MET 6208 Autumn 2011

Contrôle I Solutions.

(1) $BaO + CO_2 = BaCO_3$

$K = 1/P_{CO_2}$ $\Delta G^\circ = -RT \ln K$

At 1566K: $\Delta G^\circ = -R(1566)\ln(1/0.10) = -29983\ J.$

At 1820K: $\Delta G^\circ = -R(1820)\ln(1/1) = 0$

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

$-29983 = \Delta H^\circ - 1566\ \Delta S^\circ$

$0 = \Delta H^\circ - 1820\ \Delta S^\circ$

$\Delta S^\circ = -118.043\ J/K$

$\Delta H^\circ = -214.84\ kJ.$

Assumptions: ΔH°, ΔS° independent of T

(2) $Ag + CuS_{1/2} = Cu + AgS_{1/2}$

$$\Delta G^{o}_{1600^{\circ}C} = -1771 + 787 = -984 \text{ J.}$$

$$= -RT \ln K$$

$$K = 1.076 = \frac{X_{AgS_{1/2}} (0.3088)}{X_{CuS_{1/2}} (0.8433)}$$

$$X_{CuS_{1/2}} = (1 - X_{CuS_{1/2}})(0.34007)$$

$$\begin{cases} X_{CuS_{1/2}} = 0.254 \\ X_{AgS_{1/2}} = 0.746 \end{cases}$$

(3)

$$\begin{cases} 2A + 8B \rightarrow \text{Solution I} & \Delta H = 10(w)(0.2)(0.8) \\ & \quad = 1.6\,w \\ 7A + 3B \rightarrow \text{Solution II} & \Delta H = 10(w)(0.7)(0.3) \\ & \quad = 2.1\,w \\ 9A + 11B \rightarrow (\text{Final Solution}) & \Delta H = 20(w)(9/20)(11/20) \\ & \quad = 4.95\,w \end{cases}$$

Solution I + Solution II $\rightarrow$ (Final Solution)

$$\Delta H = 4.95w - 1.6w - 2.1w$$

$$\Delta H = 1.25\,w \text{ Joules}$$

4

$$g^E = (a + bT + cT\ln T)\, X_A X_B$$

$$s^E = -(dg^E/dT) = -(b + c + c\ln T)\, X_A X_B$$

$$\Delta h = g^E + Ts^E = X_A X_B (a + bT + cT\ln T - bT - cT - cT\ln T)$$

$$= X_A X_B (a - cT)$$

(Alternatively: $\Delta h = d(g^E/T)/d(\frac{1}{T})$)

(iv) $$c_p^E = d\Delta h/dT = X_A X_B (-c)$$

(ii) $$\Delta h_A = X_B^2 (a - cT)$$

(iii) $$s_A^E = -X_B^2 (b + c + c\ln T)$$

$$\Delta s_A = \Delta s_A^{ideal} + s_A^E$$
$$= -R\ln X_A - X_B^2 (b + c + c\ln T)$$

(i) $$\Delta g_A = \Delta g_A^{ideal} + g_A^E$$
$$= RT\ln X_A + X_B^2 (a + bT + cT\ln T)$$
$$= RT\ln a_A$$

(Note: $\Delta g_A = \Delta h_A - T\Delta s_A$)

$$\ln a_A = \ln X_A + \frac{X_B^2}{RT}(a + bT + cT\ln T)$$

$$a_A = X_A \exp\left(\frac{X_B^2}{RT}(a + bT + cT\ln T)\right)$$

(5)

$$Pb + Cl_2 = PbCl_2 \qquad K_1 = \frac{a_{PbCl_2}}{a_{Pb} \cdot P_{Cl_2}}$$

$$Sn + Cl_2 = SnCl_2 \qquad K_2 = \frac{a_{SnCl_2}}{a_{Sn} \cdot P_{Cl_2}}$$

At minimum point:

$$K_1 = \frac{1}{1.57 \times 10^{-16}} = \frac{\cancel{\xi}}{\cancel{\xi}(\gamma_{Pb}) \cdot P'_{Cl_2}}$$

$$K_2 = \frac{1}{2.74 \times 10^{-16}} = \frac{\cancel{(1-\xi)}}{\cancel{(1-\xi)}\gamma_{Sn} \cdot P'_{Cl_2}}$$

$$RT\ln \gamma_{Pb} = 5520 X_{Sn}^2 \qquad \ln \gamma_{Pb} = 0.830(1-\xi)^2$$

$(T=800K)$

$$RT\ln \gamma_{Sn} = 5520 X_{Pb}^2 \qquad \ln \gamma_{Sn} = 0.830\xi^2$$

$$\frac{1}{P'_{Cl_2}} = \frac{\gamma_{Pb}}{1.57 \times 10^{-16}} = \frac{\gamma_{Sn}}{2.74 \times 10^{-16}}$$

$$\ln \gamma_{Pb} - \ln \gamma_{Sn} = -0.5569 = 0.830\left[(1-\xi)^2 - \xi^2\right]$$

$$1 - 2\xi = \qquad -0.6710$$

$$\underline{\xi = 0.8\ 36}$$

$$\underline{P_{Cl_2} = 1.54 \times 10^{-16} \quad \text{bar}}$$

(6) (i) See figure

(ii) $C = 4$
$P = 3$ (3 solids)
$F = 4 - 3 + 2 = 3$

[Alternatively: $C=4$, $P=4$ (3 solids + gas)
$F = 4-4+2 = 2$
T is fixed
$F=1$]

Temperature and total pressure fixed (assume no gas phase)

$F = \underline{1}$ (Not invariant. Point will be found on similar diagrams at other temperatures.

(6)

Figure 2

Phase diagram of the Fe-Cr-S_2-O_2 system at 925° C showing equilibrium S_2 and O_2 partial pressures at constant molar ratio Cr/(Cr + Fe) = 0.5