Chapter 14 Problems

These problems basically ask you to do the calculations summarized in Chapter 14.

1. Calculate the stoichiometric (12 oxygen) composition of the garnet in Table 1.

SiO_2	37.57
Al_2O_3	20.93
FeO*	34.62
MnO	2.58
MgO	3.35
CaO	1.92
Total	100.97

Table 1: Sevigny and Ghent (1989), sample S130. FeO* = total iron reported as FeO.

2. Use SUPCRT92 to calculate the P-T position of the anorthite breakdown curve. Use the univariant curve option, and a pressure interval of 20 to 34 kb.

$$3\,\mathrm{CaAl_2Si_2O_8^{\mathit{plag}}} = \mathrm{Ca_3Al_2Si_3O_{12}^{\mathit{garnet}}} + 2\,\mathrm{Al_2SiO_5^{\mathit{kyanite}}} + \mathrm{SiO_2^{\mathit{qtz}}}$$

3. Hensen et al. (1975) used experimental data in the literature to determine the anorthite breakdown curve, summarized in the equation

$$P = -1200 + 23.3\,T$$

where P is in bars and T is degress Celcius. Use both the SUPCRT92 results and this equation in the following, for comparison. You will find that neither position of the anorthite curve gives activity coefficient results exactly in accord with the published ones. Why might that be?

4. If the activity of the grossular component of garnet is lowered by mixing Mg and Ca on the cubic site, the equilibrium pressure of the breakdown reaction is lowered. Use the compositions (x_{Ca}) and experimental pressures of Hensen et al. (1975) in Table 2 to calculate the activity coefficient and the excess Gibbs energy w_G of the grossular component of each garnet composition. Compare with the values in the Table. Are they using 12 or 4 oxygens?

5. Plot w_G vs. T to determine w_H and w_S as Hensen et al. (1975) did.

6. Plot the calorimetric data of Newton et al. (Table 3) and calculate the values of the excess enthalpies. These depend on how you fit the experimental curve. Newton et al. used a two-parameter Margules equation,

$$G^{\mathrm{EX}}_{sol'n} = x_1(w_{G_2}x_1x_2) + x_2(w_{G_1}x_1x_2)$$

T	P	x_{Ca}	γ	w_G
°C	kbar			cal mol^{-1}
1300	16	0.11	1.154	565
1300	21	0.22	1.153	731
1200	15	0.10	1.353	1092
1200	16.5	0.12	1.408	1293
1200	18.5	0.18	1.260	1006
1200	19	0.19	1.287	1126
1100	15	0.11	1.554	1518*
1100	17.3	0.16	1.527	1637
1100	18.5	0.21	1.418	1527
1000	17	0.20	1.656	1994
1000	17	0.22	1.574	1886

Table 2: Results of the experiments of Hensen et al. (1975). * = corrected from 1581 in the original.

where Grossular is component 1 and Pyrope component 2, with the fit parameters $w_{G_1} = 3.82\,\text{kcal mol}^{-1}$ and $w_{G_2} = 2.0\,\text{kcal mol}^{-1}$. If you are very ambitious you can use a spreadsheet to fit the curve yourself, using that or some other equation. A useful reference in this regard is Billo (2001).[1]

Sample	$\Delta_{sol'n}H$ kcal mol^{-1}	$\Delta_{sol'n}H$ kcal mol^{-1}
Pyrope 1	27.73±0.28(5)	
Pyrope 2	27.19±0.24(3)	
Pyrope 3	27.44±0.11(2)	
Pyrope mean value	27.45±0.38(10)	0
$Py_{91}Gr_9$	27.11±0.34(5)	1.67
$Py_{82}Gr_{18}$	28.33±0.24(5)	1.78
$Py_{72.5}Gr_{27.5}$	29.29±0.28(4)	2.22
$Py_{53}Gr_{47}$	32.55±0.25(4)	1.84
$Py_{20}Gr_{80}$	38.37±0.19(6)	0.89
$Py_{10}Gr_{90}$	39.75±0.15(4)	0.98
Grossular	42.21±0.41(7)	0

Table 3: Enthalpies of solution of pyrope-grossular garnets at 970 K. From Newton et al., 1977, Table 3. $H^{EX} = \Delta_{sol'n}H - \Delta_{ideal\ sol'n}H = \Delta_{mix}H$

7. Cryogenic heat capacity measurements of pyrope, grossular, and one intermediate composition were carried out by Haselton and Westrum (1980). From these they determined the Third Law entropies of these phases. (Table 4).

[1] Billo, E.J., 2001, EXCEL™ for Chemists. 2nd edition. New York, Wiley-VCH, 483 pp.

Mineral	Composition	S $\mathrm{J\,mol^{-1}\,K^{-1}}$	S $\mathrm{cal\,mol^{-1}\,K^{-1}}$
Pyrope	$Mg_3Al_2Si_3O_{12}$	266.27	63.64
Grossular	$Ca_3Al_2Si_3O_{12}$	260.12	62.17
$Py_{0.6}Gr_{0.4}$	$(Mg_{0.6}Ca_{0.4})_3Al_2Si_3O_{12}$	268.32	64.13

Table 4: Third Law entropies of garnets from Haselton and Westrum (1980).

Calculate the excess entropy and the excess parameter w_S of their intermediate garnet ($Gr_{0.4}Py_{0.6}$) from these data.

8. How would you determine w_V?

9. Why is it useful to determine the excess parameters w_H, w_S and w_V?