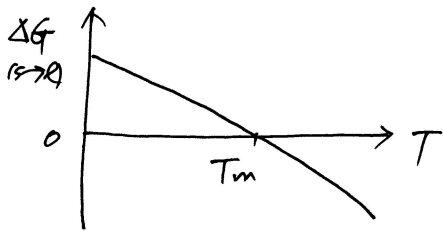


1. (a)



$$\left(\frac{\partial \Delta G}{\partial T}\right) = -\Delta S < 0, \text{ at } T = T_m, \Delta G = 0.$$

$$\left(\frac{\partial \Delta G}{\partial T}\right) = -\frac{\Delta G}{T} < 0, \quad T_m = 0^\circ\text{C at } 1 \text{ atm.}$$

at  $T < T_m \rightarrow$  solid ~~stable~~ is stable

at  $T > T_m \rightarrow$  liquid is stable.

(b) condensed phase  $\rightarrow$  vapor phase.  $\Delta V = V_v - V_c \approx V_v$ .

from Clapeyron equation, ~~(∂P/∂T)~~  $\left(\frac{\partial P}{\partial T}\right)_{eq} = \frac{\Delta H}{T \Delta V}$

$$\frac{dP}{dT} = \frac{\Delta H}{T V_v} = \frac{\Delta H}{RT^2} P.$$

rearranging gives,

$$\frac{dP}{P} = \frac{\Delta H}{RT^2} dT. \quad \therefore d \ln P = \frac{\Delta H}{RT^2} dT.$$

if  $\Delta H$  is independent of temperature,  $C_{p(v)} = C_{p(c)}$ , integration gives

$$\ln P = -\frac{\Delta H}{RT} + \text{constant.} //$$

$\rightarrow$  explains an exponential increase in the saturation vapor pressure exerted by a condensed phase with increasing temperature.

(c)

$$(i) \ln p(\text{atm}) = -\frac{15780}{T} - 0.155 \ln T + 19.25$$

$$(ii) \ln p(\text{atm}) = -\frac{15250}{T} - 1.255 \ln T + 21.19$$

$$\text{for (i), } \frac{d \ln p}{dT} = \frac{15780}{T^2} - \frac{0.155}{T} = \frac{\Delta H_{(i)}}{RT^2}$$

$$\therefore \Delta H_{(i)} = R(15780 - 0.155T).$$

$$\text{for (ii), } \frac{d \ln p}{dT} = \frac{15250}{T^2} - \frac{1.255}{T} = \frac{\Delta H_{(ii)}}{RT^2}$$

$$\therefore \Delta H_{(ii)} = R(15250 - 1.255T).$$

since  $\Delta H_{S \rightarrow v} > \Delta H_{L \rightarrow v} \leftrightarrow \Delta H_{(i)} > \Delta H_{(ii)}$

$\therefore$  (i) is for solid  $\rightarrow$  v

2. (a). when the solute B obeys Henry's law.  $\rightarrow a_B = k_B X_B$ .

$$\rightarrow \ln a_B = \ln k_B + \ln X_B$$

$$d \ln a_B = d \ln X_B$$

by using Gibbs-Duhem equation,  $X_A d \ln a_A + X_B d \ln a_B = 0$ .

$$d \ln a_A = - \frac{X_B}{X_A} d \ln a_B = - \frac{X_B}{X_A} d \ln X_B.$$

$$= - \frac{X_B}{X_A} \frac{dX_B}{X_B} = - \frac{dX_B}{X_A}.$$

$$\text{and, } - \frac{dX_B}{X_A} = \frac{dX_A}{X_A} = d \ln X_A \quad \leftarrow dX_A + dX_B = 0.$$

$$\therefore d \ln a_A = d \ln X_A$$

$$\ln a_A = \ln X_A + \text{constant.}$$

$$a_A = \text{constant} \times X_A.$$

$$= X_A. \quad (X_A = 1, a_A = 1. \therefore \text{constant} = 1.)$$

(b)

$$\Delta G'^M = (n_A \bar{G}_A + n_B \bar{G}_B) - (n_A G_A^\circ + n_B G_B^\circ)$$

$$= n_A (\bar{G}_A - G_A^\circ) + n_B (\bar{G}_B - G_B^\circ)$$

$$= n_A \Delta \bar{G}_A^M + n_B \Delta \bar{G}_B^M$$

$$= RT (n_A \ln a_A + n_B \ln a_B).$$

when ideal,  $a_A = X_A$ ,  $a_B = X_B$ , 1 mole of solution,

$$\therefore \Delta G'^{M, \text{id}} = RT (X_A \ln X_A + X_B \ln X_B). //$$

from the Gibbs-Helmholtz equation,

$$\left[ \frac{\partial (\Delta \bar{G}_i^M / T)}{\partial T} \right]_{P, \text{comp}} = - \frac{\Delta \bar{H}_i^M}{T^2}, \quad \Delta \bar{G}_i^M = RT \ln X_i$$

$$\therefore \frac{d(R \ln X_i)}{dT} = - \frac{\Delta \bar{H}_i^M}{T^2}, \quad \text{and, as } X_i \text{ is independent of } T.$$

$$\therefore \Delta \bar{H}_i^M = 0. \quad \therefore \Delta H'^{M, \text{id}} = 0. \quad (\Delta H'^M = n_A \Delta \bar{H}_A^M + n_B \Delta \bar{H}_B^M).$$

$$\left(\frac{\partial \Delta G^M}{\partial T}\right)_{P, \text{comp}} = -\Delta S^M$$

$$\Delta S^{\text{M, id}} = -R(X_A \ln X_A + X_B \ln X_B) //$$

(c). mixing of  $N_A$  particles of A with  $N_B$  particles of B,

$$\Delta S'_{\text{conf}} = k \ln \frac{(N_A + N_B)!}{N_A! N_B!}$$

$$= k[\ln(N_A + N_B)! - \ln N_A! - \ln N_B!]$$

Application of Stirling's theorem gives,

$$\Delta S'_{\text{conf}} = -k \left[ N_A \ln \left( \frac{N_A}{N_A + N_B} \right) + N_B \ln \left( \frac{N_B}{N_A + N_B} \right) \right].$$

Now,  $\frac{N_A}{N_A + N_B} = \frac{n_A}{n_A + n_B} = X_A$ ,  $\frac{N_B}{N_A + N_B} = X_B$ .

$$\Delta S'_{\text{conf}} = -k N_0 (n_A \ln X_A + n_B \ln X_B)$$

$$\therefore \Delta S_{\text{conf}} = -R(X_A \ln X_A + X_B \ln X_B).$$

which is identical with  $\Delta S^{\text{M, id}}$ .

(d) ideal solution:  $\Delta \bar{H}_i^M = 0$ ,  $\Delta \bar{S}_i^M = -R \ln X_i$ .

regular solution:  $\Delta \bar{H}_i^M \neq 0$ ,  $\Delta \bar{S}_i^M = \Delta \bar{S}_i^{\text{M, id}} = -R \ln X_i$ .

3. (a). The critical value of  $\alpha$  is seen to be that which makes  $\frac{\partial^2 \Delta G^M}{\partial X_B^2}$ , and  $\frac{\partial^3 \Delta G^M}{\partial X_B^3}$  simultaneously equal to zero at that composition at which immiscibility becomes imminent.

$$\Delta G^M = RT(X_A \ln X_A + X_B \ln X_B) + RT\alpha X_A X_B$$

$$\frac{\partial \Delta G^M}{\partial X_B} = RT \left[ \ln \frac{X_B}{X_A} + \alpha(X_A - X_B) \right]$$

$$\frac{\partial^2 \Delta G^M}{\partial X_B^2} = RT \left( \frac{1}{X_A} + \frac{1}{X_B} - 2\alpha \right) \quad - \textcircled{1}$$

$$\frac{\partial^3 \Delta G^M}{\partial X_B^3} = RT \left( \frac{1}{X_A^2} - \frac{1}{X_B^2} \right) \quad - \textcircled{2}$$

$\textcircled{2}$  equals to zero when  $X_A = X_B = 0.5$

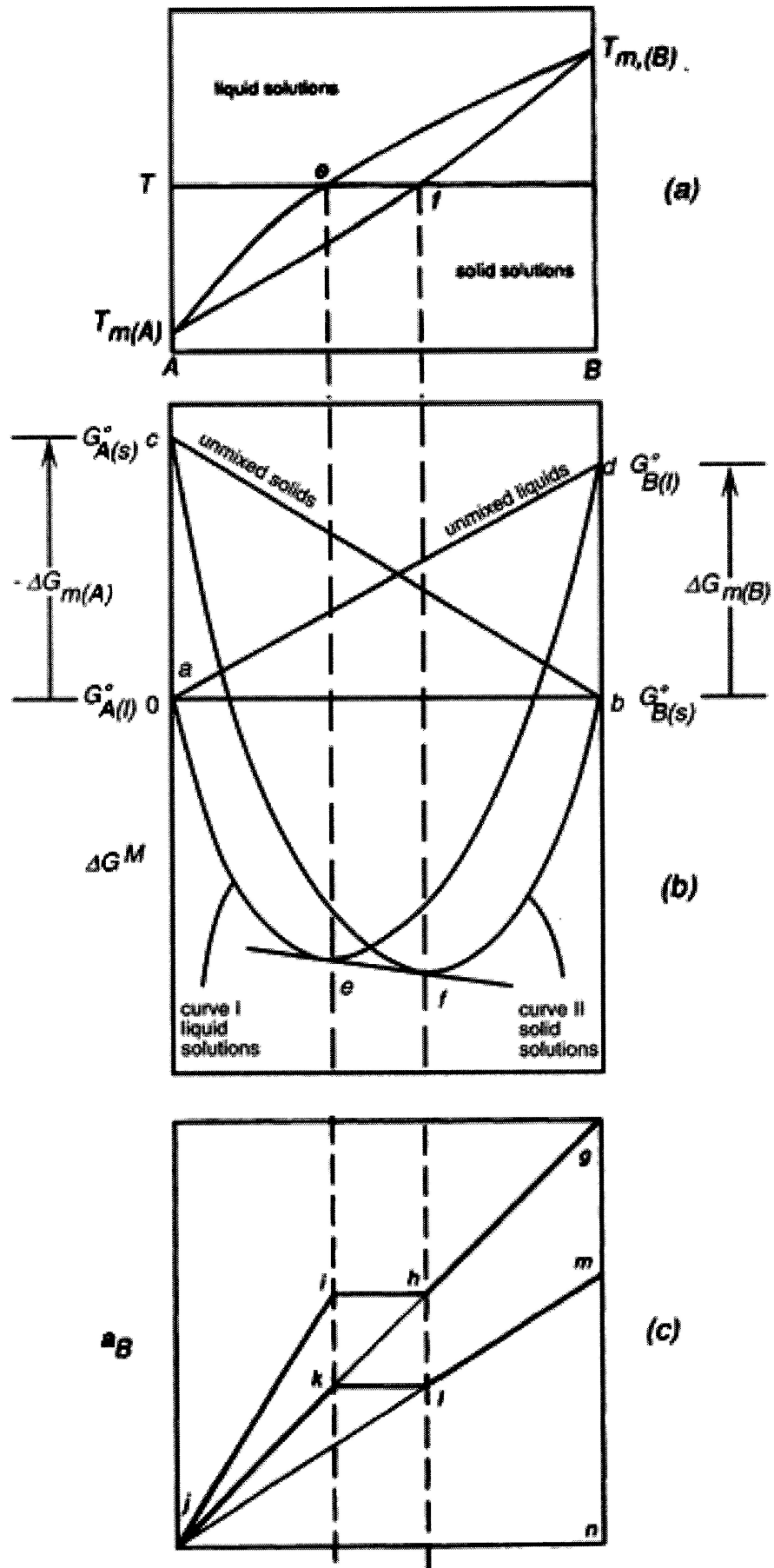
$\textcircled{1}$  equals to zero at  $X_A = X_B = 0.5$  when  $\alpha = 2$ .

$\alpha = 2$  is thus the critical value.

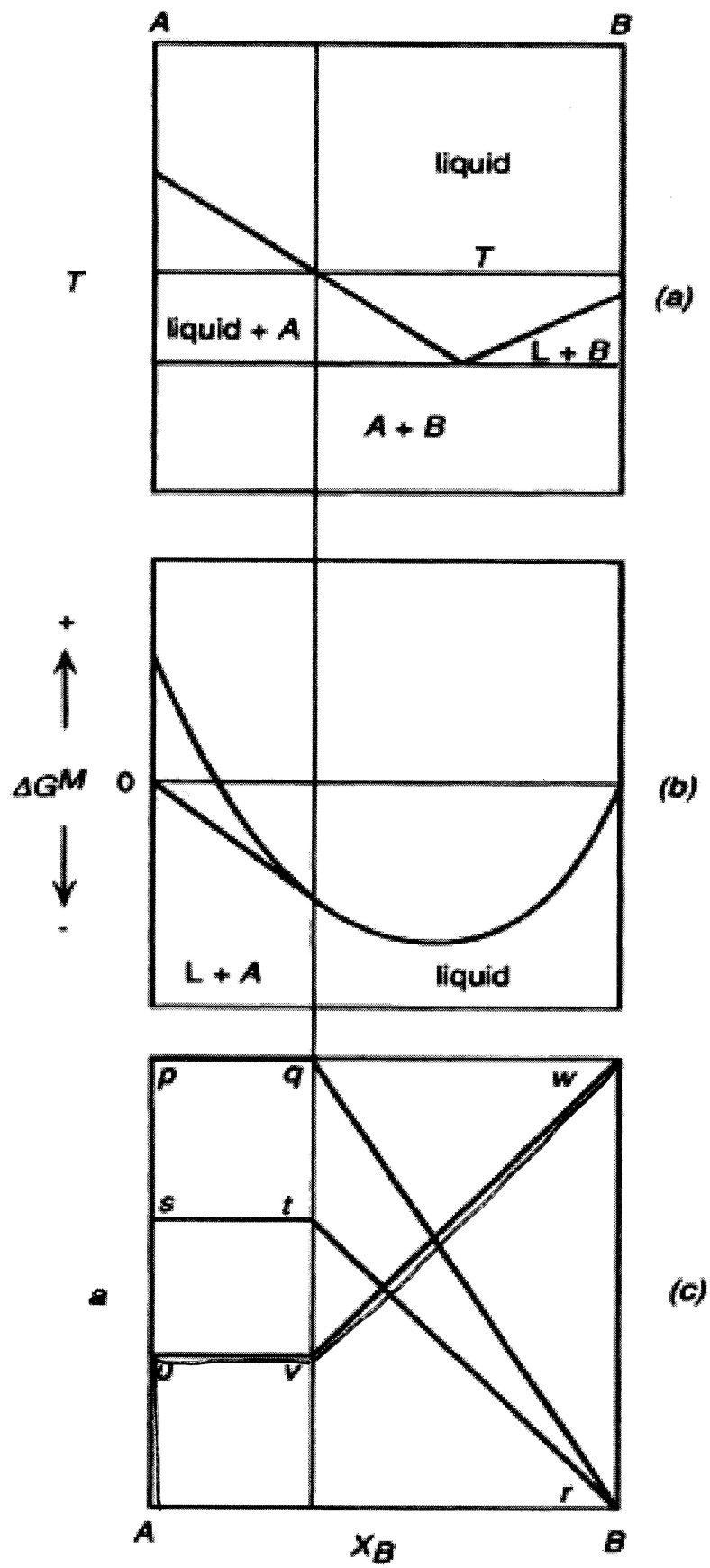
Since  $\Omega = RT\alpha$ , The critical temperature  $T_{cr} = \frac{\Omega}{2R}$ .



3.(b)



3. (c)



4. (a) Gibbs-Helmholtz equation.

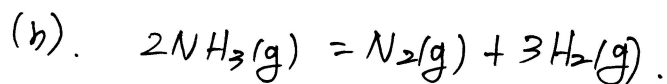
$$\left[ \frac{\partial(\Delta G^\circ/T)}{\partial T} \right]_P = - \frac{\Delta H^\circ}{T^2}$$

As  $\Delta G^\circ = -RT \ln K_p$ , then

$$\frac{\partial \ln K_p}{\partial T} = \frac{\Delta H^\circ}{RT^2} \quad \text{or} \quad \frac{\partial \ln K_p}{\partial (1/T)} = - \frac{\Delta H^\circ}{R}$$

If  $\Delta H^\circ > 0$ ,  $K_p$  increases with increasing temperature.

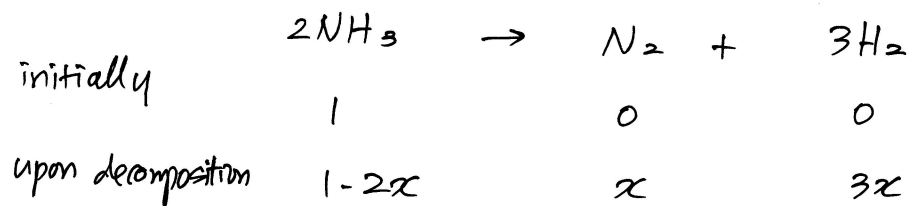
If  $\Delta H^\circ < 0$ ,  $K_p$  decreases with increasing temperature.



constant total pressure of 1 atm, at 400°C (673 K).

$$\Delta G^\circ = 87030 - 25.8 T \ln T - 31.7 T \text{ J.}$$

$$\Delta G^\circ_{673\text{K}} = -47370 \text{ J}, \quad K_{p,673\text{K}} = 4748.$$



$$n_T = 1 - 2x + x + 3x = 1 + 2x \text{ moles,}$$

$$P_{\text{H}_2} = \frac{3x}{1+2x}, \quad P_{\text{N}_2} = \frac{x}{1+2x}, \quad P_{\text{NH}_3} = \frac{1-2x}{1+2x}.$$

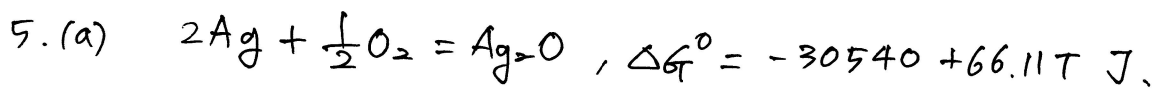
$$K_{p,673\text{K}} = \frac{P_{\text{H}_2}^3 P_{\text{N}_2}}{P_{\text{NH}_3}^2} = \frac{27x^4}{(1+2x)^2 (1-2x)^2}$$

$$= \frac{27x^4}{[1-(2x)^2]^2} \quad \text{or} \quad K_p^{1/2} = \frac{5.196x^2}{(1-4x^2)}$$

$$\therefore x = 0.4954.$$

$$P_{\text{H}_2} = \frac{3x}{1+2x} = 0.7465 \text{ atm}$$

$$P_{\text{N}_2} = \frac{x}{1+2x} = 0.2488 \text{ atm,} \quad P_{\text{NH}_3} = \frac{1-2x}{1+2x} = 0.0047 \text{ atm.}$$



$$\Delta G^\circ = -RT \ln K, \text{ where } K = 1/p_{\text{O}_2}^{1/2}.$$

(i) pure oxygen at 1 atm.

$$\Delta G^\circ = -30540 + 66.11T = -RT \ln 1 = 0.$$

$$\therefore T = 462 \text{ K}.$$

(ii) in air

$$\Delta G^\circ = -30540 + 66.11T = -8.3144 \times T \times \ln \left( \frac{1}{(0.21)^{1/2}} \right)$$

$$= \frac{1}{2} \times 8.3144 \times T \times \ln 0.21$$

$$\therefore T = 421 \text{ K}.$$

(b) From the Ellingham diagram, ~~lines~~ line for  $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$  (i) and line for  $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$  (ii) intersect each other at  $856^\circ\text{C}$  ( $1123 \text{ K}$ ).

$T > 1123 \text{ K}$ ,  $\Delta G^\circ_{(ii)} < \Delta G^\circ_{(i)} \rightarrow \text{H}_2$  is the more efficient reducing agent.

$T < 1123 \text{ K}$ ,  $\Delta G^\circ_{(i)} < \Delta G^\circ_{(ii)} \rightarrow \text{CO}$  is the more efficient reducing agent.

$$(c). (i) \text{CO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO}_2 \quad \Delta G^\circ_{(i)} = -282400 + 86.81 T \text{ J}$$

$$(ii) \text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O} \quad \Delta G^\circ_{(ii)} = -241500 + 55.85 T \text{ J}.$$

$$(iii) \text{CoO (s)} = \text{Co (s)} + \frac{1}{2} \text{O}_2(\text{g}) \quad \Delta G^\circ_{(iii)} = 233900 - 71.85 T \text{ J}.$$

$$\text{for } \text{CoO} + \text{H}_2 = \text{Co} + \text{H}_2\text{O} \quad \Delta G^\circ_{(iv)} = \Delta G^\circ_{(ii)} + \Delta G^\circ_{(iii)}$$

$$= -13600 - 16 T \text{ J}.$$

$$\text{at } 1673 \text{ K}, \quad \Delta G^\circ_{(iv)} = -40368 \text{ J}.$$

$$K_{(iv), 1673 \text{ K}} = \exp\left(\frac{40368}{8.3144 \times 1673}\right) = 18.2 = \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}\right)_{\text{eq}}.$$

$$\frac{18.2}{19.2} = 0.95. \quad \text{and thus 1 mole of } \text{H}_2 \text{ is required to reduce}$$

$$0.95 \text{ moles of } \text{CoO}.$$

$$\text{at } 873 \text{ K}, \quad \Delta G^\circ_{(iv)} = -27568 \text{ J}.$$

$$K_{(iv), 873 \text{ K}} = 44.6.$$

$$\frac{44.6}{45.6} = 0.98. \quad 0.98 \text{ moles of } \text{CoO} \text{ is reduced.}$$

$$\text{for } \text{CoO} + \text{CO} = \text{Co} + \text{CO}_2, \quad \Delta G^\circ_{(v)} = \Delta G^\circ_{(i)} + \Delta G^\circ_{(iii)}$$

$$= -48500 + 14.96 T \text{ J}.$$

$$\text{at } 1673 \text{ K}, \quad \Delta G^\circ_{(v)} = -23470 \text{ J}.$$

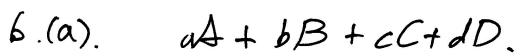
$$K_{(v), 1673 \text{ K}} = 5.40.$$

$$\frac{5.4}{6.4} = 0.84. \quad 0.84 \text{ moles of } \text{CoO} \text{ is reduced.}$$

$$\text{at } 873 \text{ K}, \quad \Delta G^\circ_{(v)} = -35440 \text{ J}.$$

$$K_{(v), 873 \text{ K}} = 132.$$

$$\frac{132}{133} = 0.99. \quad 0.99 \text{ moles of } \text{CoO} \text{ is reduced.}$$



$$\Delta G = c\bar{G}_c + d\bar{G}_d - a\bar{G}_A - b\bar{G}_B \quad - \textcircled{1}$$

$$\Delta G^\circ = cG_c^\circ + dG_d^\circ - aG_A^\circ - bG_B^\circ \quad - \textcircled{2}$$

$$\textcircled{1} - \textcircled{2}$$

$$\Delta G - \Delta G^\circ = c(\bar{G}_c - G_c^\circ) + d(\bar{G}_d - G_d^\circ) - a(\bar{G}_A - G_A^\circ) - b(\bar{G}_B - G_B^\circ)$$

$$\text{since, } \bar{G}_i = G_i^\circ + RT \ln a_i,$$

$$\Delta G - \Delta G^\circ = c(RT \ln a_c) + d(RT \ln a_d) - a(RT \ln a_A) - b(RT \ln a_B)$$

$$= RT \ln \left( \frac{a_c^c a_d^d}{a_A^a a_B^b} \right) = RT \ln Q.$$

Reaction equilibrium is established when  $\Delta G = 0$ .

$$\therefore \Delta G^\circ = -RT \ln Q^{\text{eq}}.$$

$$\text{and } \Delta G^\circ = -RT \ln K.$$

$$\therefore Q^{\text{eq}} = K.$$



$$\ln K_p = -\frac{\Delta G^\circ}{RT} = \ln \left( \frac{P_{\text{CO}}}{P_{\text{CO}_2}} \times \frac{a_{\text{FeO}}}{a_{\text{Fe}}} \right)$$

at  $1600^\circ\text{C}$  (1873 K)

$$\ln \left( \frac{P_{\text{CO}}}{P_{\text{CO}_2}} \times a_{\text{FeO}} \right) = -\frac{\Delta G^\circ}{RT} = \frac{-28370}{-8.3144 \times 1873} \quad \cancel{6.18}$$

$$a_{\text{FeO}} = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \times \exp\left(\frac{28370}{8.3144 \times 1873}\right) = 6.18.$$

$$\therefore a_{\text{FeO}} = 6.18 \times 10^{-5}.$$

$$(c). \quad F = \frac{P(C+1)}{\ominus} - \frac{(P-1)(C+2)}{\omin�}$$

$$= C+2+P$$

①.  $P$  phases is determined by specification of its  $T, P,$  and  $(C-1)$  compositions.

$\therefore P(C+1)$  variables are fixed, when the state of the entire system is specified.

② The conditions that the entire system be at complete equilibrium are

$T_\alpha = T_\beta = T_\gamma = \dots (P-1)$  equalities of temperature

$P_\alpha = P_\beta = P_\gamma = \dots (P-1)$  equalities of pressure

$a_{i(\alpha)} = a_{i(\beta)} = a_{i(\gamma)} = \dots (P-1)$  equalities of the activity of the species  $i$ .

and so on for each  $C$  chemical species.

Thus the total number of equilibrium conditions is

$$(P-1)(C+2).$$