

GG325 -- PRINCIPLES OF GEOCHEMISTRY

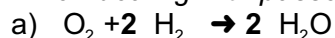
Fall 2007

Homework set #1 (answers)

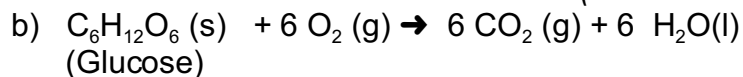
each problem is worth 15 points except numbers 5 and 6, which are worth 20

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

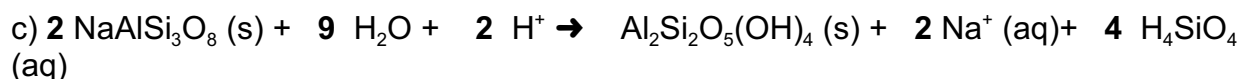
When dealing with passes, we normally write them as partial pressures (i.e., P_{O_2} , P_{H_2})



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



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

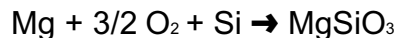


(Albite)

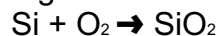
(kaolinite)

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

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



$\Delta H = -1497.4 \text{ kJ/mol}$ (multiply this rxn by 2)



$\Delta H = -859.4 \text{ kJ/mol}$ (reverse the order of this rxn)



$\Delta H = -2042.6 \text{ kJ/mol}$ (reverse the order of this rxn)

.... 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, $F = C - P + 2$, $0 = 2 - P + 2$, $P = 4$

GG325 -- PRINCIPLES OF GEOCHEMISTRY

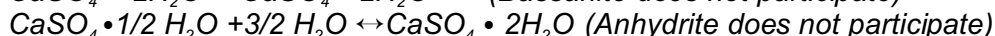
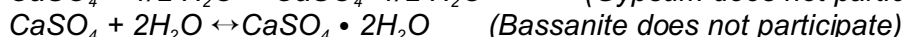
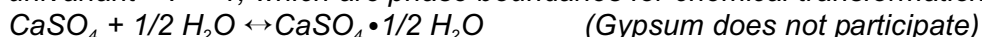
Fall 2007

Homework set #1 (answers)

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

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

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 "free" 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 PARAMETERS

T°C	A	B (10 ⁸)
0	0.4911	0.324
25	0.5092	0.328
50	0.5336	0.332
75	0.5639	0.337
100	0.5998	0.342
125	0.6416	0.347
150	0.6898	0.353
175	0.7454	0.359
200	0.8099	0.365
225	0.8860	0.372
250	0.9785	0.379
275	1.0960	0.387
300	1.2555	0.396

from Helgeson and Kirkham (1974).

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.

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

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

"B" 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)

GG325 -- PRINCIPLES OF GEOCHEMISTRY

Fall 2007

Homework set #1 (answers)

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

b) calculate the temperatures at which the olivine crystallized using both MgO and FeO. (*Hint: Use the attached example 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 subtracting 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 liquid*).

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 ₂ O ₃	14.05	14.09
Fe as FeO	11.49	11.42
MgO	7.27	7.74
CaO	11.49	10.96
Na ₂ O	2.3	2.38
K ₂ O	0.10	0.13
MnO	0.17	0.20
TiO ₂	1.46	1.55
olivine Mole % Fo (=mole % Mg)	79	81
<i>answers - based on example spreadsheet</i> K_D	0.331	0.313
T_{MgO}	1104°C	1112°C
T_{FeO}	1092°C	1111°C