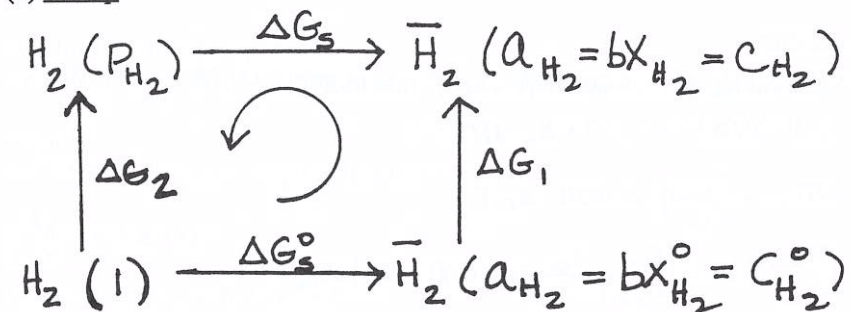## Chapter 6

[6.1] Derive an expression equivalent to Sievert's law, [6-72b], for solution of hydrogen gas in an aqueous solution. Assume Henry's law.

Solution

(1) Set Up

$$H_2\,(P_{H_2}) \xrightarrow{\ \Delta G_s\ } \overline{H}_2\,(a_{H_2} = bX_{H_2} = C_{H_2})$$

with ΔG_2 (upward left), ΔG_1 (upward right), and

$$H_2\,(1) \xrightarrow{\ \Delta G_s^0\ } \overline{H}_2\,(a_{H_2} = bX_{H_2}^0 = C_{H_2}^0)$$

(2) Sum

$$\Sigma \Delta G_{TL} = 0 = \Delta G_S^0 + \Delta G_1 - \Delta G_s - \Delta G_2$$

(3) Substitute

$\Delta G_S^0 = \Delta H_S^0 - T\Delta S_S^0,\ \Delta G_S = 0$ (equilibrium)

$$\Delta G_1 = RT\ln\left(C_{H_2}/C_{H_2}^0\right)$$

$$\Delta G_2 = RT\ln\left(P_{H_2}\right)$$

Substituting into $\Sigma \Delta G_{TL} = 0$,

$$0 = \Delta H_S^0 - T\Delta S_S^0 + RT\ln\left(C_{H_2}/C_{H_2}^0\right) - RT\ln\left(P_{H_2}\right)$$

(4) Solve

$$\ln\left[\left(C_{H_2}/C_{H_2}^0\right)/P_{H_2}\right] = \left(-\Delta H_S^0 + T\Delta S_S^0\right)/RT$$

$$\underline{C_{H_2} = k\,P_{H_2}}\ \text{where cons}\tan t\ k = C_{H_2}^0 \cdot \exp\left[\left(-\Delta H_S^0 + T\Delta S_S^0\right)/RT\right].$$

[6.2] Sievert's constant for solution of oxygen in liquid silver is $k \approx 193.6$ cm³·atm$^{-0.5}$/100 gm Ag at 1075°C (Darken and Gurry, 1953, p. 513). Calculate the solubility of Ag at the same temperature if $P_{O_2} = 50$ mm Hg.

Solution

$$C_{Ag} = 193.6 \, (50/760)^{1/2}$$
$$= \underline{49.7 \, cm^3/100 \, gm \, Ag}.$$

[6.3] Referring to Example Problem 6-5, show from the Gibbs-Duhem equation that $\overline{H}_{Au}^{m} = -20,083(1 - X_{Au})^2$ J/mol.

Solution

Substituting $\overline{H}_{Cu}^{m} = -20,083(1 - X_{Cu})^2$ into [6-57],

$$X_{Cu}d[-20,083(1 - X_{Cu})^2] + X_{Au} \, d\overline{H}_{Au}^{m} = 0$$

$$d\overline{H}_{Cu}^{m} = -\frac{X_{Cu}}{X_{Au}} d\left[-20,083(1 - X_{Cu})^2\right]$$

$$\int_{X_{Au}=1}^{X_{Au}} d\overline{H}_{Cu}^{m} = -\int_{X_{Cu}=0}^{X_{Cu}} \frac{X_{Cu}}{1 - X_{Cu}}(40,166)(1 - X_{Cu})dX_{Cu}$$

$$= -\frac{X_{Cu}}{2}(40,166)$$

$$\underline{\overline{H}_{Au}^{m} = -20,083(1 - X_{Au})^2 \, J/mol.}$$

[6.4] Calculate the composition (a/o) of a binary A-B alloy in equilibrium with oxides A_2O and BO at 627°C. Given $\Delta G_{A_2O}^0 = -15,000$ cal/mol and $\Delta G_{BO}^0 = -25,000$ cal/mol. Assume solvent A is ideal. Solute B is Henrian with γ_B = constant = 1.15. The metallic phases are completely soluble in each other, whereas the oxides are insoluble.

Solution

(1) Set Up
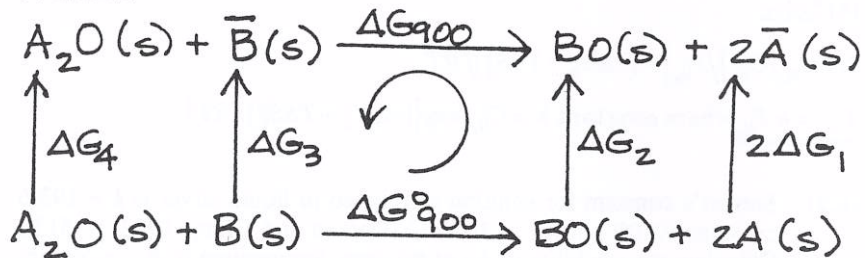
(2) Sum

$$\Sigma \Delta G_{TL} = 0 = \Delta G_{900}^0 + 2\Delta G_1 + \Delta G_2 - \Delta G_{900} - \Delta G_3 - \Delta G_4$$

(3) Substitute

$$\Delta G_{900}^0 = -25,000 - (-15,000) = -10,000 \, cal/mol$$

$$2\Delta G_1 = 2\overline{G}_A^m = 2RTln(a_A) = RTln(X_A^2)$$
$$\Delta G_2 = \Delta G_4 = 0 \text{ (pure condensed phases)}$$
$$\Delta G_{900} = 0 \text{ (equilibrium)}$$

$$\Delta G_3 = \overline{G}_B^m = RT \ln (\gamma_B X_B) = RTln(1.15X_B)$$

Substituting into $\Sigma \Delta G_{TL} = 0$,
$$0 = -10,000 + 1.987(900) \ln(X_A^2) - 0 - 1.987(900) \ln[1.15(1 - X_A)]$$

(4) Solve
$$1788.3[\ln(X_A^2) - \ln(1 - X_A)] = 10,249.94$$

$$\frac{X_A^2}{1 - X_A} = 308.483$$

$$X_A^2 + 308.483X_A - 308.483 = 0$$
$$X_A = 0.997 \Rightarrow \underline{99.7 \, a/o \, A};$$
$$X_B = 0.003 \Rightarrow \underline{0.3 \, a/o \, B}.$$

[6.5] For the binary liquid alloy system Cu-Zn, the zinc vapor pressure at 1060°C is given as a function of composition in the following partially completed table (Darken and Gurry, 1953, p. 512):

X_{Zn}	0.05	0.10	0.15	0.20	0.30	0.45	1.0
P_{Zn} (atm)	0.0289	0.0592	0.1184	0.2368	0.6000	1.2763	4.000*
a_{Zn}							
γ_{Zn}							
$\overline{G}_{Zn}^m$							
$\overline{G}_{Zn}^{m,XS}$							
$\overline{G}_{Zn}^{m,id}$							
Ω_{Zn}							

* Value is high compared to data in Appendix A, Table A.5.

(a) Complete the table (use metric units).
(b) Does the system obey the ideal, Henrian, or regular solution model?

Solution

(a)

a_{Zn} $a_{Zn} = \gamma_{Zn}X_{Zn} = P_{Zn}/P^o_{Zn} = P_{Zn}/4$

γ_{Zn} $\gamma_{Zn} = a_{Zn}/X_{Zn}$

$\overline{G}^m_{Zn}$ (J/mol) $\overline{G}^m_{Zn} = RT\ln(a_{Zn}) = 11{,}083.1 \ln(a_{Zn})$

$\overline{G}^{m,XS}_{Zn}$ (J/mol) $\overline{G}^{m,XS}_{Zn} = \overline{G}^m_{Zn} - \overline{G}^{m,id}_{Zn} = RT\ln(\gamma_{Zn}X_{Zn}) - RT\ln(X_{Zn})$
$$= RT\ln(\gamma_{Zn}) = 11{,}083.1 \ln(\gamma_{Zn})$$

$\overline{G}^{m,id}_{Zn}$ (J/mol) $\overline{G}^{m,id}_{Zn} = \overline{G}^m_{Zn} - \overline{G}^{m,XS}_{Zn} = RT\ln(\gamma_{Zn}X_{Zn}) - RT\ln(\gamma_{Zn})$
$$= RT\ln(X_{Zn}) = 11{,}083.1 \ln(X_{Zn})$$

Ω_{Zn} $\overline{G}^{XS}_{Zn} = RT\ln(\gamma_{Zn}) = \overline{G}^m_{Zn} - \overline{G}^{m,id}_{Zn} = \overline{H}^m_{Zn} - T\overline{S}^m_{Zn} - \overline{G}^{m,id}_{Zn}$
$$= \Omega_{Zn}(1 - X_{Zn})^2 + RT\ln(X_{Zn}) - RT\ln(X_{Zn})$$

$$\Omega_{Zn} = \frac{RT\ln(\gamma_{Zn})}{(1 - X_{Zn})^2} = \frac{11{,}083.1\ln(\gamma_{Zn})}{(1 - X_{Zn})^2}$$

X_{Zn}	0.05	0.10	0.15	0.20	0.30	0.45	1.0
P_{Zn} (atm)	0.0289	0.0592	0.1184	0.2368	0.600	1.2763	4.0
a_{Zn}	0.00723	0.0148	0.0296	0.0592	0.150	0.319	1.0
γ_{Zn}	0.1446	0.148	0.197	0.296	0.500	0.709	1.0
$\overline{G}^m_{Zn}$ (J/mol)	−54,634	−46,695	−39,012	−31,330	−21,026	−12,663	0.0
$\overline{G}^{m,XS}_{Zn}$ (J/mol)	−21,432	−21,175	−18,005	−13,493	−7682	−3811	0.0
$\overline{G}^{m,id}_{Zn}$ (J/mol)	−33,202	−25,520	−21,026	−17,838	−13,344	−8850	0.0
Ω_{Zn}	−26,603	−26,142	−24,921	−21,082	−15,678	−12,600	undef.

(b) $\overline{G}^{m,XS}_{Zn}$ decreases as $X_{Zn} \to 1$ hence, the solution becomes ideal with respect to Zn. The solution is regular for approximately $0.05 < X_{Zn} < 0.30$ and deviates for $X_{Zn} > 0.30$. Data is insufficient to compute the dilute solution activity coefficient although examination of the table suggests that γ_{Zn} approaches a constant value (hence the solution is Henrian) below $X_{Zn} \approx 0.05$.

[6.6] One mole of solid A at 1200°C is added to a large quantity of a liquid solution comprised of components A and B ($X_A = 0.8$). The liquid solution is also at 1200°C. If A and B form ideal solutions, calculate the Gibbs free energy change resulting from the addition of solid A to the mixture. Assume C^A_p (liquid) $\approx C^A_p$ (solid) and C^A_p is independent of temperature. $\Delta H^f_A = 24{,}000$ J/mol at 1800°C.

Solution

Since solid A is added to the solution, the heat of fusion must be included in the final result. Note that the notation $\overline{G}^m_A$ implies that pure A is in the same state of aggregation as the solution. This is not the case here hence, the Gibbs free energy of mixing cannot be computed directly from $\overline{G}^m_A = (1) RT\ln(X_A)$.

Equations characterizing the addition of A to the solution are:
(1) $A^{0,S} \to A^{0,L} \quad \Delta G^f_A = \Delta H^f_A - T^f \Delta S^f_A$
(2) $A^{0,L} \to \overline{A}^L \quad \overline{G}^L_A - G^{0,L}_A = \overline{G}^m_A - (1)RT\ln(X_A)$

The result of adding A is found by combining (1) and (2):

(3) $A^{0,S} \to \overline{A}_L \quad \overline{G}^L_A - G^{0,S}_A$
$$\overline{G}^L_A - G^{0,S}_A = \Delta H^f_A - T^f \Delta S^f_A + (1)RT\ln(X_A)$$

At T = 1800°C, solid A melts, hence

$A^{0,S} \to A^{0,L} \quad \Delta G^f_A = 0$

$\Delta G^f_A = 0 = \Delta H^f_A - T^f \Delta S^f_A$

$\Delta S^f_A = \dfrac{\Delta H^f_A}{T^f} = \dfrac{24{,}000}{2073} = 11.58$ J/(mol·K)

Since $\Delta C_p = 0$ from the problem statement, ΔH^f_A and ΔS^f_A are constants. Substituting into
$\Delta G^f_A = \Delta H^f_A - T^f \Delta S^f_A$
$\overline{G}^L_A - G^{0,S}_A = 24{,}000 - 1473(11.58) + (1)8.3144(1473)\ln(0.8)$
$$= \underline{4210\,\text{J/mol}}.$$

[6.7] The molar heat of formation of liquid brass according to the reaction $(1 - X)Cu + XZn \to \overline{CuZn}$ is given by $H^m = -7100X(1 - X)$ cal/mol (Upadhyaya and Dube, 1977, p. 139). Determine the expressions relating the partial molar heats of mixing of copper and zinc in liquid brass to the alloy composition.

Solution

Since Ω is a solution constant, it is applicable to the partial properties of both components. Hence,

$$\overline{H}^m_{Cu} = -7100(1 - X_{Cu})^2 ; \quad \overline{H}^m_{Zn} = -7100(1 - X_{Zn})^2.$$

[6.8] The solubility limit of component A in B is 1.5 w/o at 760°C. If an alloy contains 0.5 w/o A, calculate the activity of A. Assume Henrian solution behavior in the composition range.

Solution

From [6-34] and defining b in terms of w/o, $a_A = 1.0$ at the solubility limit:

$$1 = b(1.5)$$

$$b = 2/3(w/o)_A^{-1}$$

$$a_A = 2/3(0.5)$$

$$= \underline{0.33}.$$

[6.9] Antimony is removed from lead during the refining process by selective oxidation (Darken and Gurry, 1953, p. 513). Estimate the Sb content obtained for air agitation of the bath at 1173 K. State assumptions and use the following data: $\Delta G_{1100}^{0,f} = -417,600$ J/mol Sb_2O_3 and $\Delta G_{1200}^{0,f} = -395,000$ J/mol Sb_2O_3 (Wicks and Block, 1963, p. 13).

Solution

There are two approaches to the problem. The first approach <u>assumes</u> direct oxidation of Sb in solution by O_2. The second approach <u>assumes</u> Pb is oxidized to PbO which then oxidizes Sb in solution. Both approaches are presented and the results discussed. For the purpose of comparing approaches, <u>assume</u> that Sb behaves ideally at dilute concentration.

Method 1
(1) <u>Set Up</u>
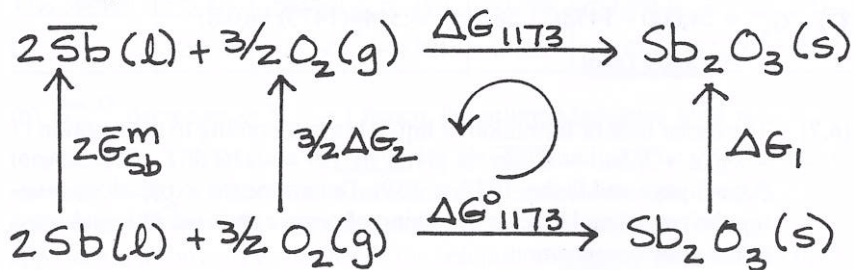
(2) <u>Sum</u>

$$\Sigma\Delta G_{TL} = 0 = \Delta G_{1173}^0 + \Delta G_1 - \Delta G_{1173} - 3/2\Delta G_2 - 2\overline{G}_{Sb}^{m,l}$$

(3) <u>Substitute</u>

$\Delta G_1 = 0$ (pure condensed phase)
$\Delta G_{1173} = 0$ (equilibrium)

$$3/2\Delta G_2 = RTln\left(P_{O_2}^{3/2}\right)$$

$$2\overline{G}_{Sb}^{m,l} = 2RTln(a_{sb}) = 2RT\ ln(X_{sb})$$

To find ΔG_{1173}^0, use $\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0$ and the given data to calculate ΔH_T^0 and ΔS_T^0. Assume ΔH_T^0 and ΔS_T^0 are constant between 1100–1200 K. Subtracting:

$$-417,600 = \Delta H_T^0 - 1100\ \Delta S_T^0$$

$$-395,000 = \Delta H_T^0 - 1200\ \Delta S_T^0$$

$-22,600 = 100\ \Delta S_T^0 \Rightarrow \Delta S_T^0 = -226$. Substituting into the first equation,

$$-417,600 = \Delta H_T^0 - 1100(-226)$$

$$\Delta H_T^0 = -666,200$$

$$\Delta G_T^0 = -666,200 + 226T$$

At 1173 K, $\Delta G_{1173}^0 = -666,200 + 226(1173) = -401,102$ J/mol

Substituting into $\Sigma\Delta G_{TL} = 0$,
$$0 = -401,102 - RTln(0.21)^{3/2} - 2RTln(X_{sb})$$

(4) <u>Solve</u>

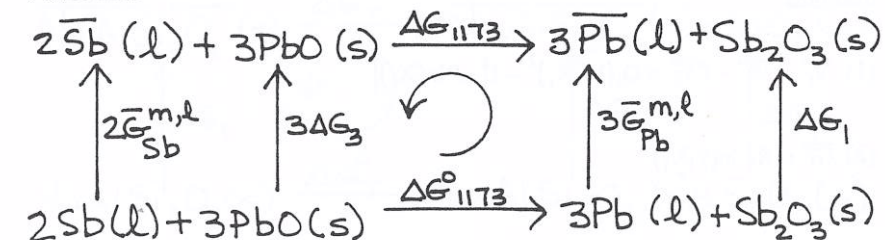$$X_{sb} = exp\left(\frac{-401,102}{2(8.3144)1173} + \frac{2.27}{2}\right)$$

$$= exp\ (-19.43)$$
$$X_{sb} \approx 3.65 \times 10^{-9}$$

From Example Problem 6-3, [6-5b],

$$(w/o)_{sb} = \frac{3.65 \times 10^{-9} \times 121.76 \times 100}{3.65 \times 10^{-9} \times 121.76 + 1 \times 207.2}$$

$$= \underline{0.21 \times 10^6\ w/o \approx 2\ ppb}$$

Method 2
(1) <u>Set Up</u>

(2) Sum

$$\Sigma \Delta G_{TL} = 0 = \Delta G^0_{1173} + \Delta G_1 + 3\overline{G}^{m,l}_{Pb} - \Delta G_{1173} - 3\Delta G_3 - 2\overline{G}^{m,l}_{Sb}$$

(3) Substitute

$\Delta G_1 = 3\Delta G_3 = 0$ (pure condensed phases)

$3\overline{G}^{m,l}_{Pb} = 0$ ($X_{Pb} \approx 1.0$)

$\Delta G_{1173} = 0$ (equilibrium)

$2\overline{G}^{m,l}_{Sb} = 2RT\ln(X_{Sb})$

Assuming Table A.4 data for $\Delta G^{0,f}_{PbO(s)}$ is accurate at ≈ 1173 K,

$$\Delta G^0_{1173} = -401,102 - 3[-229,930 - 33.68(1173)\log(1173) + 209.64(1173)] = -85,262 \text{ J/mol}$$

Substituting into $\Sigma \Delta G_{TL} = 0$,
$0 = -85,262 - 2RT\ln(X_{Sb})$

(4) Solve
$2RT\ln(X_{Sb}) = -85,262$

$$X_{Sb} = \exp\left[\frac{-85,262}{2(8.3144)(1173)}\right] = 0.013 \text{ or } \underline{0.8 \text{ w/o}} \approx 8000 \text{ ppm}.$$

Discussion: The answer using Method 1 appears unrealistically low. In practice, the rate of oxidation of Sb by direct contact with O_2 at the surface would be low because of the very low Sb concentration. Method 2 seems more realistic thermodynamically because both Pb and Sb readily oxidize in air. Agitation would rapidly promote contact between PbO and Sb throughout the solution.

[6.10] Show for a regular binary solution that

$$\Omega_i = \frac{RT\ln(\gamma_i)}{(1 - X_i)^2}$$

Solution

(1) $\overline{G}^m_i = \overline{H}^m_i - T\overline{S}^m_i = \Omega_i(1 - X_i)^2 - T[-R\ln(X_i)]$

(2) $\overline{G}^m_i = RT\ln(\gamma_i X_i)$

Equating (1) and (2) and rearranging,
$\Omega_i(1 - X_i)^2 = RT\ln(\gamma_i X_i) - RT\ln(X_i)$ or

$$\Omega_i(1 - x_i)^2 = RT\ln(\gamma_i) \Rightarrow \underline{\underline{\Omega_i = \frac{RT\ln(\gamma_i)}{(1 - x_i)^2}}}.$$

[6.11] Show that if a solution component i exhibits ideal behavior at constant temperature, $\overline{V}^{m,id}_i = 0$.

Solution

By analogy with [4-14], $d\overline{G}^{m,id}_i = \overline{V}^{m,id}_i dP - \overline{S}^{m,id}_i dT$.

At constant temperature, $d\overline{G}^{m,id}_i = \overline{V}^{m,id}_i dP$ or

$$\left(\frac{\partial \overline{G}^{m,id}_i}{\partial P}\right)_{T,X_i} = \overline{V}^{m,id}_i$$

Substituting [6-26] for component i,

$$RT\left(\frac{\partial \ln(X_i)}{\partial P}\right)_{T,X_i} = \overline{V}^{m,id}_i = 0.$$

[6.12] During low temperature-high pressure metamorphism, the albite component in the mineral plagioclase breaks down to form the mineral quartz and jadeite, a component in the mineral omphacite. Quartz occurs as a separate phase during metamorphism, hence $a_{SiO_2} = 1$. Referring to Exercise Problem [4.22]:
(a) Calculate ΔG_T as a function of temperature, activity of albite, a_{Ab}, in plagioclase, and activity of jadeite, a_{Jd}, in omphacite.
(b) Assuming ideal mixing, determine ΔG_T as a function of temperature, X_{Ab}, and X_{Jd}.

Solution

(a) An isothermal loop is used as follows:
(1) Set Up
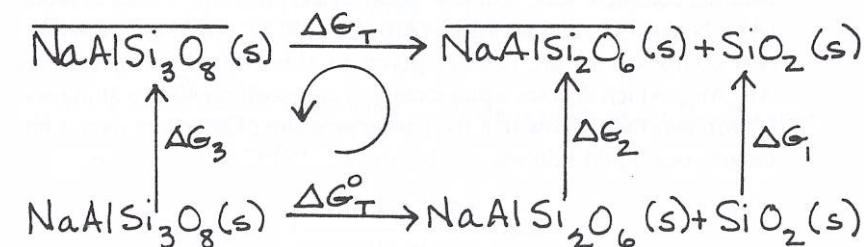
(2) Sum

$$\Sigma \Delta G_{TL} = 0 = \Delta G_T^0 + \Delta G_1 + \Delta G_2 - \Delta G_T - \Delta G_3$$

(3) Substitute

$$\Delta G_T^0 (J/mol) = 53.21 \times 10^3 - 2000.4T + 238.21T\ln(T)$$
$$-70.349 \times 10^{-3}T^2 + 3.791 \times 10^{-6}T^3$$
$$+17.478 \times 10^3 T^{0.5} + 2460.4 \times 10^3 T^{-1}$$

$\Delta G_1 = 0$ (pure condensed phase)
$\Delta G_2 = RT\ln(a_{Jd})$
$\Delta G_T = 0$ (equilibrium)
$\Delta G_3 = RT\ln(a_{Ab})$
Substituting into $\Sigma \Delta G_{TL} = 0$,

$$0 = 53.21 \times 10^3 - 2000.4T + 238.21T\ln(T) - 70.349 \times 10^{-3} T^2$$
$$+3.791 \times 10^{-6}T^3 + 17.478 \times 10^3 T^{0.5} + 2460.4 \times 10^3 T^{-1}$$
$$+RT\ln(a_{Jd}) - \Delta G_T - RT\ln(a_{Ab})$$

(4) Solve

$$\underline{\Delta G_T(J/mol)} = 53.21 \times 10^3 - 2000.4T + 238.21T\ln(T)$$
$$-70.349 \times 10^{-3}T^2 + 3.791 \times 10^{-6}T^3 + 17.478 \times 10^3 T^{0.5} +$$
$$2460.4 \times 10^3 T^{-1} + RT\ln\left(\frac{a_{Jd}}{a_{Ab}}\right)$$

(b) Assuming ideal mixing, $a_d = X_{Jd}$ and $a_{Ab} = X_{Ab}$, hence
$$\underline{\Delta G_T(J/mol)} = 53.21 \times 10^3 - 2000.4T + 238.21T\ln(T)$$
$$-70.349 \times 10^{-3}T^2 + 3.791 \times 10^{-6} T^3 + 17.478 \times 10^3 T^{0.5} +$$
$$2460.4 \times 10^3 T^{-1} + RT\ln\left(\frac{X_{Jd}}{X_{Ab}}\right).$$

[6.13] Plagioclase feldspar, one of the most common rock forming minerals, exhibits complete solid solution between the pure end members albite (Ab), $NaAlSi_3O_8$, and anorthite (An), $CaAl_2Si_2O_8$. Solid solution mineral compositions are usually given in abbreviated form, such as $Ab_{40}An_{60}$, which denotes a plagioclase of composition 40 w/o albite and 60 w/o anorthite. Show that the partial pressure of anorthite over a homogeneous liquid solution of $Ab_{20}An_{80}$ at 1350°C is:

$$P_{An} = \exp\left(\frac{-\Delta G_{1623}^0 - 383R}{1623R}\right)$$

where ΔG_{1623}^0 is the standard Gibbs free energy change at 1623 K for the phase transformation An(l) → An(g). The molecular weights of albite and anorthite are 262.23 and 278.21 respectively. State assumptions.

Solution

(1) Set Up
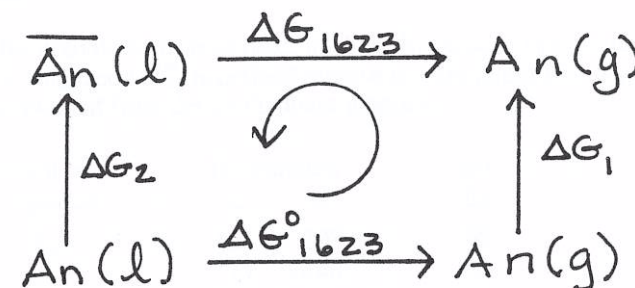
(2) Sum

$$\Sigma \Delta G_{TL} = 0 = \Delta G_{1623}^0 + \Delta G_1 - \Delta G_{1623} - \Delta G_2$$

(3) Substitute
$\Delta G_1 = RT\ln(P_{An})$
$\Delta G_{1623} = 0$ (equilibrium)
$\Delta G_2 = \overline{G}_{An}^{m,l} = RT\ln(a_{An}) = RT\ln(X_{An})$, assuming ideal mixing.

$$X_{An} = \frac{n_{An}}{n_{Ab} + n_{An}} = \frac{80\left(\frac{1}{278.21}\right)}{20\left(\frac{1}{262.23}\right) + 80\left(\frac{1}{278.21}\right)} = 0.79$$

hence, $\Delta G_2 = RT\ln(0.79)$
Substituting into $\Sigma\Delta G_{TL} = 0$
$$0 = \Delta G_{1623}^0 + RT\ln(P_{An}) - RT\ln(0.79)$$

(4) Solve
$$RT\ln(P_{An}) - RT\ln(0.79) = -\Delta G_{1623}^0$$

$$\ln(P_{An}) = \frac{-\Delta G_{1623}^0 + (1623)[\ln(0.79)]R}{1623R}$$

$$\underline{P_{An}} = \exp\left(\frac{-\Delta G_{1623}^0 - 383R}{1623R}\right) \text{ assuming anorthite is stable in the gaseous state}$$

at 1350°C.