

GG325 -- PRINCIPLES OF GEOCHEMISTRY

Fall 2013

Homework set #1 (Due on Friday 13 Sept.)

each problem is worth 15 points except numbers 5 and 6, which are worth 20

Note to all: Please watch your reporting of significant figures on all of your answers (homework, exams, etc...) If you don't remember what "sig figs" are, or how to determine them, let me know.

In a simple example, $10.0 + 20.1$, the answer is 30.1 (not 30.100000)
Also, $10.0 + 20.10001 = 30.1$ (not 30.10001). The level of sig figs is set by the least precise value.

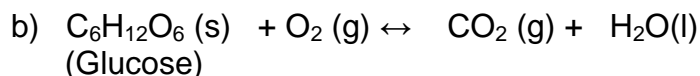
Writing down too many figures after the decimal place implies that you know a value to much greater precision than you actually do.

If you use a spreadsheet or calculator to make calculations, please only record (or show) the correct number of sig figs.

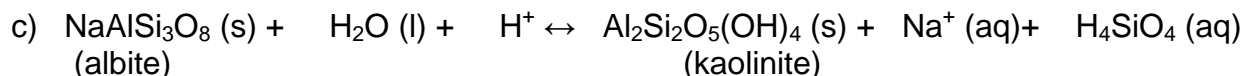
1. write an equilibrium constant expression for the following equilibria. Make sure each of them is balanced and consider the nature of the phase (solid, liquid, gas) before writing the expression. For instance, vapors and gasses are written as partial pressures and aqueous solutes are written as activities or molarities.



$$K_{eq} =$$



$$K_{sp} =$$



$$K_{eq} =$$

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



3. Suppose you found sillimanite and andalusite 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 $550^\circ C$, use the data in Figure 4-14 of your lecture 6 notes (Geothermometry and Geobarometry section) to determine the pressure at which this rock equilibrated.

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4. Consider the following minerals:

anhydrite: CaSO_4

bassanite: $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ (the stuff of which plaster of paris is made)

gypsum: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

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.

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 (not the some Trusdale-Jones eqn) and the data in Table 3.2 to the right, calculate the practical activity coefficients for each of these ions at 0°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 $\text{MgO} \leftrightarrow \text{FeO}$ exchange reaction

b) calculate the temperatures at which the olivine crystallized using both MgO and FeO. Glass (melt) compositions given as wt % oxides- except Olivine (which is as mol%):

Samples	TR3D-1	DS-D8A
SiO_2	50.32	49.83
Al_2O_3	14.05	14.09
$\Sigma\text{Fe as FeO}$	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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HINT: you will need to calculate the mole fraction of MgO and FeO in the liquid. I suggest you set up the calculation in a spreadsheet. I have some instructions on how to do this in a document on the class website, next to the HW1 assignment.

Use this example from White, "Geochemistry" as a guide. Assume Fe₂O₃ to be 10 mole% of total iron present (the analysis below includes only the total iron, calculated as FeO; you need to calculate from this the amount of FeO by subtracting an appropriate amount to be assigned as Fe₂O₃). Note that the mole % Fo in olivine is equivalent to the mole % Mg or MgO.

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 ₂ O ₃	14.3
ΣFeO	11.1
MgO	7.8
CaO	11.5
Na ₂ O	2.6
K ₂ O	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 (Fe₂O₃), so we will have to assign 10% of the total iron to Fe₂O₃. To do this, we get the weight percent FeO simply by multiplying the total FeO by 0.9. To get weight percent Fe₂O₃, we multiply total FeO (11.1%) by 0.1, then multiply by the ratio of the molecular weight of Fe₂O₃ to FeO and divide by 2 (since there are 2 Fe atoms per molecule).

	wt%	w/10% ferric	Mol. wt	moles	mol frac.
SiO ₂	50.3	50.3	60.09	0.8371	0.5265
Al ₂ O ₃	14.3	14.3	102	0.1402	0.0882
total FeO	11.1	11.1			
FeO		9.99	71.85	0.1390	0.0875
Fe ₂ O ₃		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
Na ₂ O	2.6	2.6	61.98	0.0419	0.0264
K ₂ O	0.23	0.23	94.2	0.0024	0.0015
MnO	0.2	0.2	70.94	0.0028	0.0018
TiO ₂	1.71	1.71	79.9	0.0214	0.0135
Total	99.74	99.85		1.590	1.000
X _{MgO-Ol}					0.82
X _{FeO-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-Ol}. Thus X_{MgO-Ol} = 0.82 and X_{FeO-Ol} = 0.18. Now we are ready to calculate temperatures. We can calculate 2 temperatures: one from MgO, and the other from FeO. The temperature based on the FeO exchange is:

$$T_{FeO} = \frac{3911}{\log \frac{[X_{FeO}^{ol}]}{[X_{FeO}^{liq}]} + 2.50} \quad \text{and that based on MgO is: } T_{MgO} = \frac{3740}{\log \frac{[X_{MgO}^{ol}]}{[X_{MgO}^{liq}]} + 1.87}$$

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.