Earth & Atmospheric Sciences 455: Geochemistry

Prelim Examination Oct. 24, 2007

Name ___________________________________

Show all work for partial credit. The value of R is 8.314 J/mol-K.

1. a.) What is the minimum number of components needed to describe a system which contains the phases Mg_2SiO_4 – $MgSiO_3$–$MgCaSi_2O_6$–SiO_2? (Explain your answers). *(10 points)*

3 components, which could be Mg_2SiO_4–$MgCaSi_2O_6$–SiO_2 (forsterite, diopside and quartz) or MgO, CaO, and SiO_2.

b.) How many phases would have to be present to fix both P and T?

The phase rule is $f = c - \phi + 2$

To fix both P and T, the system would have to be invariant, i.e., f = 0. Solving the equation for f=0, we find we would need **5 phases** present (e.g., a melt plus the 4 above).

2. Consider a liquid solution of plagioclase ($NaAlSi_3O_8$–$CaAl_2Si_2O_8$). *15 points.*
   (a) Write a general expression for the chemical potential of albite ($NaAlSi_3O_8$) in this solution assuming the solution is ideal.

   $$\mu = \mu^o_{Ab} + RT \ln X_{Ab}$$

   (b) Write a general expression for chemical potential if the solution is not ideal.

   $$\mu = \mu^o_{Ab} + RT \ln a_{Ab} \quad \text{or} \quad \mu = \mu^o_{Ab} + RT \ln(\lambda_{Ab} X_{Ab})$$

   (c) If plagioclase liquid and plagioclase solid are in equilibrium, what can you say about the relationship between the chemical potential of albite in the two solutions?

   The chemical potentials of albite in the two solutions are equal.

3. Use the following data to answer this question *20 points.*

Phase	Formula	H^o_f (J/mol)	S° (J/K-mol)	$\overline{V}$ (cc/mol)
water	H_2O	-285850	69.92	18.10
Kaolinite	$Al_2Si_2O_5(OH)_4$	-4119600	205.0	99.52
Gibbsite	$Al(OH)_3$	-1293335	68.45	31.96
Quartz	SiO_2	-910650	41.34	22.69

a. Write a reaction relating quartz and gibbsite to kaolinite and water.

$2Al(OH)_3 + 2SiO_2 = Al_2Si_2O_5(OH)_4 + H_2O$

b. Which side is stable at 25°C and 0.1 MPa? Why?

Whichever side has the lowest G. We calculate ΔG as:

$$\Delta G_r = G_{ka} + G_{H_2O} - 2G_{Qz} - 2G_{Gi}$$

where G for each phase is calculated as G = H – TS. ΔG is -13.91 kJ, so the right side is stable.

c. Which side is favored by increasing pressure? Why?

Since $\frac{\partial G}{\partial P} = \Delta V$, whichever side has the lowest V will be favored by increasing pressure; i.e., if the ΔV_r is negative, the r.h.s. is favored. ΔV_r calculated by Hess's Law is 8.32 cc/mol, so the left side is favored by increasing pressure.

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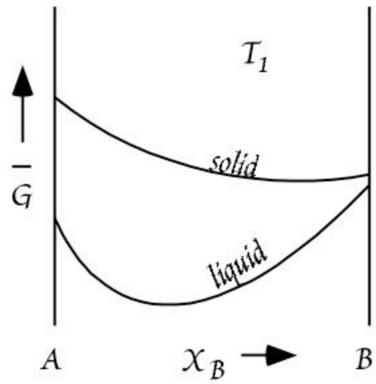
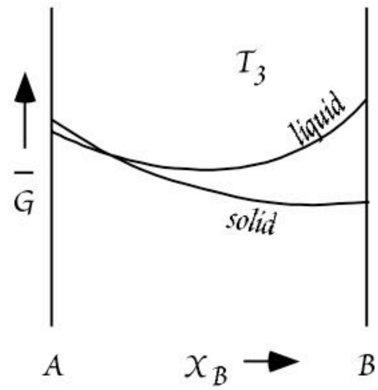
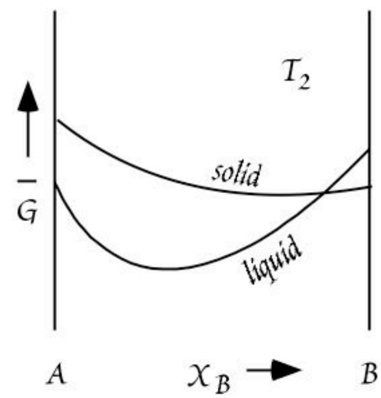
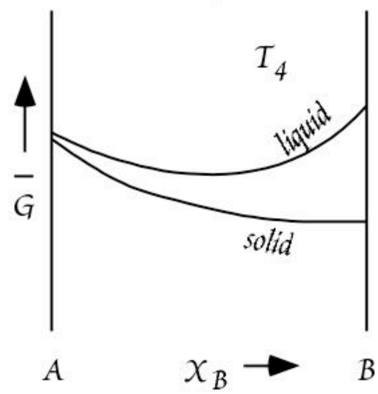
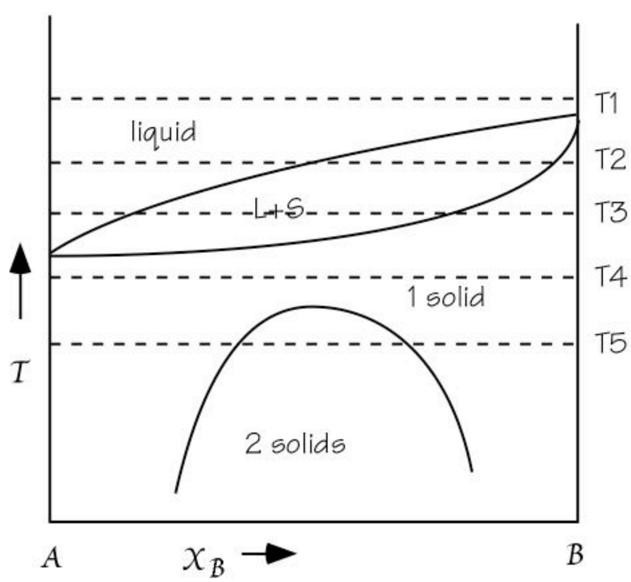
4. Shown below are G-X diagrams for a 2 component system at 5 temperatures which decrease from T_1 (highest) to T_5 (lowest). From these 5 G-X diagrams, sketch the T-X phase diagram for the system in the space provided, labeling each field. *20 points*

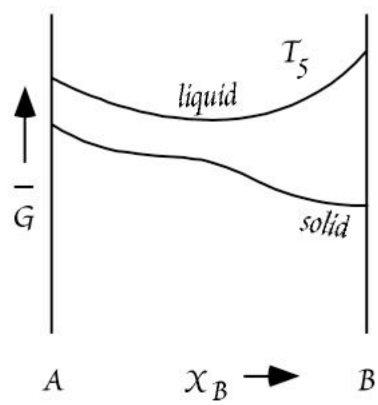












5. Using the free energies listed below, construct a pε-pH diagram showing stability fields for aqueous IrO_4^{2-} and solids of IrO_2 and Ir at 25° C and 0.1 MPa. Assume a dissolved IrO_4^{2-} activity of 10^{-8} M. Use the graph below with the upper and lower stability limits of water already drawn. *20 points*

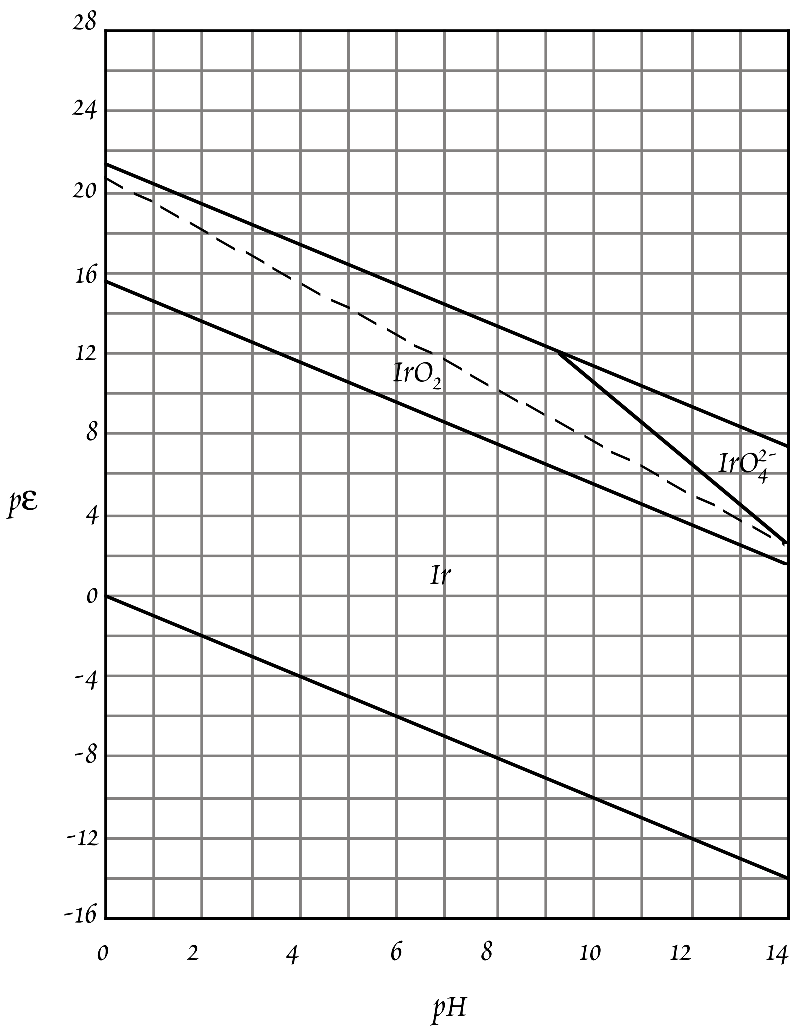
Species	ΔG_f^o (J/mol)	Species	ΔG_f^o (J/mol)
H_2O	-237191	Ir	0
IrO_2	-117152	H^+	0
IrO_4^{2-}	-196650	e^-	0

The reactions of interest are:

$Ir + 2H_2O = IrO_2 + 4H^+ + 4e^-$

$IrO_2 + 2H_2O = IrO_4^{2-} + 4H^+ + 2e^-$

$Ir + 4H_2O = IrO_4^{2-} + 8H^+ + 6e^-$



	ΔG_r	log K=log (exp(-ΔG/RT))
$Ir + 2H_2O = IrO_2 + 4H^+ + 4e^-$	357.23	-62.62
$IrO_2 + 2H_2O = IrO_4^{2-} + 4H^+ + 2e^-$	394.88	-69.22
$Ir + 4H_2O = IrO_4^{2-} + 8H^+ + 6e^-$	752.114	-131.84

Log equilibrium constant expressions are:

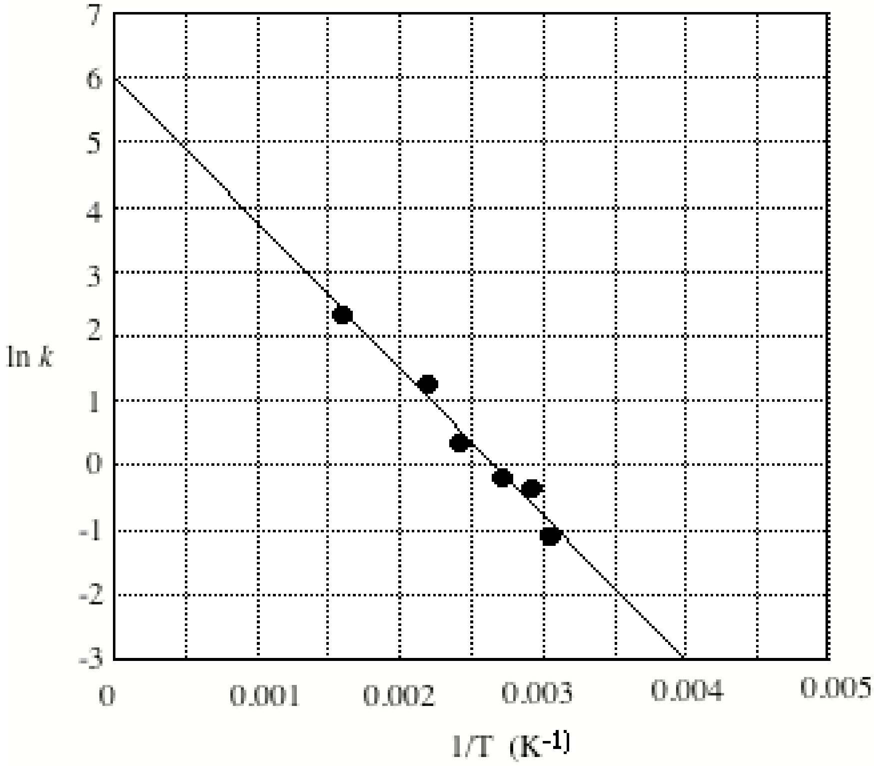
Log K = -4pH - 4pe pe = -pH - (log K)/4 = 15.65-pH

Log K = a_{IrO_4} -4pH - 2pe = -8 - 4pH -2pe pe = -2pH - 4 - (logK)/2 = 30.61-2pH

Log K = a_{IrO_4} -8pH - 6pe = -8 - 8pH -6pe pe = -8/6-(log K)/6-8/6pH = 20.63-4/3pH

The last reaction does not occur on the graph because Ir will convert to IrO_2 at lower concentrations of aqueous IrO_4^{2-} than 10^{-8}. So this equilibrium is shown by the dashed line.

6. The graph below shows the results a series of reaction rate experiments. The log of the rate constant, *k*, is plotted on the Y (vertical) axis and inverse temperature (i.e., 1/T in kelvins) is plotted on the X axis. The result of each experiment is shown as a dot; a line has been fitted to the results. *Estimate* the frequency factor and the activation, or barrier, energy for this reaction. *15 points*



In log form, the Arhenius relation is: $\ln k = \ln A - \frac{E_A}{RT}$

So on this plot, the slope is $-E_A/R$ and the intercept is ln A. The slope is 9/0.004 = 2250 and E_A = 2250*R = 18.71 kJ. The frequency factor is e^6 = 403.43.