Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET TWO SOLUTIONS DUE SEPTEMBER 19, 2007

1. In the previous problem set, you should have found that calcite is the stable form of $CaCO_3$ at 298 K and 0.1 MPa.

a.) At what pressure are calcite and aragonite in equilibrium at 298 K?

Calcite and aragonite will be in equilibrium when pressure increases enough that ΔG decreases from the standard state value of 0.94 kJ/mole to 0. To find this point, we integrate:

$$\Delta G_r^o = -0.94\,kJ = \int_{0.1}^{P'} \Delta V_r dP$$

and solve for P'. Since we have no other information, we assume ΔV is independent of pressure and hence the integral reduces to:

$$-940J=\Delta V(P'-0.1)$$

Rearranging: $-940/\Delta V + 0.1 = P'$

Substituting -2.78 cc/mol (which converts to J/MPa), we find P' = 338 MPa.

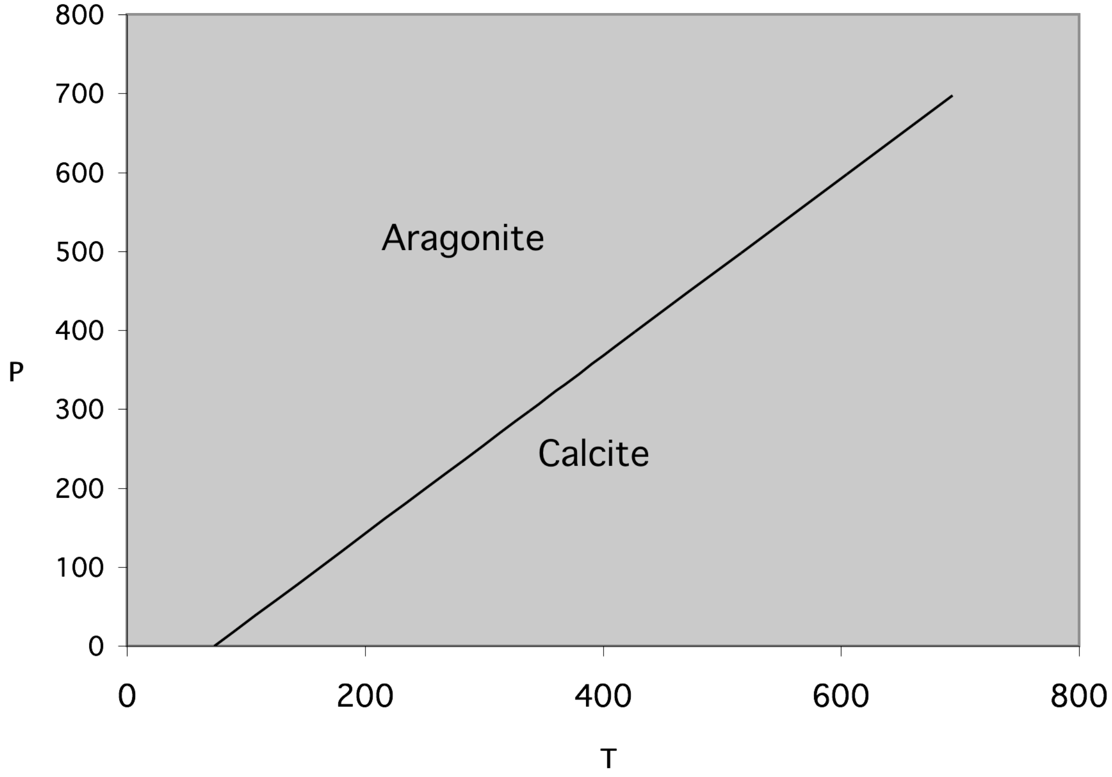
So the phase boundary is located at 298K and 338 MPa.

The slope of the phase boundary is given by the Clapeyron equation (equ. 3.3):

$$\frac{dT}{dP} = \frac{\Delta V_r}{\Delta S_r}$$

Substituting values obtained in Problem Set 1, we find the slope is 1.125 K/MPa.

b.) Using your result from a.) and the Clapeyron slope, construct a phase diagram showing the stability fields of calcite and aragonite as a function of T and P.



3. For the reaction:

$$\text{NaAlSi}_3\text{O}_8 \rightleftarrows \text{NaAlSi}_2\text{O}_6 + \text{SiO}_2$$

$$\text{albite} \rightleftarrows \text{jadite} + \text{quartz}$$

which assemblage (side of the equation) is stable at 600°C and 1 MPa? Use the thermodynamic data in Table 2.2 and assume the volume change of the reaction is independent of pressure and temperature.

This question is similar to example 2.8. Whichever side of the reaction has the lowest Gibbs Free Energy will be the stable assemblage. If ΔG for the reaction is positive, the reactants (left side) are stable, if it is negative, the products (right side) are stable. So we want to calculate ΔG at 873 K and 1 MPa (= 10 bars). Since G is a state function, we can do the pressure and temperature calculations separately, and the order doesn't matter. To determine how ΔG_r changes with temperature, we can use equation 2.139 (since the heat capacities are given in Meier-Kelley form):

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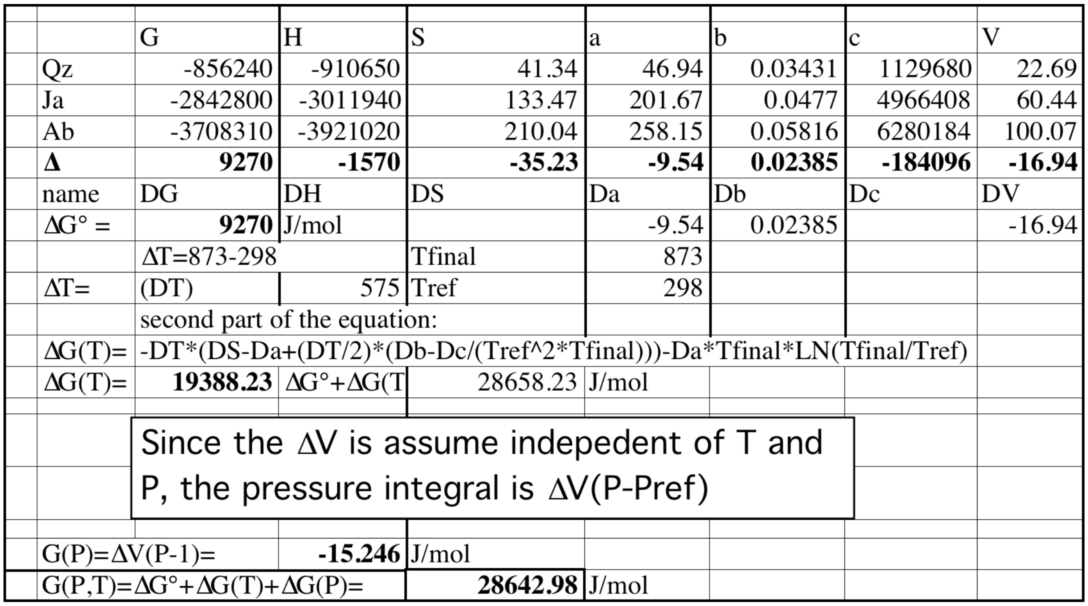
$$\Delta G_{T,P_{ref}} = \Delta G^o - \Delta T\left[\Delta S_{T_{ref}} - \Delta a + \frac{\Delta T}{2}\left(\Delta b - \frac{\Delta c}{T_{ref}^2 T}\right)\right] - \Delta a T ln\left(\frac{T}{T_{ref}}\right)$$

We need to calculate ΔG^o and Δa, Δb, and Δc. Let's set up a spreadsheet to do this calculation



	G	H	S	a	b	c	V
Qz	-856240	-910650	41.34	46.94	0.03431	1129680	22.69
Ja	-2842800	-3011940	133.47	201.67	0.0477	4966408	60.44
Ab	-3708310	-3921020	210.04	258.15	0.05816	6280184	100.07
Δ	**9270**	**-1570**	**-35.23**	**-9.54**	**0.02385**	**-184096**	**-16.94**
name	DG	DH	DS	Da	Db	Dc	DV
ΔG° =	**9270**	J/mol		-9.54	0.02385		-16.94
	ΔT=873-298		Tfinal	873			
ΔT=	(DT)	575	Tref	298			
	second part of the equation:						
ΔG(T)=	-DT*(DS-Da+(DT/2)*(Db-Dc/(Tref^2*Tfinal)))-Da*Tfinal*LN(Tfinal/Tref)						
ΔG(T)=	**19388.23**	ΔG°+ΔG(T	28658.23	J/mol			
	Since the ΔV is assume indepedent of T and P, the pressure integral is ΔV(P-Pref)						
G(P)=ΔV(P-1)=		**-15.246**	J/mol				
G(P,T)=ΔG°+ΔG(T)+ΔG(P)=			**28642.98**	J/mol			

Here we have set up the parameters H, S, a, b, c, and V in a matrix. To calculate the Δ's, we just sum the values for Ja and Qz and subtract from that the values for Al. ΔΔG° is then easy to calculate from the ΔH and ΔS.

We have assigned names to each of the Δ's, e.g., ΔH is DH, etc. This allows us to set up an equation to calculate ΔG(T) that makes some sense.

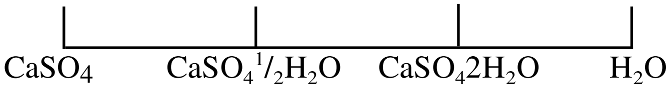
Since the answer is positive, the assemblage on the left (albite) is stable.

4. Consider the following minerals:

anhydrite:	$CaSO_4$
bassanite:	$CaSO_4.{}^1/_2H_2O$ (the stuff of which plaster of paris is made)
gyspum:	$CaSO_4.2H_2O$

a.) If water vapor is the only phase of pure water in the system, how many phases are there in this system and how many components are there?

2 components: CaSO4 and H2O, 4 phases



b.) How many phases are present at invariant points in such a system? How many univariant reactions are possible? Write all univariant reactions, labeling each according to the phase that does not participate in the reaction.

We can use the Gibbs phase rule to answer the first part of this, setting $f = 1$, with c =2, then $\phi = 4$, so four phases must be present at invariant points.

Univariant reactions:

$2CaSO_4 + H_2O \rightleftarrows 2CaSO_4{}^1/_2H_2O$	gypsum
$2CaSO_4{}^1/_2H_2O + 3H_2O \rightleftarrows CaSO_42H_2O$	anhydrite
$CaSO_42H_2O + 3CaSO_4 \rightleftarrows 4CaSO_4{}^1/_2H_2O$	water
$CaSO_4 + 2H_2O \rightleftarrows CaSO_42H_2O$	bassanite

5. The following analysis of water is from the Rhine River as it leaves the Swiss Alps:

HCO_3^-	113.5 ppm	SO_4^{2-}	36.0 ppm
Cl^-	1.1 ppm	NO_3^-	1.9 ppm
Ca^{2+}	40.7 ppm	Mg^{2+}	7.2 ppm
Na^+	1.4 ppm	K^+	1.2 ppm

a. Calculate the ionic strength of this water. (Recall that concentrations in ppm are equal to concentrations in mmol kg^{-1} multiplied by formula weight.)

b. Using the Debye-Hückel equation and the data in Table 3.1 , calculate the practical activity coefficients for each of these species at 25°C.

This problem involves repeated calculations of the same formulae, so it is easiest to do it in a spreadsheet. The first step is to calculate the concentrations in moles (millimoles are most convenient here) by dividing by the molecular weight of each ion. Then we multiply that by the square of the charge and sum over all ions to get the ionic strength, I. We use the square root if I (note it has been converted back to molar) the solvent parameters A and B for water at 20°C, and the hydrated ionic radius to calculate log gamma using the Debye-Huckel equation.

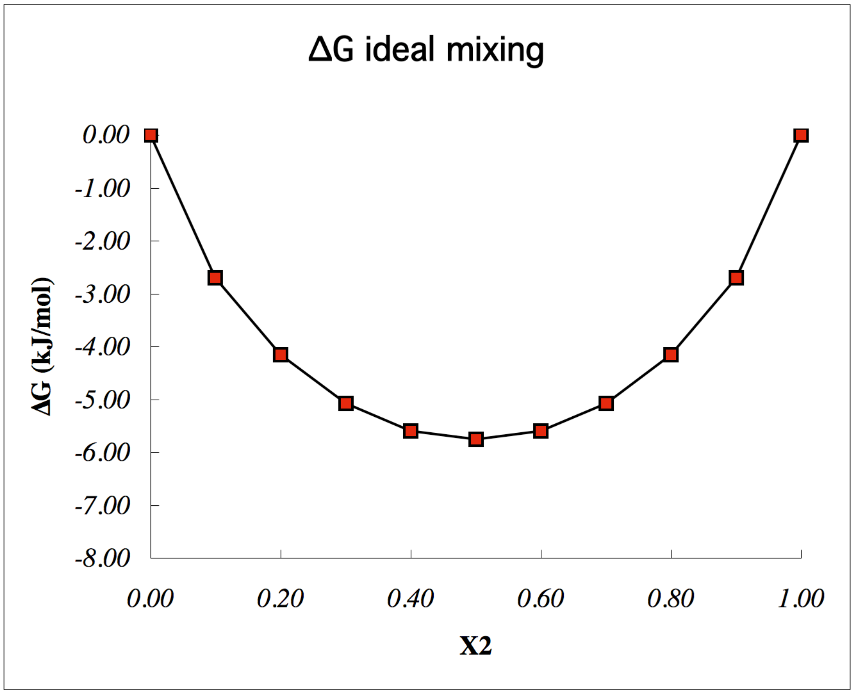
	z	conc ppm	mol. wt.	conc mmol	mmol*z^2	å	log gamm	gamma	activity
HCO3	-1	113.5	61	1.861	1.861	4.25	-0.0309	**0.931**	1.7331
Cl	-1	1.1	35.4	0.031	0.031	3	-0.0316	**0.93**	0.0289
Ca	2	40.7	40.08	1.015	4.062	6	-0.1193	**0.76**	0.7716
Na	1	1.4	23	0.061	0.061	4.25	-0.0309	**0.931**	0.0567
SO4	-2	36	96.06	0.375	1.499	4.25	-0.1234	**0.753**	0.2821
NO3	-1	1.9	62	0.031	0.031	3	-0.0316	**0.93**	0.0285
Mg	2	7.2	24.3	0.296	1.185	8	-0.1148	**0.768**	0.2275
K	1	1.2	39.1	0.031	0.031	3	-0.0316	**0.93**	0.0285
	A	0.5092		**I, mmol**	**4.38003**				
	B	0.3283		root I, mol	0.06618				

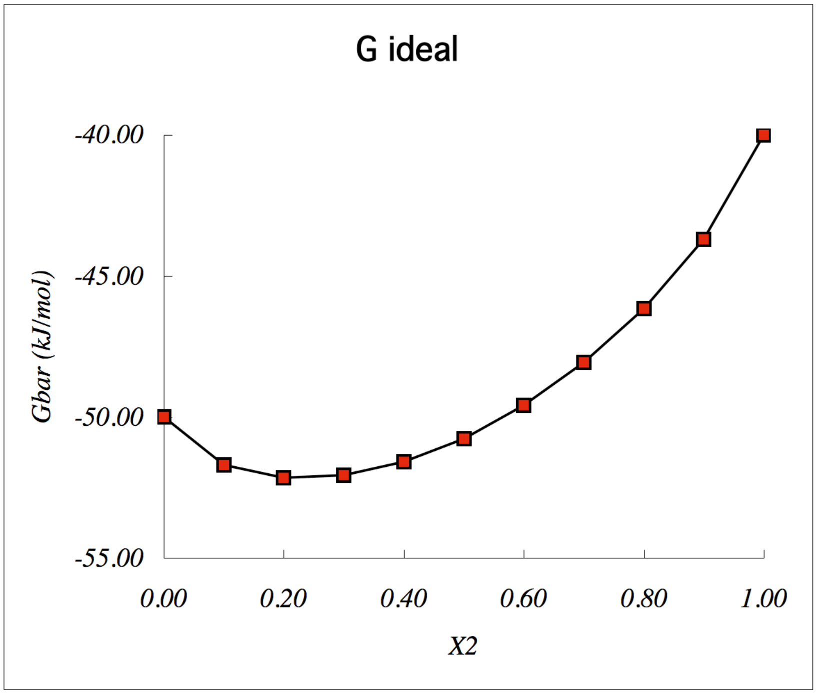
6. Consider the following hypothetical solution: components 1 and 2 form an ideal binary solution; at 1000 K, the free energies of formation from the elements are -50kJ/mol for component 1 and -40kJ/mol for component 2.

   a.) Calculate ΔG_{mixing} for the solution at 0.1 increments of X_2. Plot your results.
   b.) Calculate $\bar{G}$ for *ideal* solution at 0.1 increments of X_2. Plot your results.
   c.) Using the method of intercepts, find μ_1 and μ_2 in the solution at $X_2 = 0.2$

This problem also involves repeated calculations of the same formulae, so it is ideal for a spreadsheet:

X1	X2	ln(x1)	ln(x2)	ΔGid. mix.	Gideal	slope	µ1	µ2
1.00	0.00	0.00	-16.12	0.00	-50.00			
0.90	0.10	-0.11	-2.30	-2.70	-51.70			
0.80	0.20	-0.22	-1.61	-4.16	-52.16	-1.5	-51.86	-53.38
0.70	0.30	-0.36	-1.20	-5.08	-52.08			
0.60	0.40	-0.51	-0.92	-5.60	-51.60			
0.50	0.50	-0.69	-0.69	-5.76	-50.76			
0.40	0.60	-0.92	-0.51	-5.60	-49.60			
0.30	0.70	-1.20	-0.36	-5.08	-48.08			
0.20	0.80	-1.61	-0.22	-4.16	-46.16			
0.10	0.90	-2.30	-0.11	-2.70	-43.70			
0.00	1.00	-20.72	0.00	0.00	-40.00			
	formulae:		ΔGideal mixing=RTsum(xln x)					
			Gideal=sum(xµ)+ΔGmixing					
			slope=dG/dX2=RTln(X2/X1)+µ2-µ1					


ΔG ideal mixing
0.00
-1.00
-2.00
-3.00
-4.00
-5.00
-6.00
-7.00
-8.00
ΔG (kJ/mol)
0.00
0.20
0.40
0.60
0.80
1.00
X2


G ideal
-40.00
-45.00
-50.00
-55.00
Gbar (kJ/mol)
0.00
0.20
0.40
0.60
0.80
1.00
X2