GG325 -- PRINCIPLES OF GEOCHEMISTRY
Fall 2009
Homework set #1 (Due in 1 week)
each problem is worth 15 points except numbers 5 and 6, which are worth 20

1. balance the following equilibria expressions and write an equilibrium constant expression for each of them.

a) $O_2 + H_2 \rightarrow H_2O$ (all in the vapor phase)

$K_{eq} =$

b) $C_6H_{12}O_6$ (s) + O_2 (g) $\rightarrow$ CO_2 (g) + H_2O(l)
(Glucose)

$K_{sp} =$

c) $KAlSi_3O_8$ (s) + H_2O (l) + H^+ $\rightarrow$ $Al_2Si_2O_5(OH)_4$ (s) + K^+ (aq)+ H_4SiO_4 (aq)
(Orthoclase) (kaolinite)

$K_{eq} =$

2. Find ΔH in Joules for: $Mg_2SiO_4 + SiO_2 \rightarrow 2\ MgSiO_3$ given the following standard data:

$Mg + 3/2\ O_2 + Si \rightarrow MgSiO_3$ $\Delta H = -1497.4$ kJ/mol
$Si + O_2 \rightarrow SiO_2$ $\Delta H = -859.4$ kJ/mol
$2Mg + 2O_2 + Si \rightarrow Mg_2SiO_4$ $\Delta H = -2042.6$ kJ/mol

3. Suppose you found kyanite and andulusite coexisting in the same rock and that you had reason to believe this was an equilibrium assemblage. If you had also independently determined the temperature of equilibrium to be 400°C, use the data in Figure 4-14 of your week 2 lecture notes (Geothermometry and Geobarometry section) to determine the pressure at which this rock equilibrated.

4. Consider the following minerals:
anhydrite: $CaSO_4$
bassanite: $CaSO_4 \cdot 1/2\ H_2O$ (the stuff of which plaster of paris is made)
gyspum: $CaSO_4 \cdot 2H_2O$

a) If all of the pure water in the system is vapor (i.e., no liquid water too), how many phases are there in this system and how many components are there?

b) How many phases are present at invariant points in such a system?

c) Write all univariant reactions in this system, and note the phase that does not participate in that reaction.

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5. Seawater has the following composition:

Na^+	0.481 M	Cl^-	0.560 M
Mg^{2+}	0.0544 M	SO_4^{2-}	0.0283 M
Ca^{2+}	0.0105 M	HCO_3^-	0.00238 M
K^+	0.0105 M		

a) Calculate the ionic strength.

b) Using the Davies equation and the data in Table 3.2 to the right, calculate the practical activity coefficients for each of these ions at 25°C.

Table 3.2a Debye-Huckel Solvent

T°C	A	B (10^8 cm)
0	0.4911	0.3244
25	0.5092	0.3283
50	0.5336	0.3325
75	0.5639	0.3371
100	0.5998	0.3422
125	0.6416	0.3476
150	0.6898	0.3533
175	0.7454	0.3592
200	0.8099	0.3655
225	0.8860	0.3721
250	0.9785	0.3792
275	1.0960	0.3871
300	1.2555	0.3965

from Helgeson and Kirkham (1974).

6. Given the following 2 analyses in the table below of basaltic glass and coexisting, equilibrium composition olivine phenocrysts in 2 rock samples (rock1 is TR3D-1 and rock 2 is DS-D8A)
a) determine the K_D for the MgO ↔ FeO exchange reaction

b) calculate the temperatures at which the olivine crystallized using both MgO and FeO. *(Hint: Use the example on the next page, which is from White, "Geochemistry").* Assume Fe_2O_3 to be 10 mole% of total iron (the analysis below includes only the total iron, calculated as FeO; you need to calculate from this the amount of FeO by substracting an appropriate amount to be assigned as Fe_2O_3). Note that the mole % Fo in olivine is equivalent to the mole % Mg or MgO. *(HINT: you will need to calculate the mole fraction of MgO and FeO in the liqui*d).

Glass (melt) compositions given as wt % oxides)- except Olivine (which is as mol%):

Sample	TR3D-1	DS-D8A
SiO_2	50.32	49.83
Al_2O_3	14.05	14.09
ΣFe as FeO	11.49	11.42
MgO	7.27	7.74
CaO	11.49	10.96
Na_2O	2.3	2.38
K_2O	0.10	0.13
MnO	0.17	0.20
TiO_2	1.46	1.55
olivine Mole % Fo (=mole % Mg)	79	81

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Example 4.3. Calculating Magma Temperatures Using the Olivine Geothermometer

From the electron microprobe analysis of glass of a mid-ocean ridge basalt and its coexisting olivine microphenocryst, calculate the temperature at which the olivine and liquid equilibrated:

SiO_2	50.3
Al_2O_3	14.3
ΣFeO	11.1
MgO	7.8
CaO	11.5
Na_2O	2.6
K_2O	0.23
MnO	0.20
TiO_2	1.71
Total	99.02
Mol % Fo in Ol	82

Answer: We will answer this assuming the glass composition represents that of the liquid and using equations 4.47 and 4.48. To use the equations, we will have to convert the analysis of the glass from weight percent to mole fraction.

Let's setup a spreadsheet to do these calculations. First we must deal with the Fe analysis. The analysis reports only iron as FeO. Generally, about 10% of the iron in a basaltic magma will be present as ferric iron (Fe_2O_3), so we will have to assign 10% of the total iron to Fe_2O_3. To do this, we get the weight percent FeO simply by multiplying the total FeO by 0.9. To get weight percent Fe_2O_3, we multiply total FeO (11.1%) by 0.1, then multiply by the ratio of the molecular weight of Fe_2O_3 to FeO and divide by 2 (since there are 2 Fe atoms per molecule).

	wt%	w/10% ferric	Mol. wt	moles	mol frac.
SiO2	50.3	50.3	60.09	0.8371	0.5265
Al2O3	14.3	14.3	102	0.1402	0.0882
total FeO	11.1	11.1			
FeO		9.99	71.85	0.1390	**0.0875**
Fe2O3		1.22	157.7	0.0077	0.0049
MgO	7.8	7.8	40.6	0.1921	**0.1208**
CaO	11.5	11.5	56.08	0.2051	0.1290
Na2O	2.6	2.6	61.98	0.0419	0.0264
K2O	0.23	0.23	94.2	0.0024	0.0015
MnO	0.2	0.2	70.94	0.0028	0.0018
TiO2	1.71	1.71	79.9	0.0214	0.0135
Total	99.74	99.85		1.590	1.000
XMgO-Ol					**0.82**
XFeO-Ol					**0.18**
	TMgO	**1384**	**kelvin**	**1111**	°C
	TFeO	**1390**	**kelvin**	**1117**	°C

Now we are ready to calculate the mole fractions. We'll set up a column with molecular weights and divide each weight percent by the molecular weight to get the number of moles per 100 grams. To convert to mole fraction, we divide the number of moles by the sum of the number of moles.

Since the mole fraction of Mg in olivine is equal to the mole fraction of forsterite, we need only convert percent to fraction (i.e., divide by 100). The mole fraction of FeO in olivine is simply 1 − X_{MgO}. Thus $X_{MgO(ol)}$ = 0.82 and $X_{FeO(ol)}$ = 0.18. Now we are ready to calculate temperatures. We can calculate 2 temperatues: one from MgO, and the other from FeO. The temperature based on the FeO exchange is:

$$T_{FeO} = \frac{3911}{\log\frac{[X^{Ol}_{FeO}]}{[X^{liq}_{FeO}]} + 2.50}$$

and that based on MgO is:

$$T_{MgO} = \frac{3740}{\log\frac{[X^{Ol}_{MgO}]}{[X^{liq}_{MgO}]} + 1.87}$$

We find that the temperatures of the two methods agree within 6, which is fairly good. This indicates the analyzed olivine probably was in equilibrium with the liquid.