

## **Problem Set - Pre-Course Preparation Geochemistry for Ground-Water Systems**

The following problems assume you have a copy of Hem's Water Supply Paper for reference, a copy of thermodynamic data from Stumm and Morgan, and a reprint of Nordstrom and others (Revised chemical equilibrium data for major water-mineral reactions and their limitations, ACS Symposium Series 416, 1990) for log Ks for reactions. All but Hem's Water Supply Paper should have been forwarded to you as PDF files.

Unfortunately, the units of thermodynamic data are in transition. Some data are in kilocalories and some are in kilojoules. The conversion is kilojoules=kilocalories x 4.184. Two constants that are dependent on the units are the gas constant,  $R=0.001987 \text{ kcal mol}^{-1} \text{ K}^{-1}$  or  $0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$ ; the Faraday constant,  $F=23.06 \text{ kcal volt}^{-1} \text{ gram-equivalent}^{-1}$  or  $96.490 \text{ kJ volt}^{-1} \text{ gram-equivalent}^{-1}$ . Note that the units are important in converting free energy of reaction to equilibrium constants. Be careful to keep correct units in all calculations.

We will be using the geochemical model PHREEQC for speciation, inverse, reaction, and transport modeling. The problems below were originally intended to be worked by hand from tables of thermodynamic data. However, PHREEQC can be used to solve many of the problems and if you wish, you can solve problems 2 (easier by hand), 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 19, 20, and 21 by using this code. NETPATH can be used for problem 21, although only PHREEQC will be used during the course. The keyword data blocks needed to solve these problems with PHREEQC are listed parenthetically after each problem. PHREEQC version 2.17 has recently been released along with an complete graphical user interface, PhreeqcI. PHREEQC (batch) and PhreeqcI (interactive for PC) are available at [http://wwwbrr.cr.usgs.gov/projects/GWC\\_coupled](http://wwwbrr.cr.usgs.gov/projects/GWC_coupled), or from me at [dlpark@usgs.gov](mailto:dlpark@usgs.gov) (303) 236 5098.

You must be familiar with the concept of "moles" of chemical substances. All geochemical models work in terms of moles. Here are a couple of exercises to convert units from mass (mg/L, ppm, etc.) to moles and to use several different concentration units. A concept related to moles is equivalents which is used particularly in measurements of alkalinity. (Hem, pp. 54-57)

1. Seawater contains 400 ppm calcium. Express this concentration in units of formality (mol/kg solution), molarity (mol/liter solution), molality (mol/kg water), and mg/L. The density of seawater is 1.023 kg/L, total dissolved solids is 35 o/oo (35 g solute per 1000 g solution).

2. Central Lab reports the total alkalinity of a water sample to be 100 mg/L (as  $\text{CaCO}_3$ ). Convert this value to milliequivalents per liter. (Be careful with the number of equivalents per mole of  $\text{CaCO}_3$ .) Derive the relationship to express this value of total alkalinity in mg/L as  $\text{HCO}_3^-$ . (SOLUTION keyword, see GFW or AS).

Most of the work we do involves balanced chemical reactions. A balanced reaction conserves moles of each element and the charge between the sides of the equation. Balancing reactions that involve a change in redox state can be difficult, but the following strategy is effective. (1) Write the half reaction for each element based on the change in valence state, including the proper number of electrons [for example, sulfate to sulfide is  $\text{S(VI)} + 8\text{e}^- = \text{S(-II)}$ ], (2) sum the half reactions so that electrons are eliminated, (3) replace the valence states with an aqueous species of that valence [for example  $\text{HS}^-$  for  $\text{S(-II)}$ ], (4) balance the charge by adding  $\text{H}^+$  or  $\text{OH}^-$ , (5) balance oxygen by adding water, and (6) check your result to see if hydrogen balances. (Appelo and Postma, Chapter 7 has balanced redox reactions for several redox environments.).

3. Balance the oxidation of organic matter [assumed to be  $\text{CH}_2\text{O}$ ,  $\text{C(0)}$ ] to carbon dioxide,  $\text{CO}_2$  [ $\text{C(IV)}$ ], with the reduction of organic matter to methane,  $\text{CH}_4$  [ $\text{C(-IV)}$ ]

4. Balance the oxidation of organic matter to  $\text{HCO}_3^-$  coupled with the reduction of  $\text{SO}_4^{2-}$  to  $\text{S}_{(s)}$  [Native sulfur,  $\text{S(0)}$ ].

All thermodynamic geochemical models (PHREEQC, MINTEQA2, Geochemists' Workbench, and others) rely on the theory of chemical thermodynamics. A fundamental result of chemical thermodynamics is that reactions will proceed in a manner that decreases a quantity called "free energy". In simple terms given a choice between a set of products and a set of reactants in a reaction, the set that contains the least free energy will be favored. Equilibrium obtains when there is no net decrease in free energy favoring the reactants or products. Saturation indices for minerals

indicate the direction of free-energy decrease, negative indicates dissolution is favored, positive indicates precipitation is favored. If these concepts are not familiar to you, you must read more in one of the references. (Hem pp. 10-20)

5. Is gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or anhydrite ( $\text{CaSO}_4$ ) the stable form of calcium sulfate at 25 °C and 1.0 atmosphere total pressure? Hint: write a balanced chemical reaction and calculate the standard free energy of reaction. (SOLUTION and EQUILIBRIUM\_PHASES keywords).

6. Which pair of minerals would you expect to observe together at the Earth's surface: (a)  $\text{CaCO}_3$ (calcite) and  $\text{SrSO}_4$ (celestite) or (b)  $\text{CaSO}_4$ (anhydrite) and  $\text{SrCO}_3$ (strontianite)?

7. The first ferric compound to precipitate upon oxidation of ferrous-rich waters is usually  $\text{Fe}(\text{OH})_3$ . Is this compound the stable iron oxide phase at 25 °C and 1.0 atmosphere? If not, which iron phase is stable? (SOLUTION and EQUILIBRIUM\_PHASES keywords).

Ion-association geochemical models calculate “activities” of aqueous species by using a quantity called the “ionic strength”. Activities of aqueous species can be thought of as thermodynamic concentrations. The difference between activity and concentration is related to the excess free energy needed to form the aqueous species in question. For ion-association models, the relation between activity and concentration (in molality) is quite simple,  $a = gm$ , where  $g$  is the activity coefficient. The equations used for the activity coefficients in ion-association models are based on Debye-Hückel theory. One formulation for activity coefficients (Davies equation) as a function of ionic strength is

$$\log \gamma = -Az^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

where  $z$  is charge on the ion and  $A$  is a constant at a given temperature, about 0.5085 at 25 °C. (Hem pp. 15-18)

8. Calculate ionic strength for a 0.01 molal solution of (a) sodium chloride, (b) calcium chloride, and (c) calcium sulfate. Calculate activity coefficients for calcium and chloride ions over a range of ionic strength including 0, 0.01, 0.1, 0.5, 1.0, and 2.0. (SOLUTION, REACTION, and USE keywords).

Standard free energies of reaction can be combined to form an equilibrium constant for a reaction. At equilibrium, the reaction quotient (activities of products divided by activities of reactants, each raised to their stoichiometric coefficient power) is equal to the equilibrium constant. These equations are called mass-action equations and apply to aqueous species, minerals, and gases. In practice, pure solids are assigned activities of 1.0, and activities of gases are called fugacities, which for a good approximation are equal to the partial pressure of the gas. The activity of water is approximately 1.0 for most naturally occurring solutions, provided the ionic strength is relatively small. Assume activity coefficients are 1.0 for all of the following problems. The equilibrium constants and reaction quotients can be used to calculate saturation indices for minerals, which are extremely useful quantities in determining the reactions occurring in ground water (Hem pp. 10-20, 25-26, 60-66, 22-23).

9. Calculate the pH of a solution in equilibrium with gibbsite  $[Al(OH)_3(s)]$  and pure water if the  $Al^{3+}$  activity is  $10^{-3}$  at 25 °C by using the equation

$Al(OH)_3(s) + 3H^+ = Al^{3+} + 3H_2O(l)$ . First calculate the log K for the reaction from free energy data, then calculate the pH of the solution. (SOLUTION keyword). Remember the activity of a pure solid is 1.0 and the activity of water is also nearly unity.

10. Assuming pure water dissociates to  $H_2$  and  $O_2$  gas at 25 °C and 1.0 atmospheres total pressure, calculate  $P_{H_2}$  at the upper stability limit of water ( $P_{O_2}=1.0$ ). Conversely, what is  $P_{O_2}$  at the lower stability limit of water ( $P_{H_2} = 1.0$ )? What is the  $P_{H_2}$  in equilibrium with water and air? (SOLUTION keyword).

11. A ground water sample is found to be saturated with respect to calcite, anhydrite, and celestite. Strontianite is present in the formation in contact with the water. What is the saturation index of strontianite in the water? Would you expect strontianite to be dissolving or precipitating in the formation? Use log Ks from Nordstrom and others (1990). (SOLUTION and EQUILIBRIUM\_PHASES keywords).

Thermodynamic speciation models calculate the distribution of aqueous species in solution, that is, they calculate the concentrations of all the ions and complexes that exist at the molecular scale in an aqueous solution. The models solve a series of mass-action equations for the

formation of aqueous complexes (one for each complex), mass-balance equations (one for each element or redox state of an element), and possibly a charge-balance equation. The dominant aqueous species for an element can often be calculated by hand provided some simplifying assumptions are made. Assume activity coefficients are 1.0 for all of the following problems. (Hem pp. 57-58, 25-26, 18-19, and others)

12. The first, second, and third dissociation constants for phosphoric acid ( $\text{H}_3\text{PO}_4$ ) are  $\log K = -2.15$ ,  $-7.21$ , and  $-12.35$ , respectively. In the normal pH range of ground water (6-9), what are the dominant dissolved species of phosphorus? Explain why. (SOLUTION keyword).

13. An aquifer contains siderite ( $\text{FeCO}_3$ ) in bedrock. The waters are devoid of oxygen, have a pH of 6, and a total dissolved carbon content of  $10^{-2.5}$  molal. First estimate the concentration of  $\text{CO}_3^{2-}$  under these conditions considering the species  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ . What would you expect the dissolved iron concentration of the waters to be if they are in equilibrium with siderite? (SOLUTION keyword).

14. Rainwater infiltrates into a deposit of sand composed of quartz and feldspar. In the soil zone, the water is in contact with soil air that has a  $\text{CO}_2$  partial pressure of  $10^{-1.5}$  atmospheres. The system has a temperature of  $25^\circ\text{C}$ . Estimate the pH of the soil water. Assume that reactions between the water and the sand are so slow that they do not significantly influence the chemistry of the water. Hint: You must use two mass-action expression and a charge balance relation. (SOLUTION keyword).

Equilibrium constants are functions of temperature. There are analytical expressions for some equilibrium constants that are fit to experimental data; temperature dependence of other equilibrium constants can be calculated from the Van't Hoff expression if an enthalpy of reaction is known. (Hem p. 18)

15. What is the Ca/Mg ratio in ground water from an aquifer flowing through a dolomitic limestone at  $25^\circ\text{C}$ ? How might this ratio vary with changes in temperature? (SOLUTION, EQUILIBRIUM\_PHASES, and REACTION\_TEMPERATURE keywords).

16. Sub-geothermal ground water from a quartz sandstone is in equilibrium with barite at 75 °C. This water is pumped into a heat exchanger where it cools to 25 °C. How might the properties of the heat exchanger be affected in prolonged use? (SOLUTION, EQUILIBRIUM\_PHASES, and REACTION\_TEMPERATURE keywords).

One of the most difficult processes to understand and model in geochemical systems is redox reactions. The Nernst equation provides a relationship between chemical concentrations and the potential difference that can, in principal, be measured by a pH, specific ion, or redox electrode. Under certain conditions a platinum electrode can be used to measure a redox potential or Eh. Another indicator of oxidation/reduction potential that is directly proportional to Eh is the pe. At 25 °C  $pe = 16.7Eh$ , where Eh is measured in Volts. pe is analogous to pH in that it used for the activity of electrons in mass-action equations, it differs from pH in that free electrons do not truly exist in natural waters as hydronium ions do. (Hem pp. 20-22)

17. Using a glass electrode with silver-silver chloride reference electrode, the following potentials were measured: pH 6.86 buffer, -41.3 mV; pH 4.00 buffer, -209.6mV; unknown ground water sample, +2.9 mV. What is the  $E^0$  and slope of the electrode pair? Do you think that the electrode pair is operating correctly? What is the pH of the unknown ground-water sample?

18. Complete and balance the following oxidation-reduction reaction, use only the given species plus  $H^+$  and  $H_2O$ .  $Fe^{2+} + UO_2^{2+} = Fe^{3+} + U^{4+}$  (strongly acid solution).

19. Of the species  $U^{4+}$  ( $\Delta G_f^o = -579.1 \frac{kJ}{mol}$ ) and  $UO_2^{2+}$  ( $\Delta G_f^o = -989.1 \frac{kJ}{mol}$ ) (data converted to joules from Garrels and Christ), which would predominate in a slightly oxidizing ground water environment at pH 7? (SOLUTION keyword, *wateq4f.dat* database).

20. Compute the Eh and pe of a solution containing  $10^{-4}$  molal ferric ion and  $10^{-6}$  molal ferrous ion. (SOLUTION keyword).

The following problem is typical of the approach of inverse modeling. Two water analyses are given, a set of reactants are hypothesized, and the mass transfers of each reactant are calculated. The mass transfers are exactly the balanced chemical reaction needed for one water composition to evolve from the other. (Additional reading in NETPATH or PHREEQC manual.)

21. Rain water passing through a coal mine spoils pile is suspected of reacting with pyrite, calcite, gypsum, carbon dioxide, and oxygen. Consider the rain water to be pure water. The analysis of the water at the bottom of the spoils pile is:  $\text{Fe}^{2+} = 2.0 \text{ mmol/L}$ ,  $\text{Ca}^{2+} = 1.0 \text{ mmol/L}$ ,  $\text{SO}_4^{2-} = 4.0 \text{ mmol/L}$ , total dissolved carbonate =  $0.0 \text{ mmol/L}$ . Write a balanced net chemical reaction for the evolution of the spoils pile water. Is the spoils pile open or closed to  $\text{CO}_2$  and  $\text{O}_2$  gas? (PHREEQC: SOLUTION and INVERSE\_MODELING keywords; NETPATHXL: run DBXL and then NETPATHXL).

Isotopes are additional geochemical tools that are used to determine geochemical processes in natural waters. The first hurdle in using isotope data is to understand the “d” notation. For accuracy in measurement, isotopes are measured in ratios of isotopes in a sample relative to ratios of isotopes in standards. Results are multiplied by 1000 and are reported in per mil. For example, the definition of  $\delta^{18}\text{O}$  relative to SMOW (standard mean ocean water) as follows:

$$\delta^{18}\text{O} = 1000 \left[ \frac{(\text{}^{18}\text{O}/\text{}^{16}\text{O})_{\text{sample}} - (\text{}^{18}\text{O}/\text{}^{16}\text{O})_{\text{SMOW}}}{(\text{}^{18}\text{O}/\text{}^{16}\text{O})_{\text{SMOW}}} \right]$$

This definition has the nice property that when you mix two waters, their d values mix proportionately.

22. The abundances of the isotopes of hydrogen in Vienna Standard Mean Ocean Water (VSMOW) are  $^1\text{H} = 99.984426 \text{ atom percent}$ , and  $^2\text{H} = 0.015574 \text{ atom percent}$ . What is the dD value (or  $\text{d}^2\text{H}$  value, if you prefer) relative to VSMOW of a well water sample from Antarctica that has an abundance of  $^2\text{H} = 0.0081 \text{ atom percent}$ ?