Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET FOUR SOLUTION — DUE OCTOBER 3, 2007

1. Construct G-bar–X diagrams for a regular solution with W= 12 kJ (W is the interaction parameter in a non-ideal solution) at 100° temperature intervals from 200 to 700° C. Sketch the corresponding T-X phase diagram.

The relevant equations are:

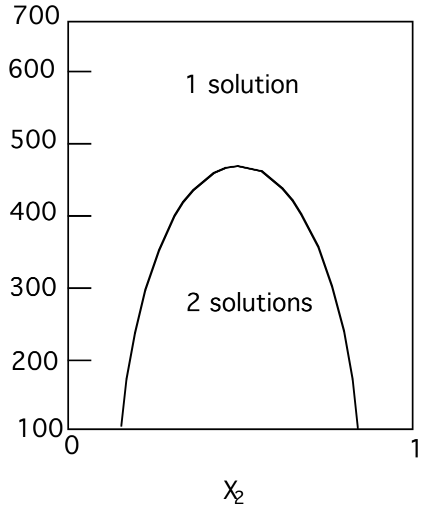
$$\bar{G}_{ex} = X_1 X_2 W_G$$

and $\bar{G}_{mixing} = G_{ideal\ mixing} + G_{ex}$, where

$$\bar{G}_{ideal\ mixing} = +RT\sum_i X_i \ln X_i$$

Phase diagram shown below:

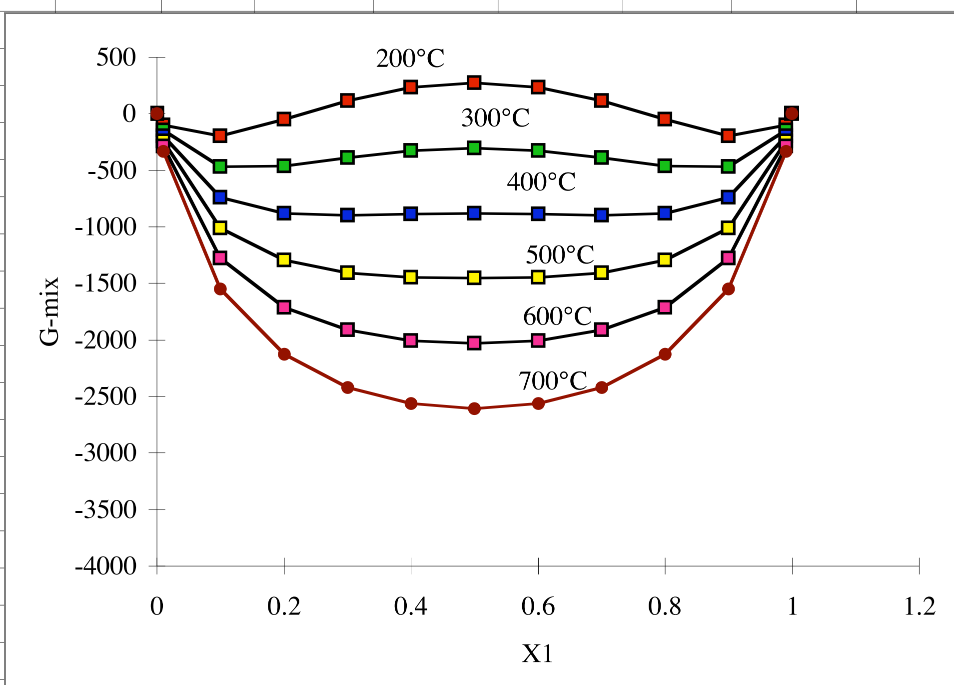
calculations are shown on the spreadsheet following:



Earth & Atmospheric Sciences 455: Geochemistry

Problem Set Four Solution — Due October 3, 2007

R	8.314	Gex=X1*X2*W							
W	12000	Gideal=RT(X1*ln(X1)+X2*ln(X2))							
Xi	Xj		T	473	573	673	773	873	973
		Gex	Gid 473	Gmix	Gmix	Gmix	Gmix	Gmix	Gmix
1	0.00	0	0	0	0	0	0	0	0
1	0.01	119	-220	-101	-148	-195	-241	-288	-334
0.9	0.10	1080	-1278	-198	-469	-739	-1009	-1279	-1550
0.8	0.20	1920	-1968	-48	-464	-880	-1296	-1712	-2128
0.7	0.30	2520	-2402	118	-390	-898	-1406	-1914	-2422
0.6	0.40	2880	-2647	233	-326	-886	-1445	-2005	-2564
0.5	0.50	3000	-2726	274	-302	-878	-1455	-2031	-2607
0.4	0.60	2880	-2647	233	-326	-886	-1445	-2005	-2564
0.3	0.70	2520	-2402	118	-390	-898	-1406	-1914	-2422
0.2	0.80	1920	-1968	-48	-464	-880	-1296	-1712	-2128
0.1	0.90	1080	-1278	-198	-469	-739	-1009	-1279	-1550
0	0.99	119	-220	-101	-148	-195	-241	-288	-334
0	1.00	0	0	0	0	0	0	0	0



Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET FOUR SOLUTION DUE OCTOBER 3, 2007

2. Show that: $G_{excess} = \left(W_{G_1} X_2 + W_{G_2} X_1\right) X_1 X_2$ may be written as a 4 term power expansion, i.e.:

$$\bar{G}_{ex} = A + BX_2 + CX_2^2 + DX_2^3$$

Substituting $X_1 = (1 - X_2)$

$$G_{excess} = \left(W_{G_1} X_2 + W_{G_2}[1 - X_2]\right)(1 - X_2)X_2$$

$$G_{excess} = \left(W_{G_1} X_2^2 + W_{G_2} X_2 - W_{G_2} X_2^2]\right)(1 - X_2)$$

Rearranging:

$$G_{ex} = W_{G_2} X_2 + (W_{G_1} - 2W_{G_2})X_2^2 + (W_{G_2} - W_{G_1}) X_2^3$$

Letting $A = 0$, $B = W_{G2}$, $C = W_{G1} - 2W_{G2}$ and $D = W_{G2} - W_{G1}$, then

$$\bar{G}_{ex} = A + BX_2 + CX_2^2 + DX_2^3$$

3. Kyanite, andalusite, and sillimanite (all polymorphs of Al_2SiO_5) are all in equilibrium at 500°C and 376 MPa. Use this information and the following to construct an approximate temperature-pressure phase diagram for the system kyanite-sillimanite-andalusite. Assume ΔV and ΔS are independent of temperature and pressure. Label each field with the phase present.

ϕ	$\bar{V}$ (cm^3)	S (J/K-mol)
kyanite	44.09	242.30
andalusite	51.53	251.37
sillimanite	49.90	253.05

The easiest way to do an approximate P-T phase diagram is to use the Clayperon slope

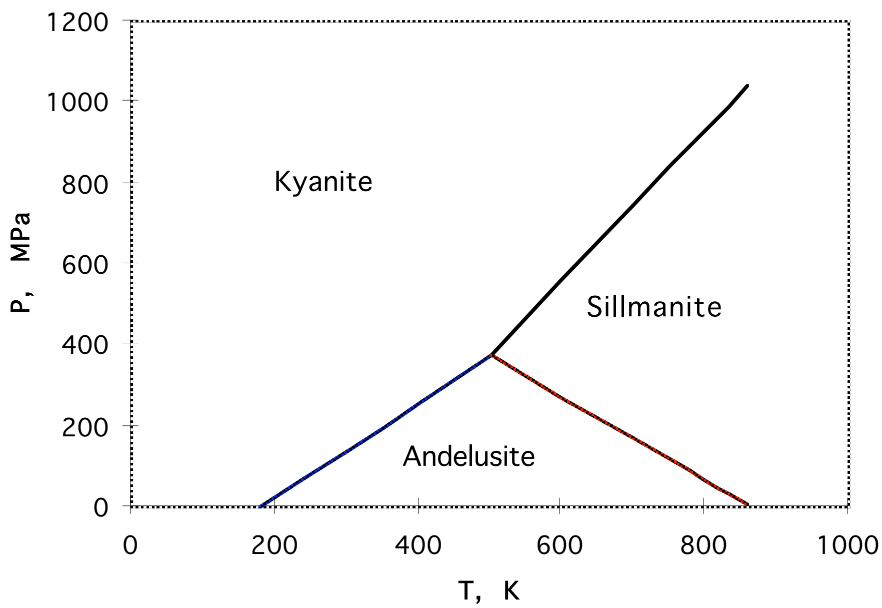
The reactions of interest and their slopes (dP/dT) are:

Andelusite-Kyanite: (242.3-251.37)/(44.09-51.53) = 1.219 MPa/K
Sillmanite-Kyanite: (242.3-253.05)/(44.09-49.90) = 1.85 MPa/K
Andelusite-Sillmanite: (253.05-251.37) /(49.90-51.53)= -1.031 MPa/K

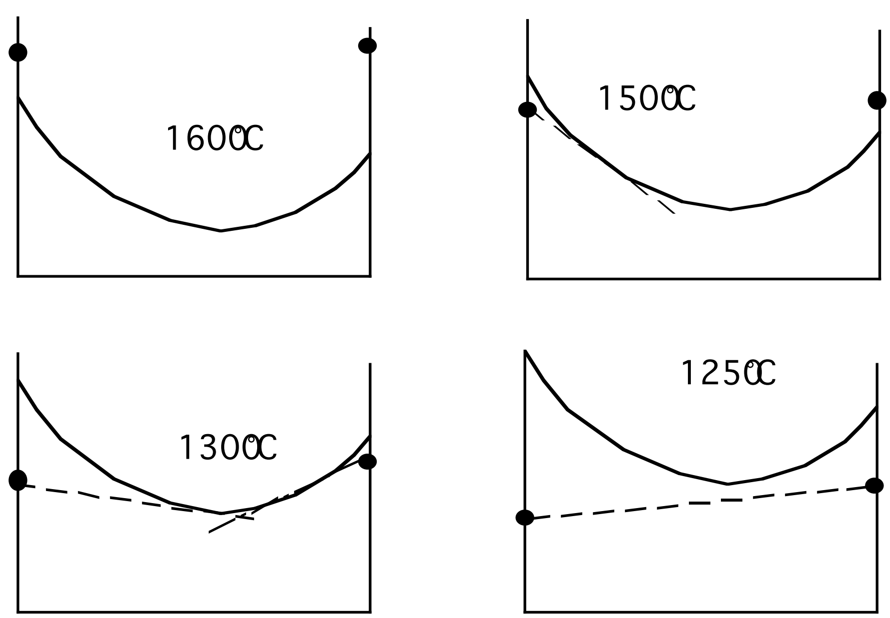
We can form equations of the form: P = 376 + slope × (T - 500) to calculate the phase boundaries.

Earth & Atmospheric Sciences 455: Geochemistry

Problem Set Four Solution — Due October 3, 2007



4. *Sketch* G-bar–X diagrams for 1600° C, 1500° C, 1300° C, and 1250° C for the system Diopside-Anorthite (Figure 4.8). Draw tangents connecting the equilibrium liquids and solids.



Points show the free energy of the pure solids. Curve shows the free energy of the liquid.

Earth & Atmospheric Sciences 455: Geochemistry

Problem Set Four Solution — Due October 3, 2007

5. Given the following 2 analyses of basaltic glass and coexisting olivine phenocrysts, determine the K_D for the MgO⇄FeO exchange reaction, and calculate the temperatures at which the olivine crystallized using both MgO and FeO. 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 (liquid) composition:

Sample	TR3D-1 (wt % oxide)	DS-D8A (wt % oxide)
SiO_2	50.32	49.83
Al_3O_2	14.05	14.09
ΣFe 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

		TR3D1				DS-D8A			
	wt%	w/10%Fe3+	Mol. wt	moles	mol frac.	wt%	w/10%Fe3+	moles	mol frac.
SiO2	50.32	50.32	60.09	0.8374	0.533	49.8	49.83	0.8293	0.528
Al2O3	14.05	14.05	102	0.1377	0.088	14.1	14.09	0.1381	0.088
total FeO	11.49	11.49				11.4	11.42		
FeO		10.341	71.85	0.1439	**0.092**		10.278	0.1430	**0.091**
Fe2O3		1.26	157.7	0.0080	0.005		1.25	0.0079	0.005
MgO	7.27	7.27	40.6	0.1791	**0.114**	7.74	7.74	0.1906	**0.121**
CaO	11.49	11.49	56.08	0.2049	0.131	11	10.96	0.1954	0.124
Na2O	2.3	2.3	61.98	0.0371	0.024	2.38	2.38	0.0384	0.024
K2O	0.1	0.1	94.2	0.0011	0.001	0.13	0.13	0.0014	0.001
MnO	0.17	0.17	70.94	0.0024	0.002	0.2	0.2	0.0028	0.002
TiO2	1.46	1.46	79.9	0.0183	0.012	1.55	1.55	0.0194	0.012
Total	98.65	98.76		1.570	1.000	98.3	98.41	1.566	0.998
XMgO-Ol					**0.79**				**0.81**
XFeO-Ol					**0.21**				**0.19**
	KD	**0.33072**				**KD**	**0.312609**		
	TMgO	**1380**	**kelvin**	**1107**	**°C**	**TMgO**	**1388**	**1115**	**°C**
	TFeO	**1368**	**kelvin**	**1095**	**°C**	**TFeO**	**1387**	**1114**	**°C**

Earth & Atmospheric Sciences 455: Geochemistry

PROBLEM SET FOUR SOLUTION DUE OCTOBER 3, 2007

6. Starting from equations 4.54, 4.56 and 4.18, use the fundamental relationships between free energy, entropy, enthalpy, and the equilibrium constant to derive the temperature dependence of the titanomagnetite–ilmenite exchange (equation 4.57)

We want to show that

$$T(K) = \frac{AW_H^{Usp} - BW_H^{Mt} - CW_H^{Il} + DW_H^{Hem} + \Delta H^o}{AW_S^{Usp} - BW_S^{Mt} - CW_S^{Il} + DW_S^{Hem} + \Delta S^o - R\ln K^{exch}}$$

given $W_G = W_H - TW_S$ (4.56) and $\overline{G}_{ex} = (W_{G_1}X_2 + W_{G_2}X_1)X_1X_2$ (4.16)

for the reaction $Fe_3O_4 + FeTiO_3 \rightleftarrows Fe_2TiO_4 + Fe_2O_3$ 4.52

We are dealing with two solutions: $FeTiO_3$– Fe_2O_3 and Fe_2TiO_4– Fe_3O_4, so the species in the above reactions are actually components in the two solutions. There will be one version of 4.16 to express the excess free energy of each solution and one version of 4.56 for each component.

The free energy change of reaction ΔG_r is:

$$\Delta G_r = G_{Usp} + G_{Hem} - G_{Mag} - G_{Ilm}$$

Let's begin by reorganizing 4.57:

$$TAW_S^{Usp} - TBW_S^{Mt} - TCW_S^{Il} + TDW_S^{Hem} + T\Delta S^o - RT\ln K^{exch} = AW_H^{Usp} - BW_H^{Mt} - CW_H^{Il} + DW_H^{Hem} + \Delta H^o$$

and

$$-RT\ln K^{exch} = AW_H^{Usp} - BW_H^{Mt} - CW_H^{Il} + DW_H^{Hem} + \Delta H^o - TAW_S^{Usp} + TBW_S^{Mt} + TCW_S^{Il} - TDW_S^{Hem} - T\Delta S^o$$

Collecting terms, we have:

$$-RT\ln K^{exch} = \Delta H^o - T\Delta S^o + A(W_H^{Usp} - TW_S^{Usp}) - B(W_H^{Mt} - TW_S^{Mt}) - C(W_H^{Il} - TW_S^{Il}) + D(W_H^{Hem} - TW_S^{Hem})$$

Substituting equation 4.56, this becomes:

$$-RT\ln K^{exch} = \Delta H^o - T\Delta S^o + AW_G^{Usp} - BW_G^{Mt} - CW_G^{Il} + DW_G^{Hem}$$

Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

We have $-RT\ln K^{exch} = \Delta G^o + AW_G^{Usp} - BW_G^{Mt} - CW_G^{Il} + DW_G^{Hem}$

Or $\Delta G^o = -RT\ln K^{exch} - AW_G^{Usp} + BW_G^{Mt} + CW_G^{Il} - DW_G^{Hem}$ (1)

According to equation 4.54:

$$-\frac{\Delta G^\circ}{RT} = \ln\left[\frac{X_{Usp}^\alpha (1 - X_{Ilm})^\alpha}{(1 - X_{Usp})^\alpha X_{Ilm}^\alpha}\right] + \ln\left[\frac{\lambda_{Usp}^\alpha \lambda_{Hem}^\alpha}{\lambda_{Mt}^\alpha \lambda_{Ilm}^\alpha}\right] \quad (4.54)$$

The first term on the right is simply $\ln K^{exch}$ as Spencer and Lindsley defined it (since $(1-X_{Ilm}) = X_{Hem}$), so this can be rewritten as:

$$\Delta G^\circ = -RT\ln K^{exch} - \alpha RT\ln\left[\lambda_{Usp}\right] + \alpha RT\ln\left[\lambda_{Mt}\right] - \alpha RT\ln\left[\lambda_{Hem}\right] + \alpha RT\ln\left[\lambda_{Ilm}\right] \qquad (2)$$

Comparing equation (2) with equation (1) above, we see that the problem is now simply to show that:

$$-\alpha RT\ln\left[\lambda_{Usp}\right] + \alpha RT\ln\left[\lambda_{Mt}\right] - \alpha RT\ln\left[\lambda_{Hem}\right] + \alpha RT\ln\left[\lambda_{Ilm}\right] = -AW_G^{Usp} + BW_G^{Mt} + CW_G^{Il} - DW_G^{Hem}$$

According to equation 4.18:

$$\alpha RT\ln\lambda_i = (2W_{G_j} - W_{G_i})X_j^2 + 2(W_{G_i} - W_{G_j})X_j^3 \qquad (4.18)$$

Let's concentrate on the first two terms on the left. Substituting equation 4.18, these two terms become:

$$-\alpha RT\ln\left[\lambda_{Usp}\right] + \alpha RT\ln\left[\lambda_{Mt}\right] = -\left[(2W_{G_{Mt}} - W_{G_{Usp}})X_{Mt}^2 + 2(W_{G_{Usp}} - W_{G_{Mt}})X_{Mt}^3\right]$$
$$+\left[(2W_{G_{Usp}} - W_{G_{Mti}})X_{Usp}^2 + 2(W_{G_{Mt}} - W_{G_{Usp}})X_{Usp}^3\right]$$

We now make the substitution $X_{MT} = (1-X_{USP})$:

$$= -\left[(2W_{G_{Mt}} - W_{G_{Usp}})(1-X_{Usp})^2 + 2(W_{G_{Usp}} - W_{G_{Mt}})(1-X_{Usp})^3\right]$$
$$+\left[(2W_{G_{Usp}} - W_{G_{Mti}})X_{Usp}^2 + 2(W_{G_{Mt}} - W_{G_{Usp}})X_{Usp}^3\right]$$

Expanding terms:

$$= -\left[(2W_{G_{Mt}} - W_{G_{Usp}})(1-2X_{Usp} + X_{Usp}^2) + 2(W_{G_{Usp}} - W_{G_{Mt}})(1-3X_{Usp} + 3X_{Usp}^2 - X_{Usp}^3)\right]$$
$$+\left[(2W_{G_{Usp}} - W_{G_{Mti}})X_{Usp}^2 + 2(W_{G_{Mt}} - W_{G_{Usp}})X_{Usp}^3\right]$$

and

$$= -(2W_{G_{Mt}} - W_{G_{Usp}}) + 2X_{Usp}(2W_{G_{Mt}} - W_{G_{Usp}}) - X_{Usp}^2(2W_{G_{Mt}} - W_{G_{Usp}})$$
$$-2(W_{G_{Usp}} - W_{G_{Mt}}) + 3X_{Usp}2(W_{G_{Usp}} - W_{G_{Mt}}) - 3X_{Usp}^2 2(W_{G_{Usp}} - W_{G_{Mt}})$$
$$+X_{Usp}^3 2(W_{G_{Usp}} - W_{G_{Mt}}) + (2W_{G_{Usp}} - W_{G_{Mti}})X_{Usp}^2 + 2(W_{G_{Mt}} - W_{G_{Usp}})X_{Usp}^3$$

and

$$= -2W_{G_{Mt}} + W_{G_{Usp}} + 4X_{Usp}W_{G_{Mt}} - 2X_{Usp}W_{G_{Usp}} - X_{Usp}^2 2W_{G_{Mt}} + X_{Usp}^2 W_{G_{Usp}}$$
$$-2W_{G_{Usp}} + 2W_{G_{Mt}} + 6X_{Usp}W_{G_{Usp}} - 6X_{Usp}W_{G_{Mt}} - 6X_{Usp}^2 W_{G_{Usp}} + 6X_{Usp}^2 W_{G_{Mt}}$$
$$+2X_{Usp}^3 W_{G_{Usp}} - 2X_{Usp}^3 W_{G_{Mt}} + 2X_{Usp}^2 W_{G_{Usp}} - X_{Usp}^2 W_{G_{Mti}} + 2X_{Usp}^3 W_{G_{Mt}} - 2X_{Usp}^3 W_{G_{Usp}}$$

Now simplifying, this becomes

$$= -W_{G_{Usp}} + 4X_{Usp}W_{G_{Usp}} - 2X_{Usp}W_{G_{Mt}} - 3X_{Usp}^2 W_{G_{Usp}} + 3X_{Usp}^2 W_{G_{Mt}}$$

Collecting terms we have:

$$= -W_{G_{Usp}}(3X_{Usp}^2 - 4X_{Usp} + 1) + W_{G_{Mt}}(3X_{Usp}^2 - 2X_{Usp}) = -AW_{G_{Usp}} + BW_{G_{Mt}}$$

Now focusing on the last two terms:

$$-\alpha RT \ln[\lambda_{Hem}] + \alpha RT \ln[\lambda_{Ilm}] = -[(2W_{G_{Ilm}} - W_{G_{Hem}})X_{Ilm}^2 + 2(W_{G_{Hem}} - W_{G_{Ilm}})X_{Ilm}^3]$$
$$+[(2W_{G_{Hem}} - W_{G_{Ilm}})X_{Hem}^2 + 2(W_{G_{Ilm}} - W_{G_{Hem}})X_{Hem}^3]$$

We now make the substitution $X_{Hem} = (1-X_{Ilm})$:

$$= -[(2W_{G_{Ilm}} - W_{G_{Hem}})X_{Ilm}^2 + 2(W_{G_{Hem}} - W_{G_{Ilm}})X_{Ilm}^3]$$
$$+[(2W_{G_{Hem}} - W_{G_{Ilm}})(1-X_{Ilm})^2 + 2(W_{G_{Ilm}} - W_{G_{Hem}})(1-X_{Ilm})^3]$$

Expanding:

$$= -[(2W_{G_{Ilm}} - W_{G_{Hem}})X_{Ilm}^2 + 2(W_{G_{Hem}} - W_{G_{Ilm}})X_{Ilm}^3]$$
$$+[(2W_{G_{Hem}} - W_{G_{Ilm}})(1-2X_{Ilm} + X_{Ilm}^2) \; + 2(W_{G_{Ilm}} - W_{G_{Hem}})(1-3X_{Ilm} + 3X_{Ilm}^2 - X_{Ilm}^3]$$

and:

$$= -[2X_{Ilm}^2 W_{G_{Ilm}} - X_{Ilm}^2 W_{G_{Hem}} + 2X_{Ilm}^3 W_{G_{Hem}} - 2X_{Ilm}^3 W_{G_{Ilm}}]$$
$$+\begin{bmatrix} (2W_{G_{Hem}} - W_{G_{Ilm}}) - 2X_{Ilm}(2W_{G_{Hem}} - W_{G_{Ilm}}) + X_{Ilm}^2(2W_{G_{Hem}} - W_{G_{Ilm}}) \\ +2(W_{G_{Ilm}} - W_{G_{Hem}}) - 6(W_{G_{Ilm}} - W_{G_{Hem}})X_{Ilm} \\ +6(W_{G_{Ilm}} - W_{G_{Hem}})X_{Ilm}^2 - 2(W_{G_{Ilm}} - W_{G_{Hem}})X_{Ilm}^3 \end{bmatrix}$$

and:

$$= -[2X_{Ilm}^2 W_{G_{Ilm}} - X_{Ilm}^2 W_{G_{Hem}} + 2X_{Ilm}^3 W_{G_{Hem}} - 2X_{Ilm}^3 W_{G_{Ilm}}]$$
$$+\begin{bmatrix} 2W_{G_{Hem}} - W_{G_{Ilm}} - 4X_{Ilm}W_{G_{Hem}} + 2X_{Ilm}W_{G_{Ilm}} + 2X_{Ilm}^2 W_{G_{Hem}} - X_{Ilm}^2 W_{G_{Ilm}} \\ +2W_{G_{Ilm}} - 2W_{G_{Hem}} - 6X_{Ilm}W_{G_{Ilm}} + 6X_{Ilm}W_{G_{Hem}} \\ +6X_{Ilm}^2 W_{G_{Ilm}} - 6X_{Ilm}^2 W_{G_{Hem}} - 2X_{Ilm}^3 W_{G_{Ilm}} + 2X_{Ilm}^3 W_{G_{Hem}}) \end{bmatrix}$$

ow collecting terms:

$$= [W_{G_{Ilm}} - 4X_{Ilm}W_{G_{Ilm}} + 2X_{Ilm}W_{G_{Hem}} + 3X_{Ilm}^2 W_{G_{Ilm}} - 3X_{Ilm}^2 W_{G_{Hem}}]$$

Rearranging

$$= W_{G_{Ilm}}(1-4X_{Ilm} + 3X_{Ilm}^2) - W_{G_{Hem}}(2X_{Ilm} - 3X_{Ilm}^2) = CW_{G_{Ilm}} - DW_{G_{Hem}}$$

Thus

$$-\alpha RT \ln[\lambda_{Usp}] + \alpha RT \ln[\lambda_{Mt}] - \alpha RT \ln[\lambda_{Hem}] + \alpha RT \ln[\lambda_{Ilm}] = -AW_G^{Usp} + BW_G^{Mt} + CW_G^{Il} - DW_G^{Hem}$$

Q.E.D.