Earth &Atmospheric Sciences 455
Geochemistry

PROBLEM SET 5 SOLUTIONS DUE OCT. 17, 2007

1. Schrott et al. (1981) found that dependence on pH of the rate of dissolution of enstatite could be expressed as:

$$\Re = k a_{H^+}^n$$

where *k* shows a typical Arrhenius temperature dependence.

a.) Reaction rates were measured at a series of pH values at constant temperature (22° C). These data are shown in the adjacent table. Using these data, estimate values of *k* and *n* for this temperature (*HINT*: try using linear regression).

RATE OF ENSTATITE DISSOLUTION

pH	Rate moles Si/g-sec
1	2.75×10^{-10}
2	7.08×10^{-11}
6	2.82×10^{-13}

The first step is to linearize the equation by taking the log. We have then:

$$\log R = \log k - n\,\text{pH}$$

The equation has the form y = a +bx; a (log k) is the intercept, b (n) is the slope. Using the slope and intercept functions in Excel, we find **n = 0.598** and log *K* = -8.958

b.) Based on your answer above, do you think this is an elementary reaction? Why or why not?

No, because it depends on the fractional power of the activity of the hydrogen ion. Should be an integer if it were elementary.

T ° C	Rate moles Si/g-sec
20	3.72×10^{-13}
50	2.34×10^{-12}
60	4.07×10^{-12}
75	8.13×10^{-12}

c.) Reaction rates were also determined at various temperatures at constant pH (6). Using these data, estimate the activation energy and frequency factor for the rate constant.

The relevant equation is:

$$k = Ae^{-E/RT}$$

where E is the activation energy. Substituting this into our equation above, we have:

Taking the log we have:

$$\log R = (\log A - (E/R \times 1/T) \times \log(e)) - n\,\text{pH}$$

or

$$\log R + n\,\text{pH} = \log A - (E \times \log(e)/R) \times 1/T$$

If we set y = log R + n pH, this is again the equation of a line with log A as intercept and -(E/R× log(e)) as slope when log R + n pH is plotted against 1/T. We find A is 0.479 and E is 47.78 kJ.

d.) Using your results from (a) and (b), estimate the rate of reaction (in moles Si released per sec per gram enstatite) at pH 4 and 30° C.

$$R = 1.13 \times 10^{-11}\ \text{moles/g/sec}$$

2. Diamond is remarkably stable at the surface of the Earth. Pearson et al. (1995) estimated that to convert 1 cc of diamond to graphite at 0.1Mpa and 1000°C would require 1 billion years, but only a million years would be required at 1200°C. From the difference in these rates, estimate the activation energy for the diamond-graphite transition.

The problem is essentially telling us that in going from 1000° C to 1200° C, the reaction rate will increase by a factor of 1000. Assuming other things, particularly the frequency factor are independent of temperature, we may write:

$$\frac{R_{1200^\circ C}}{R_{1000^\circ C}} = \frac{Ae^{-E_A/(R\times1473)}}{Ae^{-E_A/(R\times1273)}} = 1000$$

Rearranging, we have:

$$e^{-E_A/(R\times1473)+E_A/(R\times1273)} = 1000$$

Taking the log

$$\frac{E_A}{R\times1273} - \frac{E_A}{R\times1473} = \ln(1000)$$

and

$$\frac{E_A}{R}\left\{\frac{1}{1273} - \frac{1}{1473}\right\} = \ln(1000)$$

finally solving for E_A

$$E_A = \frac{R\ln(1000)}{\left\{\frac{1}{1273} - \frac{1}{1473}\right\}}$$

We calculate E_A as 538.45 kJ. Wow! Remembering most activation energies are in 10's of kJ, we can see why diamond is so stable!

3. The transformation of kaolinite to illite (muscovite) may be written as:

$$K^+ + 1.5Al_2Si_2O_5(OH)_4 \rightleftarrows H^+ + KAl_3Si_3O_{10}(OH)_2 + 1.5H_2O$$

Chermack and Rimstidt (1990) determined that the forward rate of reaction was:

$$-\frac{d[K^+]}{dt} = k_+[K^+]$$

Forward and reverse rate constants for the reaction were determined to be:

$$\ln k_+ = 12.90 - 1.87 \times 10^4/T \qquad \text{and} \qquad \ln k_- = 6.03 - 1.21 \times 10^4/T$$

a.) What are the activation energies for the forward and reverse reactions?

If the rate constant temperature dependence is expressed as an Arrhenius relation, then the terms $-1.87 \times 10^4/T$ and $-1.21 \times 10^4/T$ must be equal to $-E_A/RT$. Setting E_a/R equal to $1.87 \times 10^4/R$ and $1.21 \times 10^4/R$ we find E_a of 155.5 kJ/mol and 100.6 kJ/mol for the forward and reverse respectively.

b.) What is the equilibrium constant for this reaction at 275° C?

$$\ln K = \ln k_+ - \ln k_- = 12.80 - 1.87\times10^4/T - 6.03 + 1.21 \times 10^4/T = 6.77 - 0.66 \times 10^4/T$$

Substituting 548 for T, we calculate ln K as –5.174 and K as 0.00566.

c.) Make a plot of log $\Re_{net}$ vs. log ([H$^+$]/[K$^+$]) at 250° C assuming a K$^+$ concentration of 2.0 x 10^{-6} M , ideal solution, that muscovite, water and kaolinite are pure phases, the system is not far from equilibrium, and that the forward and reverse reactions are elementary.

We can answer this problem using equation 5.66:

$$\Re_{net} = \Re_{+}(1 - \frac{Q}{K})$$

Given the assumptions, the activity quotient can be expressed simply as:

$$Q = m_{H^+}/m_{K^+}$$

Substituting this into equation 5.66, we have:

$$R_{net} = R_{+} \times (1 - \frac{m_{H^+}}{m_{K^+}}/K)$$

The rate of the forward reaction is given by:

$$R_{+} = k_{+}m_{K^+}$$

So we have: $$R_{net} = k_{+}m_{K^+} \times (1 - \frac{m_{H^+}}{m_{K^+}}/K)$$

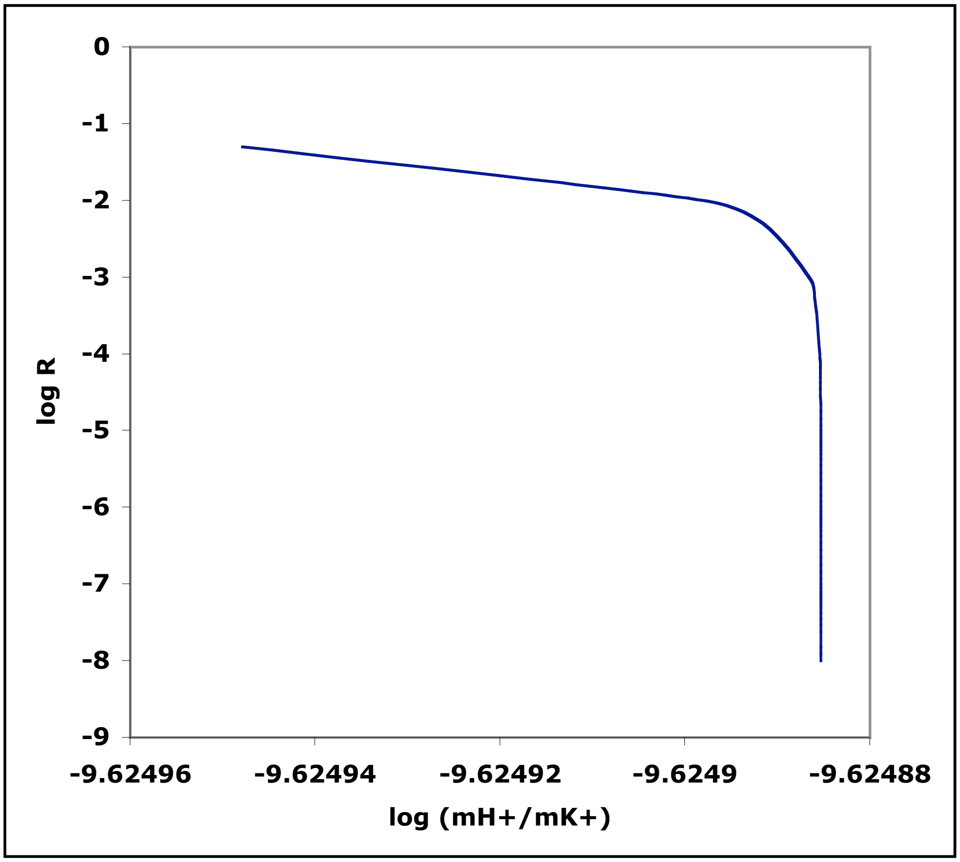
Using the equation given above for k_+ and m_{K^+} = 2.0, we calculate (k_+ m_{K^+}) to be 2.372 $\times$ 10^{-10}.

Using the equation we derived in (b) and T of 523, we calculate K as 0.00288.

Our equation is then:

$$R_{net} = 2.372 \times 10^{-10} \times (1 - m_{H^+}/m_{K^+} \times 0.00288)$$

The plot is appended.



5. Using the data in Table 5.2, determine the diffusion coefficient for diffusion of Ba in an andesitic melt for T = 1200°, 1100°, 1000°, and 900°C (assume the parameters are valid over this temperature range; remember to use thermodynamic temperature).

We solve this problem using the Arrhenius relationship in the form of Equation 5.102.

Do	Ea				
0.44	209000				
D=Do*exp(-Ea/RT)					
T °C	T, K	D			
1200	1473	1.7051E-08	cm^2/sec		
1100	1373	4.9197E-09	cm^2/sec		
1000	1273	1.1676E-09	cm^2/sec		
900	1173	2.1686E-10	cm^2/sec		

6. Crystal growth and dissolution are reactions that involve both diffusion and surface reactions occurring in series. Either of these processes can be the rate-limiting step at 25° C. Diffusion in aqueous solutions typically has an activation energy of 20 kJ/mol whereas surface reactions in aqueous solution typically have activation energies of 60-80 kJ/mol. Assuming the rates of diffusion and surface reaction for growth of a certain mineral from aqueous solution are approximately equal at 25° C, will diffusion or surface reaction be rate-limiting at 200°C?

Lets use R_D to indicate the rate of diffusion and R_S to indicate the rate of surface reaction. We have learned that both diffusion and chemical reaction rates have an Arrhenius temperature dependence of the form:

$$R \propto Ae^{-E_A/RT} \tag{1}$$

Both the surface reaction rate and the diffusion rate will depend on other things as well as activation energy and temperature (e.g., the surface reaction rate is likely to depend on concentrations of reactant and the diffusion rate will depend on the concentration gradients), but these other things are not implicitly temperature dependent and since the problem provides no information about these, let’s assume these other things are constant.

Using the Arrhenius relation, we can easily calculate that the rate of diffusion will increase by a factor of a little less than 20 over this temperature range, while (even taking an activation energy of 60 kJ) the surface reaction rate will increase by about 7000! So if both rates are similar at 25°C, then since the surface reaction rate will have increased much more than the diffusion rate in increasing temperature to 200°C, the diffusion rate will be limiting at 200°C.