



$$K = 1/P_{\text{CO}_2} \quad \Delta G^\circ = -RT \ln K$$

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

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

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

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

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

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

$$\Delta H^\circ = -214.84 \text{ kJ}$$

Assumptions: ΔH° , ΔS° independent of T

(2)



$$\begin{aligned}\Delta G_{1600^\circ\text{C}}^\circ &= -1771 + 787 = -984 \text{ J} \\ &= -RT \ln K\end{aligned}$$

$$K = 1.076 = \frac{X_{\text{AgS}_{1/2}} (0.3088)}{X_{\text{CuS}_{1/2}} (0.8433)}$$

$$X_{\text{CuS}_{1/2}} = (1 - X_{\text{CuS}_{1/2}}) (0.34007)$$

$$\begin{cases} X_{\text{CuS}_{1/2}} = 0.254 \\ X_{\text{AgS}_{1/2}} = 0.746 \end{cases}$$

③

$$2A + 8B \rightarrow \text{Solution I} \quad \Delta H = 10(w)(0.2)(0.8) \\ = 1.6w$$

$$7A + 3B \rightarrow \text{Solution II} \quad \Delta H = 10(w)(0.7)(0.3) \\ = 2.1w$$

$$9A + 11B \rightarrow (\text{Final Solution}) \quad \Delta H = 20(w)\left(\frac{9}{20}\right)\left(\frac{11}{20}\right) \\ = 4.95w$$

Solution I + Solution II \rightarrow (Final Solution)

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

$$\Delta H = 1.25w \text{ joules}$$

④

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

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

$$\begin{aligned} \Delta h &= g^E + T s^E = X_A X_B (a + bT + cT \ln T - bT - cT - cT \ln T) \\ &= X_A X_B (a - cT) \end{aligned}$$

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

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

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

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

$$\begin{aligned} \Delta s_A^A &= \Delta s_A^{\text{ideal}} + s_A^E \\ &= -R \ln X_A - X_B^2 (b + c + c \ln T) \end{aligned}$$

(i) $\Delta g_A = \Delta g_A^{\text{ideal}} + g_A^E$

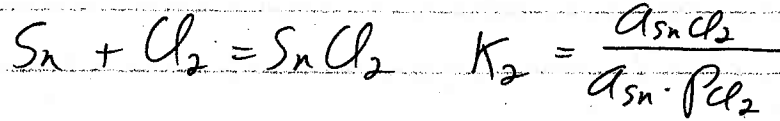
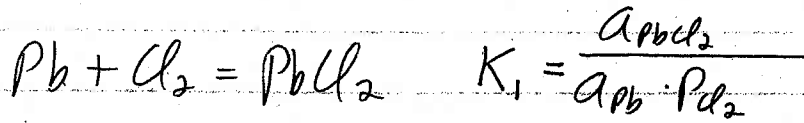
$$\begin{aligned} &= RT \ln X_A + X_B^2 (a + bT + cT \ln T) \\ &= RT \ln a_A \end{aligned}$$

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

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

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

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At minimum point:

$$K_1 = \frac{1}{1.57 \times 10^{-16}} = \frac{\xi}{\xi(\gamma_{\text{Pb}}) P_{\text{Cl}_2}}$$

$$K_2 = \frac{1}{2.74 \times 10^{-16}} = \frac{(1-\xi)}{(1-\xi)\gamma_{\text{Sn}} P_{\text{Cl}_2}}$$

$$\begin{aligned} RT \ln \gamma_{\text{Pb}} &= 5520 X_{\text{Sn}}^2 & \ln \gamma_{\text{Pb}} &= 0.830(1-\xi)^2 \\ (T=800\text{K}) \\ RT \ln \gamma_{\text{Sn}} &= 5520 X_{\text{Pb}}^2 & \ln \gamma_{\text{Sn}} &= 0.830 \xi^2 \end{aligned}$$

$$\frac{1}{P_{\text{Cl}_2}} = \frac{\gamma_{\text{Pb}}}{1.57 \times 10^{-16}} = \frac{\gamma_{\text{Sn}}}{2.74 \times 10^{-16}}$$

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

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

$$\xi = 0.836$$

$$P_{\text{Cl}_2} = 1.54 \times 10^{-16}$$

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)

$F = 1$ (Not invariant). Point will be found on similar diagrams at other temperatures.

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Figure 2

Phase diagram of the Fe-Cr-S₂-O₂ system at 925° C showing equilibrium S₂ and O₂ partial pressures at constant molar ratio Cr/(Cr + Fe) = 0.5

