

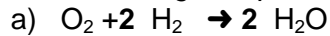
GG325 -- GEOCHEMISTRY
Fall 2009

Homework set #1 (answers)

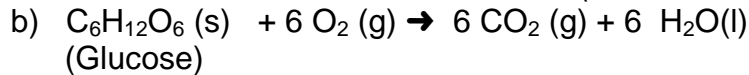
each problem is worth 15 points except numbers 5 and 6, which are worth 20

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

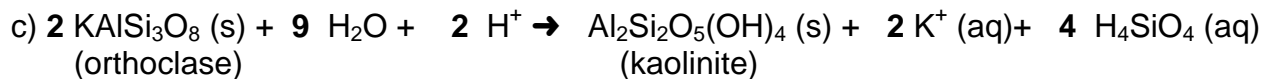
When dealing with passes, we normally write them as partial pressures (i.e., P_{O_2} , P_{H_2})



$$K_{eq} = 1 / P_{O_2} P_{H_2}^2 \text{ assuming water is a liquid. If it is a gas then } P_{H_2O} \text{ would appear in the numerator (either answer is OK since I didn't specify)}$$

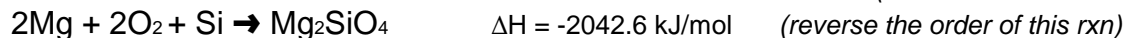


$$K_{sp} = P_{CO_2}^6 / P_{O_2}^6$$



$$K_{eq} = a_{K^+}^2 a_{H_2SiO_4}^4 / a_{H^+}^2$$

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



.... then add all 3

$$\Delta H^\circ = \Sigma(\Delta H^\circ_{rxn1} + \Delta H^\circ_{rxn2} + \Delta H^\circ_{rxn3})$$

$$\Delta H^\circ = (2 \times (-1497.4) + 859.4 + 2042.6) = -92.8 \text{ kJ/mol}$$

3. Suppose you found kyanite and andalusite coexisting in the same rock, that you had reason to believe this was an equilibrium assemblage, and that you could independently determine 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.

Reading off the phase diagram on the kyanite-andalusite boundary, when $T = 400$, $P = 260 \text{ Mpa}$.

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)

gypsum: $CaSO_4 \cdot 2H_2O$

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?

Phases = 4 [vapor and 3 solid minerals]

Components = 2 ($CaSO_4$ + water)

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

Invariant point = 0 degrees of freedom, $F = C - P + 2$, $0 = 2 - P + 2$, $P = 4$

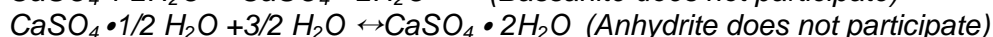
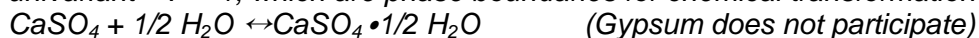
c) Write all univariant reactions in this system, and note the phase that does not participate in that reaction.

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univariant = F = 1, which are phase boundaries for chemical transformations



$[3\text{CaSO}_4 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \leftrightarrow 4 \text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}]$ (water does not participate)] although we can write the last reaction, in practice it does not occur without *Afree*® water vapor to exchange between the minerals, so I've put it in brackets.

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		

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

a) Calculate the ionic strength.

$I = \frac{1}{2} \sum m_i z_i^2$ (*m = molality, z = charge for each ion in solution*) $I = 0.5 \times (.481 + 0.0544 \times 4 + 0.0105 + 0.0105 + 0.56 + 0.0283 \times 4 + 0.00238) = \mathbf{0.713}$

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.

$-\log \gamma_i = \frac{A z_i^2 I^2}{1 + I^2} - 0.2 I$

from Helgeson and Kirkham (1974).

A= 0.5092		"B" = 0.3 (white)		"B" = 0.2 (class notes)	
ion	z	=-log γ _i	γ _i	=-log γ _i	γ _i
Na+	1	0.02	0.957	0.09	0.812
Mg2+	1	0.02	0.191	0.09	0.162
Ca2+	2	0.72	0.191	0.79	0.162
K+	1	0.02	0.957	0.09	0.812
Cl-	-1	0.02	0.957	0.09	0.812
SO42-	-2	0.72	0.191	0.79	0.162
HCO3-	-1	0.02	0.957	0.09	0.812

notes:

A is a constant from the table
AB is given in White Chap 3 as 0.3 and in the lecture notes as 0.2, so I've given you the answers both ways

Note: some of you used the Trusdale-Jones eqn instead of the Davies eqn. I would have given you credit but in each case most of the calculations were also not done correctly

6. Given the following 2 analyses of basaltic glass and coexisting olivine phenocrysts in 2 rock samples *TR3D-1 and DS-D8A)

a) determine the K_D for the MgO ↔ FeO exchange reaction

$K_D = \frac{X_{\text{FeO}}^{\text{ol}} X_{\text{MgO}}^{\text{liq}}}{X_{\text{MgO}}^{\text{ol}} X_{\text{FeO}}^{\text{liq}}}$ (see answers in Table on the next page)

b) calculate the temperatures at which the olivine crystallized using both MgO and FeO.

(Hint: Use the attached example White, AGeochemistry®). Assume Fe₂O₃ to be 10 mole% of total iron (the analysis below includes only the total iron, calculated as FeO; you need to calculate

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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. (*HINT: you will need to calculate the mole fraction of MgO and FeO in the liquid*).

The relevant answers needed for the calculations are in the bold outline boxes.

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

Sample	TR3D-1	Mole fract	DS-D8A	Mole fract
SiO ₂	50.32	0.5267	49.83	0.5216
Al ₂ O ₃	14.05	0.0866	14.09	0.0869
ΣFe as FeO	11.49		11.42	
FeO		0.0905		0.0900
Fe ₂ O ₃		0.0050		0.0050
MgO	7.27	0.1126	7.74	0.1199
CaO	11.49	0.1289	10.96	0.1229
Na ₂ O	2.3	0.0233	2.38	0.0242
K ₂ O	0.10	0.0007	0.13	0.0009
MnO	0.17	0.0015	0.20	0.0018
TiO ₂	1.46	0.0115	1.55	0.0122
olivine				
Mole % Fo (=mole % Mg)	79	0.79	81	0.81
1-Fo = mole % Fe	21	0.21	19	0.19
<i>answers - based on example spreadsheet</i>	<i>K_D</i>			
	0.331		0.313	
<i>T MgO</i>	1104°C		1112°C	
<i>T FeO</i>	1092°C		1111°C	

Everyone: 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.