 + (0.3315 \times 10^8)(9.0 \times 10^{-8})(0.12)^{1/2}} = -0.089$$

$$\gamma_{i_{\text{H}^+}} = 0.81$$

$$AP = \frac{[\text{Mg}^{2+}]^3 [\text{H}_4\text{SiO}_4(\text{aq})]^2}{[\text{H}^+]^6} = \frac{[(0.42)(8.7 \times 10^{-4})]^3 [(1.028)(1.5 \times 10^{-6})]^2}{[(0.81)(10^{-4})]^6} = 411$$

**d.** Based on these calculations, would you expect chrysotile to persist in the lungs? Explain your answer.

Lung fluids are strongly undersaturated with respect to chrysotile. Therefore, strictly from the point of view of equilibrium thermodynamics, chrysotile should readily dissolve in the lungs. Its actual rate of dissolution is a function of kinetics (see Problem 32).

**30.** Knauss et al. (2000) determined Henry's law constants for TCE and PCE at various temperatures. Henry's law is often expressed as

$$H_c = \frac{\text{Concentration vapor}}{\text{Concentration liquid}}$$

which is the form of Henry's law used by Knauss et al. (2000).

TCE		PCE	
T (K)	$H_c$ ( $\text{atm m}^3 \text{ mol}^{-1}$ )	T (K)	$H_c$ ( $\text{atm m}^3 \text{ mol}^{-1}$ )
294	0.006942	295	0.017574
323	0.025183	324	0.057607
348	0.048869	348	0.121925
372	0.067645	374	0.182980



TCE		PCE	
T (K)	H <sub>c</sub> (atm m <sup>3</sup> mol <sup>-1</sup> )	T (K)	H <sub>c</sub> (atm m <sup>3</sup> mol <sup>-1</sup> )
390	0.060473	397	0.189062

a.  $1 \times 10^{-4}$  mol m<sup>-3</sup> of TCE is dissolved in water at 294 K. Calculate the equilibrium vapor pressure.

$$P_i = C_i H_c = (1 \times 10^{-4} \text{ mol m}^{-3})(0.006942 \text{ atm m}^3 \text{ mol}^{-1}) = 6.94 \times 10^{-7} \text{ atm}$$

b.  $1 \times 10^{-5}$  mol m<sup>-3</sup> of PCE is dissolved in water at 324 K. Calculate the equilibrium vapor pressure.

$$P_i = C_i H_c = (1 \times 10^{-5} \text{ mol m}^{-3})(0.057607 \text{ atm m}^3 \text{ mol}^{-1}) = 5.76 \times 10^{-7} \text{ atm}$$

31. At 25°C and pH = 5, the following dissolution rates have been obtained for quartz, microcline, albite, diopside, forsterite, and anorthite (data from Lasaga et al., 1994). These dissolution reactions are zeroth-order reactions.

Mineral	Formula	Density g cm <sup>-3</sup>	Log rate mol m <sup>-2</sup> s <sup>-1</sup>
Quartz	SiO <sub>2</sub>	2.65	-13.39
Microcline	KAlSi <sub>3</sub> O <sub>8</sub>	2.59	-12.50
Albite	NaAlSi <sub>3</sub> O <sub>8</sub>	2.62	-12.26
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>	3.22	-10.15
Forsterite	Mg <sub>2</sub> SiO <sub>4</sub>	3.22	-9.50
Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	2.76	-8.55

Assuming a planar surface, calculate how long it will take to dissolve a 1-mm-thick layer from each of the minerals. Note that the dissolution rates are determined for a square meter of surface area, so you should do these calculations for 1 m<sup>2</sup> of surface area retreating 1 mm. You will first need to calculate the total moles of each mineral in the volume to be removed. Then calculate the dissolution times, in years, for each mineral. Compare these dissolution times to the preservation/loss of these minerals during weathering and transport. Is there a relationship between the dissolution times and the persistence of these minerals in the weathering environment?

The amount of material removed = (0.1 cm)(100 cm)(100 cm) = 1000 cm<sup>3</sup>. First determine the mass of material per 1000 cm<sup>3</sup>. Then determine the number of moles removed from a 1mm thick surface area by dividing the mass by the atomic weight of the mineral. The dissolution time is then determined by dividing the moles of material by the rate constant. The results are tabulated below.

Mineral	Mass of material (g)	Atomic Weight	Moles of material	Log rate mol m <sup>-2</sup> s <sup>-1</sup>	Dissolution time
Quartz	2650	60.084	44.10	-13.39	34.3 My
Microcline	2590	278.33	9.31	-12.50	933 ky
Albite	2620	262.22	9.99	-12.26	576 ky
Diopside	3220	216.55	14.87	-10.15	6656 y
Forsterite	3220	140.69	22.89	-9.50	2294 y
Anorthite	2760	278.21	9.92	-8.55	111.5 y

There is a relationship between dissolution rate and the persistence of these minerals in the weathering environment. Quartz is the mineral most resistant to weathering and this is reflected in its long dissolution time. The other minerals have significantly shorter dissolution times and these correspond to the weatherability of these minerals in the natural environment (see Chapter 9). The minerals that are least stable thermodynamically at surface temperatures and pressure are those that dissolve fastest.

32. Hume and Rimstidt (1992) investigated the dissolution of chrysotile in lung solutions. They found that the rate-controlling step is the release of Si to solution, and that the reaction is zeroth order. The experimentally determined rate constant is  $k = 5.9 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ . They modeled the breakdown of a fiber as if it were an infinitely long cylinder dissolving over its lateral surface. The resulting equation is

$$t = 3/4 (d/V_m k)$$

where  $t$  is the time in seconds,  $d$  is the diameter of the fiber in meters,  $V_m$  is the volume occupied by 1 mole of silica in chrysotile ( $5.4 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ ), and  $k$  is the rate constant. Calculate the dissolution time for a chrysotile fiber 1  $\mu\text{m}$  in diameter.

$$t = (0.75)[(1 \times 10^{-6} \text{ m}) / (5.4 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})(5.9 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1})] = 23,540,490 \text{ s} = 272 \text{ d}$$

33. Foos (1997) determined a first-order rate constant for the removal of  $\text{Fe}^{2+}$  from a stream (Case Study 2-1). Discharge from a point source adds  $\text{Fe}^{2+}$  to a river. Using the rate constant determined by Foos (1997) and a stream velocity of  $0.5 \text{ m s}^{-1}$ , calculate the transport distance required to achieve a 90% reduction in the amount of  $\text{Fe}^{2+}$  in solution. To do this problem you will first need to find the amount of time required to reduce the iron concentration by 90%.

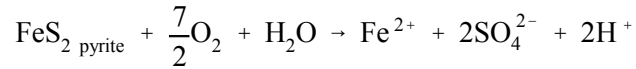
There are several ways to do this problem. One way is to set  $A_0 = 1$  and  $A = 0.1$  (to represent a 90% reduction) and then solve the equation  $\ln A = \ln A_0 - kt$  for time.

$$t = -(\ln A - \ln A_0) / k = -(-2.3026 - 0) / 2.9 \times 10^{-4} \text{ s}^{-1} = 7940 \text{ s}$$

$$\text{Transport distance} = (0.5 \text{ m s}^{-1})(7940 \text{ s}) = 3970 \text{ m}$$

34. The breakdown of pyrite (and marcasite) is important in determining the pH of waters draining from coal mines and spoils (acid mine drainage). Aqueous oxidation of pyrite by molecular oxygen can be

represented by the following reaction:



For this reaction, Williamson and Rimstidt (1994) determined the following rate constant:

$$r = 10^{-8.19} \frac{m_{\text{DO}}^{0.5}}{m_{\text{H}^+}^{0.11}}$$

where  $m_{\text{DO}}$  is the amount of dissolved oxygen,  $m_{\text{H}^+}$  is the hydrogen ion concentration, and  $r$  is the rate of pyrite destruction in  $\text{mol m}^{-2} \text{s}^{-1}$ . Assume the activation energy for this reaction is  $60 \text{ kJ mol}^{-1}$ . Spoils from a coal mine contain small pyrite cubes having an average specific surface area of  $0.01 \text{ m}^2 \text{ g}^{-1}$ . Water percolating down through this spoils pile is saturated with respect to atmospheric oxygen ( $10^{-3.6} \text{ mol L}^{-1}$ ). The water has a pH of 5.0. Assume that the breakdown of pyrite only occurs according to the preceding reaction.

- a. Calculate the rate constant for the breakdown of pyrite in contact with the water percolating through the spoils pile.

$$r = 10^{-8.19} \frac{m_{\text{DO}}^{0.5}}{m_{\text{H}^+}^{0.11}} = (10^{-8.19}) \left[ \frac{(10^{-3.6})^{0.5}}{(10^{-5})^{0.11}} \right] = 3.63 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$$

- b. Given that the reaction is pseudo-zero-order, calculate the time required ( $t_{1/2}$ ) for oxidation of half the pyrite in the spoils pile. You will first need to calculate the number of moles in 1 gram of pyrite, and then determine the moles per square meter of specific surface area. The result of this calculation is the value for  $A_0$  in the rate equation.

$$\text{Moles of pyrite in 1 gram} = 1 \text{ gram/atomic wt. of pyrite} = 1/119.98 = 8.335 \times 10^{-3}$$

$$\text{Moles of pyrite per 1 m}^2 \text{ of surface area} = (100)(8.335 \times 10^{-3}) = 0.8335 \text{ mol m}^{-2}$$

$$t_{1/2} = \frac{0.5A_0}{k} = \frac{(0.5)(0.8335)}{3.63 \times 10^{-10}} = 1.148 \times 10^9 \text{ s} = 36.38 \text{ y}$$

- c. If the reaction rate was determined at  $20^\circ\text{C}$ , calculate the reaction rate at  $30^\circ\text{C}$ .

First determine the pre-exponential term.

$$\log A = \log k + \frac{E_a}{2.303RT} = -9.44 + \frac{60}{(2.303)(8.314 \times 10^{-3})(293.15)} = -9.44 + 10.69 = 1.25$$

Use the Arrhenius equation (2-53) to find the reaction rate at  $30^\circ\text{C}$ .

$$k = A \exp\left(\frac{-E_a}{RT}\right) = (17.78) \exp\left(\frac{-60}{(8.314 \times 10^{-3})(303.15)}\right) = 8.15 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$$

- 35.** Several studies have been done on the rate at which organic matter breaks down in the marine environment. Westerich and Berner (1984) identified three types of organic matter in marine sediments - highly reactive, less reactive, and nonreactive (didn't break down during the course of their experiments). The following equation summarizes the results of their experiments:

$$G_T(t) = G_{o1}[\exp(-k_1t)] + G_{o2}[\exp(-k_2t)] + G_{nr}$$

where  $G_T$  is the total organic carbon,  $G_{o1}$  is the highly reactive fraction,  $G_{o2}$  is the less reactive fraction, and  $G_{nr}$  is the none reactive fraction. Different rate constants were determined for oxic and anoxic decay. Middelburg (1989) developed a different model that expressed the decay of organic matter in marine sediments in terms of a single first-order rate equation in which  $k$  changes with time. The following equation relates the rate constant and its change with time:

$$\log k = -0.95 \log t - 0.81$$

and

$$G_{t_1} = G_{t_0} \exp 3.2(-t^{0.05})$$

where  $G_{t_1}$  is the amount of organic carbon remaining at time  $t$ ,  $G_{t_0}$  is the amount of organic carbon initially present, and  $t$  is time.

For a number of years New York City has disposed of its sewage sludge in the New York bight.

- a.** Using the model of Westerich and Berner (1984), calculate the amount of sludge remaining 1 year after deposition in the New York Bight. Assume that the sewage consists of 45% highly reactive organic carbon, 45% less reactive organic carbon, and 10% nonreactive organic carbon. For oxic decay,  $k_1 = 18 \text{ y}^{-1}$  and  $k_2 = 2.3 \text{ y}^{-1}$ .

$$G_T(t) = (45)[\exp(-18 \times 1)] + (45)[\exp(-2.3 \times 1)] + 10 = 0 + 4.5 + 10 = 14.5\%$$

- b.** Do the same calculation as in (a) using the model of Middelburg (1989).

$$G_{t_1} = (100)[\exp(-3.2 \times 1^{0.05})] = (100)(0.041) = 4.1\%$$

- c.** Compare the two answers. Why are they different?

The Westerich and Berner model considers some of the organic carbon to be nonreactive while the Middelburg model considers all of the carbon to be reactive. The results are similar if you exclude the nonreactive carbon in part (a).

- d.** Using the equation of Middelburg (1989), calculate the length of time it will take for 50% and 99% of the organic matter to decompose. Are both of these answers realistic? You may want to read the original paper to get a better understanding of the model.

Rearranging the equation of Middelburg in order to solve for  $t$  gives

$$t = \left[ \left( \ln \frac{G_{t_1}}{G_{t_0}} \right) \left( -\frac{1}{3.2} \right) \right]^{(20)} \left( \frac{1}{0.05} \right)$$

For 50%:

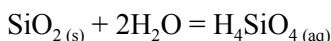
$$t = \left[ \left( \ln \frac{50}{100} \right) \left( -\frac{1}{3.2} \right) \right]^{(20)} = 5.17 \times 10^{-14} \text{ y}$$

For 1%:

$$t = \left[ \left( \ln \frac{1}{100} \right) \left( -\frac{1}{3.2} \right) \right]^{(20)} = 1452 \text{ y}$$

The first answer, for 50% degradation, is not realistic. Middelburg (1989) solved this problem by introducing an additional parameter,  $a$ , which was the apparent initial age. This parameter was eliminated from the above equation in order to simplify the problem. If the student reads Middelburg's paper, she/he will discover that what the author actually found was that all the field data showed the same reactivity decrease with time, but each data set started with a different apparent age. This apparent age presumably represents the time that elapsed before the organic matter began to decompose.

**36.** The dissolution of quartz in  $\text{H}_2\text{O}$  can be represented by the following reaction:

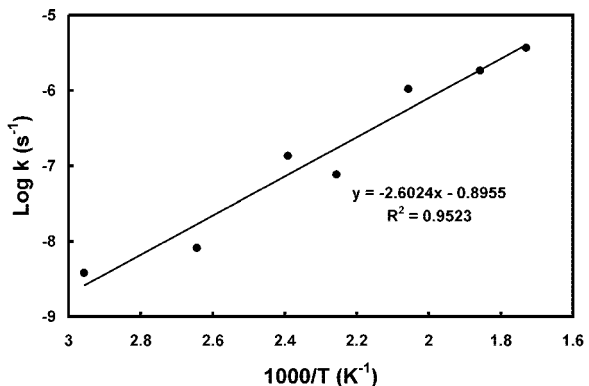


Rimstidt and Barnes (1980) determined the reaction rate for the dissolution of quartz as a function of temperature. Their data are listed in the following table:

Temperatures and reaction rates for the dissolution of quartz	
T (°C)	k (sec <sup>-1</sup> )
65	3.81 x 10 <sup>-9</sup>
105	8.15 x 10 <sup>-9</sup>
145	1.36 x 10 <sup>-7</sup>
170	7.68 x 10 <sup>-8</sup>
213	1.05 x 10 <sup>-6</sup>
265	1.85 x 10 <sup>-6</sup>
305	3.69 x 10 <sup>-6</sup>

- a. Plot  $\log k$  versus  $1/T$ . Note that temperature should be in *Kelvin*.

See spreadsheet **Problem 2-36.xls**. The line is fitted to the data points using simple linear regression (**Figure 2-36a**). The slope of the line is  $-2.6024$  and the y intercept is  $-0.8955$ .



- b. Using the graph, determine the activation energy for this reaction and the pre-exponential factor.

**Figure 2-36a.** Arrhenius plot for quartz-water reactions.

$$\text{Log } A = \text{y-intercept} = -0.8955$$

$$A = 0.13$$

$$\text{Slope (m)} = -E_a/2.303R$$

$$E_a = -m \cdot 2.303R = -(-2.6024 \text{ K})(1000)(2.303)(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) = 49.8 \text{ kJ mol}^{-1}$$

37. The bacterial reduction of organic matter in marine sediments has been investigated by Berner (1981a). The following data table, showing the variation in sulfate as a function of time, was derived from the experiments of Berner (1981).

Dissolved sulfate versus time for marine sediments	
$\text{SO}_4^{2-}$ (mmol L <sup>-1</sup> )	Time (days)
20	0
15	5
10	10
5	15
0	20

- a. Graph the data.

See spreadsheet **Problem 2-37.xls**. The line is fitted to the data points using simple linear regression (**Figure 2-37a**). The y-intercept is 20 and the slope is 1.

- b. What is the order of the reaction?

This is a zeroth-order reaction. The plot of concentration versus time yields a linear relationship.

c. Calculate the rate constant.

$$-k = \frac{dA}{dt} = 1 \text{ mmol L}^{-1} \text{ d}^{-1}$$

38. If you have read the book *Civil Action* or seen the movie, you may recall that trichloroethene (TCE) was one of the contaminants found in wells G and H. Much of the court case dealt with the source of this contaminant. Knauss et al. (1999) determined the kinetic rate law for the aqueous oxidation of TCE in aerobic, pH neutral, waters. The Arrhenius activation energy ( $E_a$ ) for the reaction was determined to be  $108.0 \pm 4.5 \text{ kJ mol}^{-1}$ . A series of experiments yielded the following concentration and rate data. Note that the data are given in log form.

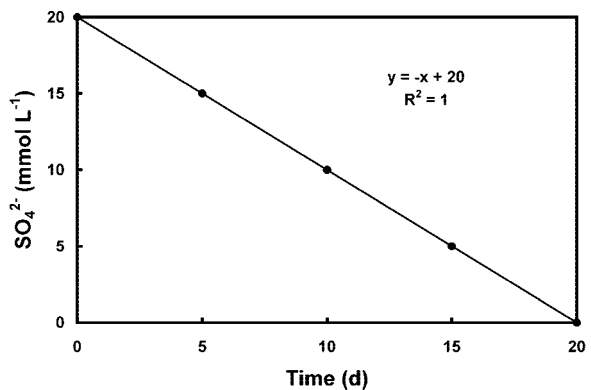


Figure 2-37a. Plot of time versus concentration. Data points fitted by simple linear regression.

Run	Log Co (mol)	Log initial rate (mol kg <sup>-1</sup> s <sup>-1</sup> )
TCE-35	-4.330	-9.748
TCE-39	-3.781	-9.724
TCE-41	-4.949	-10.300
TCE-42	-5.662	-11.261
TCE-43	-4.899	-10.195
TCE-51	-4.329	-9.741
TCE-53	-4.401	-9.770

a. Plot the data. Put *Log Co* on the *x-axis* and *Log rate* on the *y-axis*. Fit a straight line through the data points. Note that these are real data and there is scatter. The straight line can be fit either by eye or by linear regression. Linear regression is the preferred method and is most easily done using a spreadsheet. The intercept of this line with the *y-axis* gives the rate constant for this reaction at 25°C. What is the value of the rate constant? What is the slope of the line?

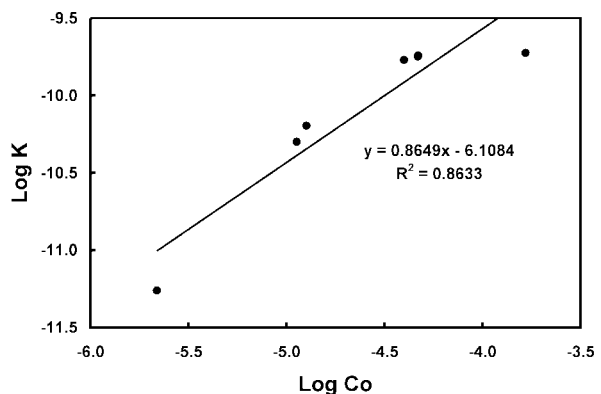


Figure 2-38a. Log Co versus Log Rate.

See spreadsheet **Problem 2-38.xls**. Simple linear regression (**Figure 2-38a**) gives  $k = 7.79 \times 10^{-7} \text{ s}^{-1}$  and slope = 0.865. Using a

polynomial curve fitting routine the authors of the paper obtained  $k = 5.77 \times 10^{-7} \text{ s}^{-1}$  and

slope = 0.85. I have used the  $k$  value obtained from the linear regression to solve the subsequent parts of the problem. If the student refers to the original paper he/she may use a different value for  $k$  ( $5.77 \times 10^{-7}$ ).

- b. Based on the slope of the line, what is the order of the reaction?

Given a slope of 0.86 this can be considered a pseudo-first order reaction.

- c. Using the rate constant from part (a), calculate the pre-exponential factor for the rate equation.

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\log A = \log k + \frac{E_a}{2.303RT} = (-6.1084) + \frac{108.0}{(2.303)(8.314 \times 10^{-3})(298.15)} = 12.81$$

- d. Calculate the rate of the reaction at 5°C. By how much does the reaction rate change in going from 25°C to 5°C?

$$\log k = \log A - \frac{E_a}{2.303RT} = 12.81 - \frac{108.0}{(2.303)(8.314 \times 10^{-3})(278.15)} = -7.47$$

$$k = 3.39 \times 10^{-8} \text{ s}^{-1}$$

$$\text{Change} = 7.79 \times 10^{-7} / 3.39 \times 10^{-8} = 23\text{X decrease in reaction rate}$$

- e. Calculate the reaction half-life at 25°C and 5°C.

$$\text{At } 25^\circ\text{C: } t_{1/2} = 0.693 / 7.79 \times 10^{-7} = 889,602 \text{ s} = 10.3 \text{ d}$$

$$\text{At } 5^\circ\text{C: } t_{1/2} = 0.693 / 3.39 \times 10^{-8} = 20,442,478 \text{ s} = 237 \text{ d}$$

- f. Assuming that the groundwater in the vicinity of wells G and H had a temperature of 5°C, what might you conclude about the transport time for TCE delivered to these wells, i.e., would it be months or years? Explain your answer. In answering this question you need to consider how long TCE would persist in the groundwater under these conditions. If it has already degraded by the time the water reaches the well, it wouldn't be found in the well water.

Given the 242 day half-life for the decomposition of TCE, one would expect TCE to persist in the groundwater system for several years, i.e., at the end of 4 years approximately 1.5% of the amount of TCE added to the system would still be present.