Ch.12 Reactions Involving Pure Condensed Phase and a Gaseous Phase

§12-1. Introduction

§12-2. Reaction Equilibrium in a system containing pure condensed phases and a gas phase

§12-3. Variation of “Standard Gibbs Free Energy Change” with T

§12-4. Ellingham Diagrams (Stability of Metals and Metal-Oxides.)

§12-5. Effect of Phase Transition

§12-6. Stability of Oxides in CO/CO_2 and H_2/H_2O Gas Mixtures

§12-7. Upper limit of $(\frac{p_{CO}}{p_{CO_2}})$ at a fixed T

§12-1. Introduction

$$\begin{cases} \text{Condensed Phase : Pure Metal} \\ \text{Gas} : O_2,\ S_2,\ Cl_2,\ H_2O,\ H_2,\ \text{etc.} \end{cases}$$

e.g. 1. Oxidation of metals.

2. At a given T, what is the maximum p_{O_2}, which can be tolerated in a gas atmosphere without oxidation of a metal. “Bright” annealing of copper.

§12-2. Reaction Equilibrium in a system containing pure condensed phases and a gas phase

Oxidation of a pure metal M at T, P=1atm

$$M_{(s)} + \frac{1}{2}O_{2(g)} = MO_{(s)}$$

$$\text{assumptions:} \begin{cases} \text{oxygen is insoluble in M.} \\ \text{MO is stoichiometric.} \end{cases}$$

$$\text{Three Equil.} \begin{cases} (1)\ M_{(s)} = M_{(g)} \\ (2)\ MO_{(s)} = MO_{(g)} \\ (3)\ M_{(g)} + \frac{1}{2}O_{2(g)} = MO_{(g)} \end{cases}$$

$$\therefore \begin{cases} (1)\ \overline{G}_M(\text{gas}) = \overline{G}_M(\text{solid}) \\ (2)\ \overline{G}_{MO}(\text{gas}) = \overline{G}_{MO}(\text{solid}) \\ (3)\ \Delta G^o = G^o_{MO(g)} - G^o_{M(g)} - \frac{1}{2}G^o_{O_2(g)} = -RT\ln\frac{p_{MO}}{p_M \cdot p_{O_2}^{1/2}} \end{cases}$$

$$\because \begin{cases} \overline{G}_M(\text{gas}) = G^o_{M(g)} + RT\ln p_{M(g)} \\ \overline{G}_M(\text{solid}) = G^o_{M(S)} + \int_{P=1}^{P=p_{M(g)}} V_{M(S)}dP \end{cases}$$

$\because V_{M(s)}$ = molar volume of solid M, it is insensitive to pressure change.

$$\text{i.e.}\quad \left|\int_{P=1}^{P=p_{M(g)}} V_{M(s)}dP\right| << \left|RT\ln p_{M(g)}\right|$$

$$\text{e.g. T=1000}\,^oC,\ \text{Fe} \begin{cases} p_{Fe(g)} \cong 6\times10^{-10}\,\text{atm} \\ V_{Fe(s)} \cong 7.34\text{cm}^3 \end{cases}$$

$$\therefore \begin{cases} RT\ln p_{Fe(g)} = -224750 \text{ J} \\ \int_{P=1}^{p} V_{Fe(s)} = -7.34 \text{ atm}\cdot\text{cm}^3 = -0.74 \text{ J} \end{cases}$$

$$\therefore G^o_{M(g)} + RT \ln p_{M(g)} \cong G^o_{M(s)}$$

$$\text{or} \quad G^o_{M(g)} = G^o_{M(s)} - RT \ln p_{M(g)}$$

Similarly, $G^o_{MO(g)} = G^o_{MO(s)} - RT\ln p_{MO(g)}$

Substitute into(3), $\Delta G^o = G^o_{MO(s)} - G^o_{M(s)} - \frac{1}{2}G^o_{O_2(g)} = -RT \ln\left(\frac{1}{p^{1/2}_{O_2}}\right)$

$\because \Delta G^o \equiv -RT\ln K$

$\therefore K = \frac{1}{p^{1/2}_{O_2}}$

and $\Delta G^o = [G^o_{MO(s)} - G^o_{M(s)} - \frac{1}{2}G^o_{O_2(g)}]$ is Standard Gibbs Free Energy Change for

reaction : $M_{(s)} + \frac{1}{2}O_{2(g)} = MO_{(s)}$

Note: 1. Equilibrium constant K can be expressed only with species in gas phase.

2. ΔG^o is f (T), and K=K(T) only.

3. $\therefore$ At fixed T, $(p_{O_2})_{eq.} = p_{O_2(eq,T)}$

$\therefore$ when $p_{O_2} > p_{O_2(eq.)} \Rightarrow$ Spontaneous oxidation of metal will occur.

$\Rightarrow$ consuming $O_{2(g)}$, $p_{O_2} \downarrow$

$\Rightarrow$ finally, $p_{O_2} = p_{O_2(eq.)}$, oxidation ceases.

e.g. Extraction metallurgy process: Reduction of oxide ores by $p_{O_2} < p_{O_2(eq.)}$

$$4Cu_{(s)} + O_{2(g)} = 2Cu_2O_{(s)}$$

$$\Delta G^o = -333000 + 141.3T \text{ (J)}$$

$$\therefore \Delta G^{o} = -RT\ \ln K = -RT\ \ln\left(\frac{1}{p_{O_2}}\right) = RT\ \ln p_{O_2}$$

$$\therefore \ln p_{O_2} = \frac{\Delta G^{o}}{RT} = -\frac{17390}{T} + 7.38$$

Figure 12.1

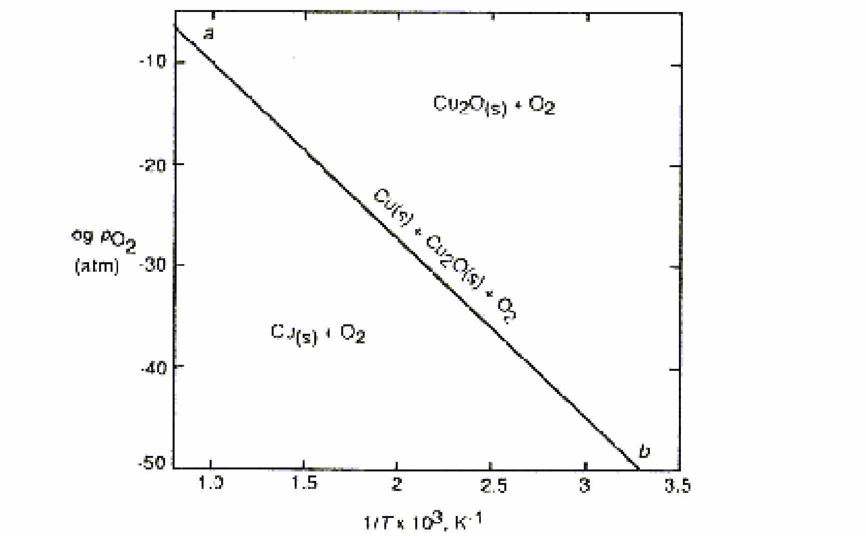


Figure 12.1 The variation, with temperature, of the oxygen pressure required for maintenance of the equilibrium $4Cu_{(s)} + O_2 = 2Cu_2O$.

§12-3. Variation of "Standard Gibbs Free Energy Change" with T

$M_{(s)} + O_{2(g)} = MO_{2(s)}$, $\Delta G^{o}(T) = ?$

$* \because \Delta G^{o} = -RT\ \ln K = RT\ \ln p_{O_2}$

$\therefore p_{O_2(eq.)}(T)$ is determined by $\Delta G^{o}(T)$

Exact calculation of $\Delta G^{o}(T)$ can be done with $C_P(T)$

$* \Delta G^{o}_{T} = \Delta H^{o}_{T} - T\Delta S^{o}_{T}$ at P=1atm

$$= [\Delta H^{o}_{298} + \int_{298}^{T} \Delta C_P dT] - T[\Delta S^{o}_{298} + \int_{298}^{T} \frac{\Delta C_P}{T} dT]$$

For $M(s) + O_2(g) = MO_2(s)$

$$\text{Given}\ \begin{cases} \Delta H^o_{298},\ \ \Delta S^o_{298} \\ C_{P,M(s)} = a_1 + b_1 T + c_1 T^{-2} \\ C_{P,O_2(g)} = a_2 + b_2 + c_2 T^{-2} \\ C_{P,MO_2(s)} = a_3 + b_3 + c_3 T^{-2} \end{cases}$$

$$\therefore \Delta C_P = (a_3 - a_2 - a_1) + (b_3 - b_2 - b_1)T + (c_3 - c_2 - c_1)T^{-2}$$

$$= \Delta a + \Delta bT + \Delta cT^{-2}$$

$$\therefore \Delta H^o_T = \Delta H^o_{298} + \int_{298}^{T} \Delta C_P \cdot dT = \Delta H_o + \Delta aT + \frac{\Delta b}{2}T^2 - \frac{\Delta c}{T}$$

$$\Delta H_o = \left\{ \Delta H^o_{298} + (\text{Lower limit of integration}) \left| \Delta aT + \frac{\Delta b}{2}T^2 - \frac{\Delta C}{T} \right|_{298} \right\}$$

Similarly, calculation of $\Delta S^o_T \Rightarrow \Delta G^o_T$ can be obtained.

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

$$\therefore \int_{298}^{T} d\left(\frac{\Delta G^o_T}{T}\right) = \int_{298}^{T} \left(-\frac{\Delta H^o}{T^2}\right)dT = \int_{298}^{T} \left(-\frac{\Delta H_o}{T^2} - \frac{\Delta a}{T} - \frac{\Delta b}{2} + \frac{\Delta c}{T^3}\right)dT$$

$$\therefore \frac{\Delta G^o_T}{T} = \mathbf{I} + \frac{\Delta H_0}{T} - \Delta a \ln T - \frac{\Delta b}{2}T - \frac{\Delta c}{2T^2}$$

$$\mathbf{I} = \text{integration constant} = \left(\frac{\Delta G^o_{298}}{298} - \frac{\Delta H_o}{298} + \Delta a \ln 298 + \frac{\Delta b}{2} \times 298 + \frac{\Delta c}{2 \times 298^2} \right)$$

$$\therefore \Delta G^o_T = \mathbf{I}\,T + \Delta H_o - \Delta aT \ln T - \frac{\Delta b}{2}T^2 - \frac{\Delta c}{2T}$$

∗ e.g. for $4Cu_{(s)} + O_{2(g)} = 2Cu_2O_{(s)}$

(1) calculate from : $\Delta H^o_{298},\ \Delta S^o_{298},\ C_P[Cu_{(s)},\ O_{2(g)},\ Cu_2O_{(s)}]$

$$\Delta G^o_T = -333200 - 4.28T \ln T - 9.3 \times 10^{-3} T^2 - 0.85 \times 10^5 T^{-1} + 174.4T$$

(2) $\because \Delta G^o = -RT \ln K = RT \ln p_{O_2(eq.)}$

Measure $p_{O_2(eq.)}(T) \Rightarrow \Delta G^{o}(T) \cong A' + B'T\ln T + C'T$

$$\Delta G^{o}_{T} = -338900 - 14.2T\ln T + 247T$$

(3) Approximate (2) to a linear form $\Delta G^{o}_{T} = A + BT$

$$\Delta G^{o}_{T} = -333000 + 141.3T$$

Compare (3) with (1), error is small !!

∴Usually, it is convenient to use approximation, " for oxidation of pure metals."

$$\boxed{\Delta G^{o}_{T} = A + BT}$$

§12-4. Ellingham Diagrams (Stability of Metals and Metal-Oxides.)

1. Ellingham: Plot ΔG^{o} vs. T for oxidation of many metals.

$\Delta G^{o} \cong A + BT$, for oxidation of pure metals.

c.p. $\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$, at constant P

$\therefore \begin{cases} A = \Delta H^{o} \\ B = -\Delta S^{o} \end{cases}$, but ΔH^{o}, ΔS^{o} is almost independent of T.

$$M_{(s)} + O_{2(g)} = MO_{2(s)}$$

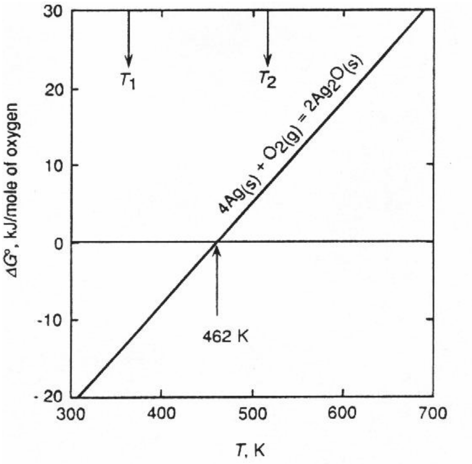


Figure 12.2 The Ellingham line for the oxidation of silver

Figure 12.2 $T=0\,^{o}K,\ \Delta G^{o}=\Delta H^{o}$ (Heat formation of oxide at $0\,^{o}K$)

$$\Delta S^{o}=S^{o}_{MO_2(s)}-S^{o}_{M(s)}-S^{o}_{O_2}\cong -S^{o}_{O_2}$$

$$\begin{cases} S^{o}_{MO_2(s)}\cong S^{o}_{M(s)} \\ S^{o}_{O_2}>>S^{o}_{MO_2(s)}\ \text{or}\ S^{o}_{M(s)} \end{cases}$$

$$\therefore(-\Delta S^{o})>0$$

(1) T= T_o, $\Delta G^{o}=0$, $\therefore M_{(s)}$ and $MO_{2(s)}$ are in equilibrium under $p_{O_2}=1\text{atm}$

$$\because \Delta G^{o}=-RT\ln K=RT\ln p_{O_2}=0,\ \therefore (p_{O_2})_{eq.}\equiv 1\text{atm}$$

(2) T= $T_1<T_0$, $\because \Delta G^{o}<0$ (oxidation reaction occurs under $p_{O_2}=1\text{atm.}$)

$\therefore G^{o}_{MO_2(s)}$ is smaller than $G^{o}_{M(s)}$

$M_{(s)}$ is spontaneously oxidized.

$$\because \Delta G^{o}_{T_1}=RT_1\ \ln p_{o_2(eq,T_1)}<0,\ \therefore p_{o_2(eq,T_1)}<1\text{atm}$$

(3) T= $T_2>T_0$, $\Delta G^{o}>0$, decompose of $MO_{2(s)}$ occurs under $p_{O_2}=1\text{atm.}$

$$p_{o_2(eq,T_2)} > 1\text{atm}$$

2. $\because \Delta S^o \cong -S^o_{O_2}$

$\therefore \Delta S^o$ corresponds with disappearance of 1 mole of $O_{2(g)}$ initially at 1atm.

Therefore, if all oxidation reactions for pure metals are expressed in terms of 1 mole of $O_{2(g)}$, then lines in Ellingham diagram have similar slopes.

$$\text{slope} = -\Delta S^o \cong S^o_{O_2}$$

$\therefore$ all lines are more or less parallel.

$$\text{e.g.} \quad \begin{cases} 2Co_{(s)} + O_{2(g)} = 2CoO_{(s)}, \ \Delta G^o = -467800 + \underline{143.7}T \\ 2Mn_{(s)} + O_{2(g)} = 2MnO_{(s)}, \ \Delta G^o = -769400 + \underline{145.6}T \end{cases}$$

$\therefore$ Relative stability of oxides CoO and MnO are determined by their ΔH^o, i.e.

More negative $\Delta H^o \Leftrightarrow$ More negative ΔG^o

$\Leftrightarrow$ More stable the oxide, or metal is more easily oxidized.

3. Consider: Two oxidation reactions with Ellingham lines intersecting one another.

$$2A_{(s)} + O_2 = 2AO_{(s)} \ldots\ldots(1)$$

$$B_{(\lambda)} + O_2 = BO_{(s)} \ldots\ldots(2)$$

$$\text{Assume:} \quad \begin{cases} \Delta H^o_{(2)} < \Delta H^o_{(1)} \\ \Delta S^o_{(2)} < \Delta S^o_{(1)} \ \text{or} \ \left|\Delta S^o_{(2)}\right| > \left|\Delta S^o_{(1)}\right| \end{cases}$$

$$\therefore \text{(2)-(1)} \Rightarrow B_{(\lambda)} + 2AO_{(s)} = 2A + BO_2 \ldots\ldots(3)$$

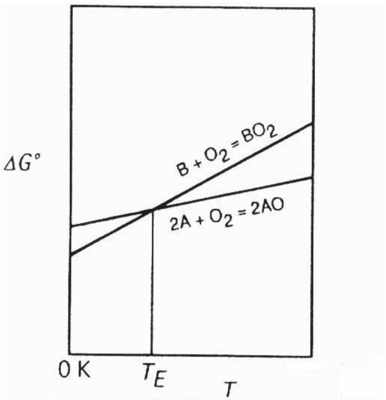


Figure 12.3 Intersecting Ellingham lines for two hypothetical oxidation reactions

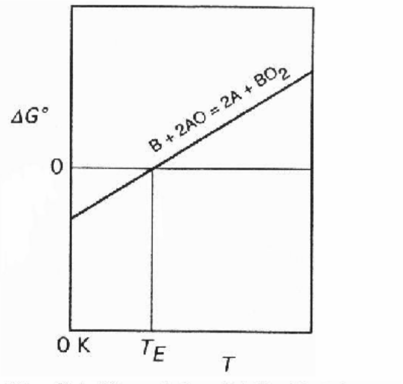


Figure 12.4 The variation of ΔG^o with T for $B + 2AO = 2A + BO_2$ from Fig. 12.4

Figure 12.3 , Figure 12.4

$$\therefore T < T_E,\ \Delta G^o < 0,\ \begin{cases} (A + BO_2)\ \text{are stable} \\ (B + AO)\ \text{are unstable} \end{cases}$$

$$T > T_E,\ \Delta G^o > 0,\ \begin{cases} (A + BO_2)\ \text{are ustable} \\ (B + AO)\ \text{are stable} \end{cases}$$

$\therefore$ If pure A were to be used as a reducing agent to reduce BO_2 to form B and AO, reduction should be conducted at $T > T_E$.

Note: In order to compare stabilities of oxides, Ellingham diagram must be drawn for oxidation reactions with consumption of one mole of $O_{2(g)}$.

4. Richardson nomographic scale of $p_{O_2(eq,T)}$

$\Delta G_T^o = -RT\ \ln K = RT\ \ln p_{O_2(eq,T)}$: for oxidation

$\because$ For $O_{2(g)}$, ideal gas model $G = G^o + RT \ln P$

G^o : Standard Gibbs Free Energy of $O_{2(g)}$ at $P=1atm$

$\therefore \Delta G_T^o$ is the Gibbs Free Energy change of $O_{2(g)}$ from 1atm to $p_{O_2(eq,T)}$ at T.

$\therefore$ For a given $p_{O_2(eq.)}$, $\Delta G_T^o = [R\ \ln p_{O_2(eq.)}] \cdot T$

a straight line of ΔG_T^o vs. T can be drawn.

$\therefore$ For different $p_{O_2(eq.)}$, a series of lines of ΔG_T^o vs. T can be drawn .

These lines radiate from the point $\Delta G^o = 0$, at $T = 0^oK$.

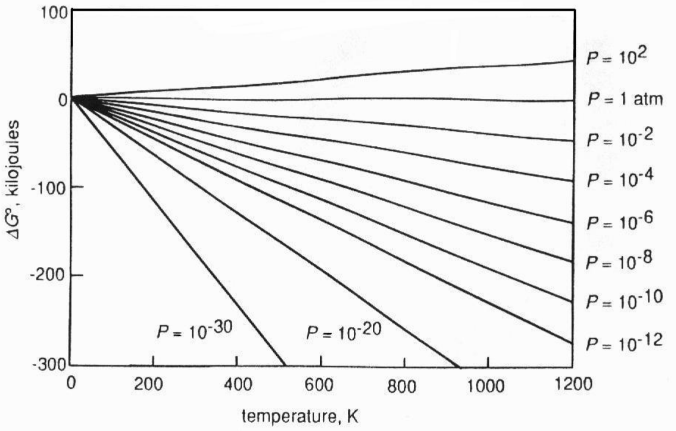


Figure 12.5 The variation, with temperature, of the difference between the Gibbs free energy of 1 mole of ideal gas in the state ($P = P$ atm, T) and the Gibbs free energy of 1 mole of ideal gas in the state ($P = 1$ atm, T)

Figure 12.5

* When $p_{O_2(eq.)} = 1atm \quad \ln p_{O_2(eq.)} = 0$

$\therefore \Delta G^o_T = R \ln p_{O_2(eq.)} \cdot T$, slope=0

when $p_{O_2(eq.)} < 1atm$, $\ln p_{O_2(eq.)} < 0$

$\therefore \Delta G^o$ vs. T line, slope < 0

$\therefore p_{O_2(eq,T)}$ nomographic scale is added to Ellingham diagram along right-hand edge and bottom edge.

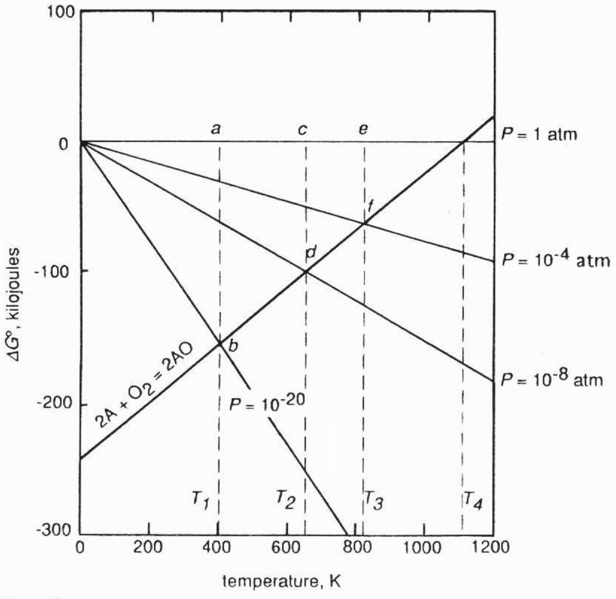


Figure 12.6 The superimposition of an Ellingham line on Figure 12.5

Figure 12.6 e.g. at T= T_1

$\overline{ab} = \Delta G^{o}_{T_1}$ =Gibbs Free Energy change of $O_{2(g)}$

from $1\text{atm} \rightarrow 10^{-20}$ atm

$\therefore$ if $p_{O_2} < p_{O_2(eq,T_1)} = 10^{-20}$ atm

oxidation of $M_{(s)}$ will not occur.

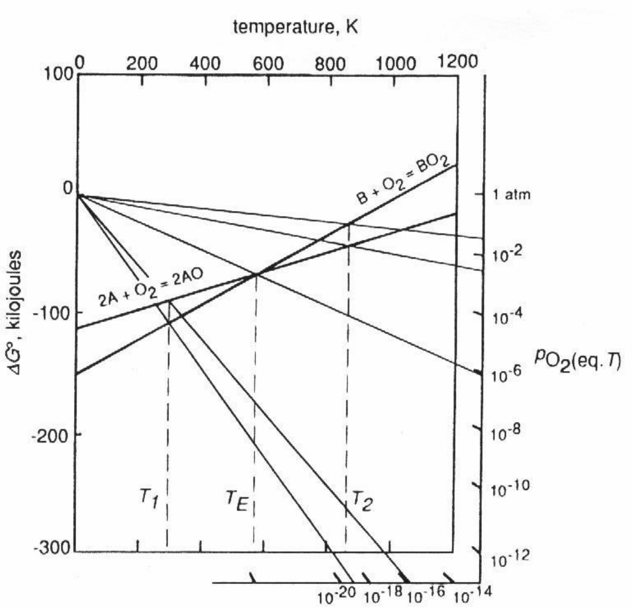


Figure 12.7 Illustration of the addition of the Richardson oxygen pressure nomographic scale to an Ellingham diagram

Figure 12.7 If $T_1 < T_E$

$p_{O_2(eq,T_1)}(2) < p_{O_2(eq,T_1)}(1)$

$\therefore$ B oxidized more easily than A.

$\ast$ Starting with p_{O_2} =1atm at T_1, (A+B+ O_2)

A and B oxidized simultaneously.

When $p_{O_2} \downarrow$ to $\leq p_{O_2(eq,T_1)}(1)$

Oxidation of A ceases and oxidation of B continues + part of $AO_{(s)}$ decomposed.

Final equilibrium: $A_{(s)} + BO_{2(s)} + p_{O_2(eq,T_1)}(2)$

§12-5. Effect of Phase Transition

$$A_{(s)} + O_{2(g)} = AO_{(s)} \ldots\ldots(1)$$

$$A_{(\lambda)} = A_{(s)} \ldots\ldots(2) \quad \text{at } T = T_{m,(A)}$$

$$(3)=(1)+(2) \quad \therefore A_{(\lambda)} + O_{2(g)} = AO_{2(s)} \ldots\ldots(3)$$

$$\therefore \Delta H^o_{(3)} = H^o_{AO_2(s)} - H^o_{A(\lambda)} - H^o_{O_2(g)}$$

$$= H^o_{AO_2(s)} - H^o_{A(s)} - H^o_{O_2(g)} - [H^o_{A(\lambda)} - H^o_{A(s)}]$$

$$\therefore \Delta H^o_{(3)} = \Delta H^o_{(1)} - \Delta H^o_{m,A}$$

Similarly, $\Delta S^o_{(3)} = \Delta S^o_{(1)} - \Delta S^o_{m,A} = -S_{O_2} - \Delta S^o_{m,A} = -(S_{O_2} + \Delta S^o_{m,A})$

$$\because \Delta H^o_{m,A} > 0 \quad \text{and} \quad \Delta S^o_{m,A} > 0$$

$$\therefore \begin{cases} \Delta H^o_{(3)} < \Delta H^o_{(1)} \\ \Delta S^o_{(3)} < \Delta S^o_{(1)} \end{cases} \Rightarrow * \text{ slope of Ellingham line=}(-\Delta S^o) > 0$$

$$\therefore (\text{slope}) \uparrow \quad \text{slope} = S_{O_2} + \Delta S^o_{m,A}$$

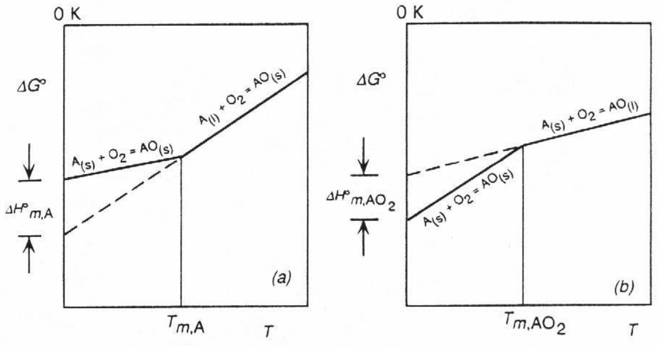


Figure 12.8 (*a*) The effect of melting of the metal on the Ellingham line for oxidation of the metal. (*b*) The effect of melting of the metal oxide on the Ellingham line for the oxidation of the metal.

Figure 12.8 $*$ intercept at T= 0^oK is lower.

$$A_{(s)} + O_{2(g)} = AO_{2(s)} \ldots\ldots(1)$$

$$AO_{2(s)} = AO_{2(\lambda)} \ldots\ldots(4) \quad \text{at } T = T_{m,AO_2}$$

(5)=(1)+(4): $A_{(s)} + O_{2(g)} = AO_{2(\lambda)} \ldots\ldots(5)$

$$\Delta H^o_{(5)} = H^o_{AO_2(\lambda)} - H^o_{A(s)} - H^o_{O_2(g)}$$

$$= H^o_{AO_2(s)} - H^o_{A(s)} - H^o_{O_2(g)} + [H^o_{AO_2(\lambda)} - H^o_{AO_2(s)}]$$

$$\Delta H^o_{(5)} = \Delta H^o_{(1)} + \Delta H^o_{m,AO_2}$$

Similarly, $\Delta S^o_{(5)} = \Delta S^o_{(1)} + \Delta S^o_{m,AO_2} = -S_{O_2} + \Delta S^o_{m,AO_2}$

$\because \Delta H^o_{m,AO_2} > 0,\ \Delta S^o_{m,AO_2} > 0$

$$\therefore \begin{cases} \Delta H^o_{(5)} < \Delta H^o_{(1)} \\ \Delta S^o_{(5)} < \Delta S^o_{(1)} \end{cases}$$

$$\therefore \begin{cases} * \ \text{intercept at } T = 0^oK \text{ is higher.} \\ * \ \text{slope}_{(5)} = (-\Delta S^o_{(5)}) < (-\Delta S^o_{(1)}),\ (\text{slope}) \text{ decreases.} \end{cases}$$

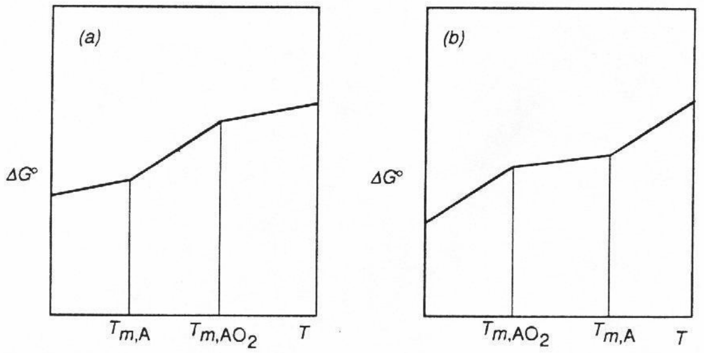


Figure 12.9 Illustration of the effects of phase changes of the reactants and products of a reaction on the Ellingham line for the reaction

Figure 12.8 , Figure 12.9

e.g. $T_{m,Fecl_2} = 969K,\ T_{b,Fecl_2} = 1298K,\ T_{m,Fe} = 1809K$

$$\text{Given} \begin{cases} Fe_{(s)} + Cl_{2(g)} = FeCl_{2(s)} \ldots\ldots(1) \\ Fe_{(s)} + Cl_{2(g)} = FeCl_{2(\lambda)} \ldots\ldots(2) \\ Fe_{(s)} + Cl_{2(g)} = FeCl_{2(g)} \ldots\ldots(3) \\ \Delta G^o_{(1)} = -346300 - 12.68T\ln T + 212.9T \ \ (J) \\ \Delta G^o_{(2)} = -286400 + 63.68T \ \ (J) \\ \Delta G^o_{(3)} = -105600 + 41.8T\ln T - 375.1T \ \ (J) \end{cases}$$

$\therefore$ (2)−(1), $FeCl_{2(s)} = FeCl_{2(\lambda)}$ ……(4)

$$\Delta G^o_{(4)} = \Delta G^o_{m,FeCl_2} = \Delta G^o_{(2)} - \Delta G^o_{(1)} = 59900+12.68T\ \ln T - 149T$$

$$\begin{cases} \Delta H^o_{m,FeCl_2} = -T^2[\dfrac{\partial(\Delta G^o_{m,FeCl_2}/T)}{\partial T}] = 59900 - 12.68T \\ \Delta S^o_{m,FeCl_2} = -[\dfrac{\partial \Delta G^o_{m,FeCl_2}}{\partial T}] = -12.68\ \ln T - 12.68 + 149 \end{cases}$$

$\therefore$ T= $T_{m,Fecl_2}$ =969K, $\begin{cases} \Delta H^o_{m,FeCl_2} = 47610\ J \\ \Delta S^o_{m,FeCl_2} = 49.13\ J/K \end{cases}$

(3)−(2), $FeCl_{2(\lambda)} = FeCl_{2(g)}$ …...(5)

$$\Delta G^o_{(5)} = \Delta G^o_{b,FeCl_2} = \Delta G^o_{(3)} - \Delta G^o_{(2)} = 180800+41.8T\ \ln T - 438.8T$$

$$\begin{cases} \Delta H^o_{b,FeCl_2} = -T^2[\dfrac{\partial(\Delta G^o_{b,FeCl_2}/T)}{\partial T}] = 180800 - 41.8T \\ \Delta S^o_{b,FeCl_2} = -[\dfrac{\partial \Delta G^o_{b,FeCl_2}}{\partial T}] = -41.8\ \ln T - 41.8 + 438.8 \end{cases}$$

$\therefore$ T= $T_{b,Fecl_2}$ =1298K, $\begin{cases} \Delta H^o_{b,FeCl_2} = 126500\ J \\ \Delta S^o_{b,FeCl_2} = 97.46\ J/K \end{cases}$

Figure 12.10

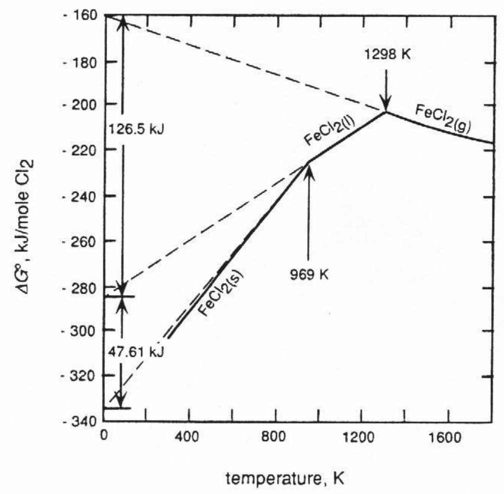


Figure 12.10 The Ellingham diagram for the chlorination of iron

§12-6. Stability of Oxides in CO/CO_2 and H_2/H_2O Gas Mixtures

＊ In order to avoid oxidation of a metal, or reducing a metal oxide, a low p_{O_2} is usually needed.

＊ A vaccum system, $p \cong 10^{-10}$ atm (10^{-7} Torr), is not enough to get a low p_{O_2}.

＊ Low p_{O_2} can be obtained by CO/CO_2 or H_2/H_2O mixture with high (p_{CO}/p_{CO_2}) or (p_{H_2}/p_{H_2O}) ratio. Nomographic scales of (p_{CO}/p_{CO_2}) and (p_{H_2}/p_{H_2O}) are added to Ellingham diagram.

1. Consider reducing of MO_2 with (CO/CO_2) gas mixture.

$$\because 2CO_{(g)} + O_{2g)} = 2CO_{2(g)} \ldots\ldots(*1)$$

$$\therefore \Delta G^o = -564800+173.62T \text{ (J)}$$

$$\Delta G^o = -RT \ln K_P = -RT \ln\left(\frac{p^2_{CO_2}}{p^2_{CO} \cdot p_{O_2}}\right)$$

$$\Delta G^o = 2RT \ln\left(\frac{p_{CO}}{p_{CO_2}}\right) + RT \ln p_{O_2}$$

at $T = T_o$

$$\therefore \ln p^{(*1)}_{O_2(eq.)} = \frac{\Delta G^o_{(T_o)}}{RT_o} - 2\ln\left(\frac{p_{CO}}{p_{CO_2}}\right)$$

For oxidation of some metal: at $T = T_o$

$$M_{(s)} + O_{2(g)} = MO_{2(s)} \ldots\ldots(*2)$$

$$\Delta G^o = -RT_0 \ln K = RT_0 \ln p^{(*2)}_{O_2(eq.)}$$

$\therefore$ If $p^{(*1)}_{O_2(eq.)} < p^{(*2)}_{O_2(eq.)}$, metal will not be oxidized (or oxide will be reduced)

2. Nomographic scale for (p_{CO}/p_{CO_2})

$$2CO_{(g)} + O_{2g)} = 2CO_{2(g)} \ldots\ldots(*1)$$

[1atm] [1atm] [1atm]

$$\Delta G^o_1 = -564800+173.62T$$

or $\Delta G_1^o = \Delta H^o_{[CO_2]} - T\Delta S^o_{[CO_2]}$

$2CO_{2(g)}$ [1atm]= $2CO_{2(g)}$ [P atm]……(*3)

$\therefore \Delta G_3^o = 2RT\ln P$

$\therefore$(*1) + (*3)=(*4) $\quad 2CO_{(g)} + O_{2g)} = 2CO_{2(g)}$

[1atm] [1atm] [P atm]

$\therefore \Delta G_4^o = \Delta G_1^o + \Delta G_3^o$

$\therefore \Delta G_4^o = \Delta H^o_{[CO_2]} - T\Delta S^o_{[CO_2]} + 2RT\ln P$

$$\boxed{\Delta G_4^o = \Delta H^o_{[CO_2]} + T[2R\ln P + (-\Delta S^o_{[CO_2]})]}$$

$\therefore$For any other pressure of $CO_{2(g)}$: P atm, or $(\frac{p_{CO}}{p_{CO_2}}) = (\frac{1}{P}) \neq 1$

ΔG_4^o vs. T is linear, originating from $\Delta H^o_{[CO_2]}$ "C" point,

with a slope $\cong (-\Delta S^o_{[CO_2]}) + 2R\ln P$

$$\therefore \begin{cases} P = p_{CO_2} > 1,\ (\dfrac{p_{CO}}{p_{CO_2}}) < 1,\ \text{slope} > (-\Delta S^o_{[CO_2]}) \\ P < 1,\ (\dfrac{p_{co}}{p_{CO_2}}) > 1,\ \text{slope} < (-\Delta S^o_{[CO_2]}) \end{cases}$$

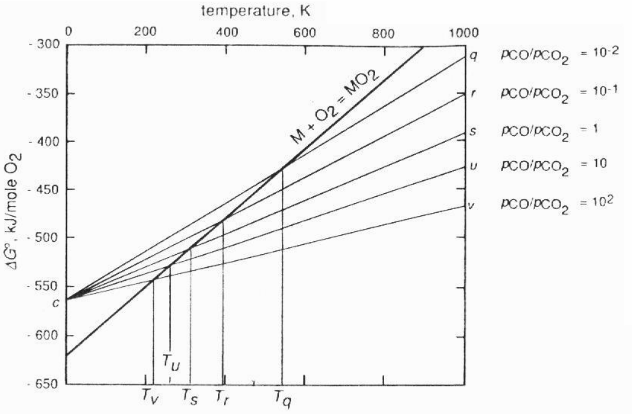


Figure 12.11 Illustration of the effect of the ratio p_{CO_2}/p_{CO} in a CO_2–CO gas mixture on the temperature at which the equilibrium M + CO_2 = MO + CO is established

Figure 12.11

3. Using CO/CO_2 gas mixture to reduce $MO_{2(s)}$

$$M_{(s)} + O_2(1atm) = MO_{2(s)} \ldots\ldots(*5)$$

$$(*1)-(*5)=(ix) \quad MO_{2(s)} + 2CO(1atm) = M_{(s)} + 2CO_2(1atm)\ldots\ldots(ix)$$

$$\therefore \Delta G^o_{(ix)} = (\Delta G^o_{(1)} - \Delta G^o_{(5)}) = -RT\ln\left(\frac{p_{CO_2}}{p_{CO}}\right)^2$$

$$\Delta G^o_{(ix)} = 2RT\ln(\frac{p_{CO}}{p_{CO_2}})$$

$\therefore$ at $T=T_s$, $(\frac{p_{CO}}{p_{CO_2}})=1$, $\Delta G^o_{(ix)}=0$, (equil.)

(a) Fix $(\frac{p_{CO}}{p_{CO_2}})=1$, $T_r > T_s$, (r)point lies below Ellingham line(*5)

$$\therefore \begin{cases} M \text{ will not be oxidized.} \\ MO_2 \text{ is reduced.} \end{cases}$$

(b) AT $T_u < T_s$

If $(\frac{p_{CO}}{p_{CO_2}})=1$, point(u) lies above line(*5) M will be oxidized.

Only when $(\frac{p_{CO}}{p_{CO_2}}) \geq 10$, M will not be oxidized. (or MO_2 can be reduced)

e.g. $2CO_2(1atm) = 2CO_2(0.1atm)\ldots\ldots(6)$

$$\Delta G^o_6 = 2RT\ln(0.1)$$

$\therefore$ (ix)+(6)=(x) $\quad MO_2 + 2CO(1atm) = M + 2CO_2(0.1atm)\ldots\ldots(x)$

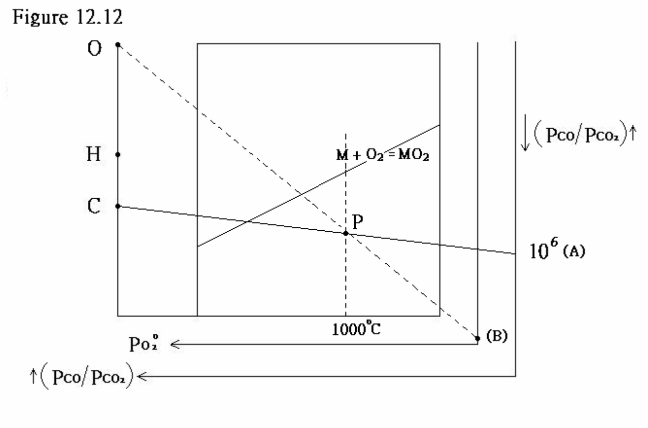
$$\therefore \Delta G^o_{(x)} = \Delta G^o_{(ix)} + 2RT\ln(0.1) = 2RT\ln(\frac{p_{CO}}{p_{CO_2}}) + 2RT\ln(0.1)$$

at T= T_u, $(\frac{p_{CO}}{p_{CO_2}})=10$ $\Delta G^o_{(x)}=0$, (equil.)

Ex.: For a given $(\frac{p_{CO}}{p_{CO_2}})$ point A= 10^6, and T=1000 ^oC, then a point P in diagram can be specified.

(1) $(p_{O_2})_{eq.}$ can be obtained by drawing $\overline{OP}$ and its intercept at p_{O_2} scale (point B= 10^{-26} atm)

(2) For an Ellingham line of some metal, if point P lies below line, metal will not be oxidized. **Figure 12.12**



§12-7. Upper limit of $(\frac{p_{CO}}{p_{CO_2}})$ at a fixed T

$$\begin{cases}(1)\ C_{(s)}+O_{2(g)}=CO_{2(g)},\ \Delta G^o_{(1)}=-394100-0.84T\\(2)\ 2C_{(s)}+O_{2(g)}=2CO_{(g)},\ \Delta G^o_{(3)}=-223400-175.3T\end{cases}$$

$$(2)-2\cdot(1)=(3)\qquad 2CO_{(g)}+O_{2(g)}=2CO_{2(g)},\ \Delta G^o_{(3)}=-564800+173.62T$$

$$(2)-(1)=(4)\qquad C_{(s)}+CO_{2(g)}=2CO_{(g)},\ \Delta G^o_{(4)}=170700-174.5T$$

1. Reaction Equilibrium of (3) (CO- CO_2**-**O_2**)**

$$\therefore \Delta G^o_{(3)}=-RT\ln K_P=-RT\ln(\frac{p^2_{CO_2}}{p^2_{CO}\cdot p_{O_2}})$$

$$\therefore 2\ln(\frac{p_{CO_2}}{p_{CO}})=\ln p_{O_2}-\frac{\Delta G^o_{(3)}}{RT}$$

$$\therefore \log\left(\frac{p_{CO_2}}{p_{CO}}\right)=\frac{1}{2}\ \log p_{O_2}-\frac{\Delta G^{o}_{(3)}}{2\times 2.3RT}$$

$$\therefore \log\left(\frac{p_{CO_2}}{p_{CO}}\right)=\frac{1}{2}\ \log p_{O_2}+\frac{564800}{2\times 2.3RT}-\frac{173.62}{2\times 2.3R}$$

For a fixed p_{O_2}, $\log(\frac{p_{CO_2}}{p_{CO}})$ vs. $(\frac{1}{T})$ is linear with same slope of $(\frac{564800}{2\times 2.3RT})$

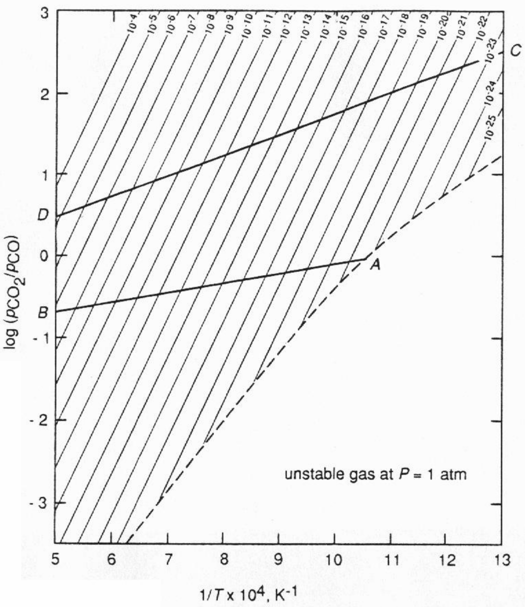


Figure 12.13 reproduced as log (p_{CO_2}/p_{CO}) vs. $1/T$

Figure 12.13

Fix p_{O_2}, as T ↑, $(\frac{1}{T})\downarrow \Rightarrow \left(\frac{p_{CO_2}}{p_{CO}}\right)\downarrow$, $\left(\frac{p_{CO}}{p_{CO_2}}\right)\uparrow$

i.e. $T\uparrow \Rightarrow \left(\frac{p_{CO}}{p_{CO_2}}\right)\uparrow$, more reducing gas.

See **Figure.12.14.**

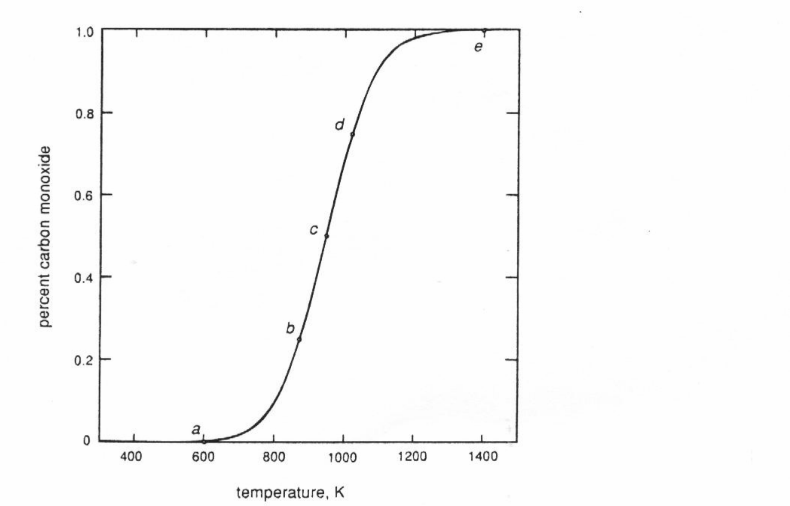


Figure 12.14 The variation, with temperature, of the composition of the CO–CO$_2$ gas mixture in equilibrium with solid graphite at $P_{total} = 1$ atm

2. At a fixed T, $(\frac{1}{T})$, there is a lower limit of $\left(\frac{p_{CO_2}}{p_{CO}}\right)$,

[upper limit of $\left(\frac{p_{CO}}{p_{CO_2}}\right)$] , because reaction (4) sets an equilibrium ,

as $\left(\frac{p_{CO}}{p_{CO_2}}\right) \uparrow \;\Rightarrow\; C_{(s)}$ precipitates

(4) $C_{(s)} + CO_{2(g)} = 2\,CO_{(g)}$

$$\Delta G^{o}_{4} = -RT \ln K = -RT \ln \left(\frac{p^{2}_{CO}}{p_{CO_2}}\right)$$

At a total pressure : P = 1 atm , $p_{CO_2} = 1 - p_{CO}$

$$K = \frac{p^{2}_{CO}}{1-p_{CO}} = \exp\left(-\frac{\Delta G^{o}_{4}}{RT}\right) = (1.3 \times 10^{9}) \exp\left(-\frac{20532}{T}\right) = x$$

$$\therefore\ p^{2}_{CO} + p_{CO}\cdot x - x = 0$$

$$\therefore\ p_{CO} = \frac{-x+\sqrt{x^{2}+4x}}{2}$$

and $p_{CO_2} = 1 - p_{CO} = \dfrac{2+x-\sqrt{x^{2}+4x}}{2}$

$$\therefore \left(\frac{p_{CO_2}}{p_{CO}}\right)_{limit} = \frac{2+x-\sqrt{x^2+4x}}{-x+\sqrt{x^2+4x}} = f(T)$$

$T \downarrow, (\frac{1}{T}) \uparrow \Rightarrow x \downarrow \Rightarrow \left(\frac{p_{CO_2}}{p_{CO}}\right)_{limit} \uparrow$, see Figure 12-13.

3. $MO_{(s)}$ reduced in CO/ CO_2 gas mixture

* $MO_{(s)} + CO_{(g)} = M_{(s)} + CO_{2(g)}$

Equilibrium line can be added into Figure12-13.

e.g. (A) $FeO_{(s)} + CO_{(g)} = Fe_{(s)} + CO_{2(g)}$

$$\Delta G^o_{(A)} = -22800 + 24.26T$$

$$\therefore \Delta G^o_{(A)} = -RT\ln K = -RT\ln\left(\frac{p_{CO_2}}{p_{CO}}\right)$$

$$\therefore \log\left(\frac{p_{CO_2}}{p_{CO}}\right) = -\frac{\Delta G^o_{(A)}}{2.3RT} = \frac{1192}{T} - 1.27 \quad (\text{ line } \overline{AB})$$

Note : * any gas state , which lies above $\overline{AB}$ is oxidizing with respect to $Fe_{(s)}$

* Point A is the lowest temperature T_A, at which FeO can be reduced by $C_{(s)}$.

Example 1 :

Given

(1) $CO_{(g)} + \frac{1}{2}O_{2(g)} = CO_{2(g)}$ $\Delta G^o_1 = -282400+86.81T$

(2) $H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(g)}$ $\Delta G^o_2 = -246400+54.8T$

(3) $Co_{(s)} + \frac{1}{2}O_{2(g)} = CoO_{(s)}$ $\Delta G^o_3 = -282400+71.85T$

Ask : 1. Which ($H_{2(g)}$ or $CO_{(g)}$) is a more efficient reducing gas ?

2. One mole $H_{2(g)}$, how many moles of $CoO_{(s)}$ can be reduced at

T = 1673 K and T = 873 K ?

3. One mole $CO_{(g)}$, how many moles of $CoO_{(s)}$ can be reduced at

T = 1673 K and T = 873 K ?

Sol :

1. $\because\ \Delta G^o_1 = \Delta G^o_2$, T_o = 1125 K = 852℃

When $T > T_o$, $\Delta G^o_1 < \Delta G^o_2$, $H_{2(g)}$ is a more efficient reducing gas.

When $T < T_o$, $CO_{(g)}$ is a more efficient reducing gas.

2. $CoO_{(s)} + H_{2(g)} = Co_{(s)} + H_2O_{(g)}$ …….(4)

(4) = (2)－(3), $\Delta G^o_4 = -12500 + 17.05\,T$

	$CoO_{(s)}$ +	$H_{2(g)}$ =	$Co_{(s)}$ +	$H_2O_{(g)}$
Initial	1	1	0	0
Final	1-x	1-x	x	x

$$\Delta G^o_4 = -RT\ln K_4 = -RT\ln\left(\frac{p_{H_2O}}{p_{H_2}}\right)$$

$$\therefore\ K_4 = \exp\left(-\frac{\Delta G^o_4}{RT}\right) = \left(\frac{p_{H_2O}}{p_{H_2}}\right)$$

$$T = 1673\ K\ ,\ K_4 = 19.1 = \frac{x}{(1-x)}$$

$$\therefore\ x = \frac{K_4}{K_4+1} = \frac{19.1}{20.1} = 0.95\ (\text{mole})$$

$$T = 873\ K\ ,\ K'_4 = 43.5$$

$$x' = \frac{K'_4}{K'_4+1} = \frac{43.5}{44.5} = 0.978\ (\text{mole})$$

3. $CoO_{(s)} + CO_{(g)} = Co_{(s)} + CO_{2(g)}$.(5)

(5) = (1)－(3), $\Delta G^o_5 = -48500 + 14.96\,T$

$$CoO_{(s)} + CO_{(g)} = Co_{(s)} + CO_{2(g)}$$

Initial	1	1	0	0
Final	1-y	1-y	y	y

$$\therefore \quad \Delta G_5^o = -RT \ln K_5 = -RT \ln\left(\frac{p_{CO_2}}{p_{CO}}\right)$$

$$\therefore \quad K_5 = \exp\left(-\frac{\Delta G_5^o}{RT}\right) = \left(\frac{p_{CO_2}}{p_{CO}}\right) = \frac{y}{(1-y)}$$

$$\begin{cases} T = 1673\ K\ ,\ K_5 = 0.52 & y = \dfrac{K_5}{K_5+1} = \dfrac{0.52}{1.52} = 0.34\ (\text{mole}) \\ T = 873\ K\ ,\ K_5^{'} = 132 & y^{'} = \dfrac{132}{133} = 0.992\ (\text{mole}) \end{cases}$$

$$\therefore \begin{cases} T = 1673\ K\ ,\ x > y\ ,\ H_{2(g)} \text{ is more efficient} \\ T = 873\ K\ ,\ x < y\ ,\ CO_{(g)} \text{ is more efficient} \end{cases}$$

Example 2 : $NiO_{(s)} + Cl_{2\ (g)} = NiCl_{2\ (s)} + \frac{1}{2} O_{2(g)}$

At T = 900 K $\Delta G^o = -15490$ J

If 90 % $Cl_{2\ (g)}$ must be converted into $O_{2(g)}$,

What is the total pressure ? P =?

Sol: $NiO_{(s)} + Cl_{2\ (g)} = NiCl_{2\ (s)} + \frac{1}{2} O_{2(g)}$

Initial	1	1	0	0
Final	1-x	1-x	x	$\frac{1}{2}x$

$$\therefore \quad \Delta G^o = -RT \ln K = -RT \ln\left(\frac{p_{O_2}^{\frac{1}{2}}}{p_{Cl_2}}\right)$$

$$\therefore \quad \left(\frac{p_{O_2}^{\frac{1}{2}}}{p_{Cl_2}}\right) = \exp\left(-\frac{\Delta G^o}{RT}\right) = 7.925$$

For gas phase : $n_T = (1\text{-}x) + \frac{1}{2}x = 1 - \frac{1}{2}x$

$$\therefore \quad \frac{\left(\frac{x/2}{1-(x/2)} \cdot P\right)^{\frac{1}{2}}}{\left(\frac{1-x}{1-(x/2)} \cdot P\right)} = 7.925$$

But $x = 90\ \% = 0.9$ $\quad \therefore \quad \frac{(0.818)^{\frac{1}{2}}}{0.182P} = 7.925$ $\quad \therefore\ P = 0.393$ atm

Example 3 : (1) $ZnO_{(s)} + CO_{(g)} = Zn_{(g)} + CO_{2(g)}$, $\quad \Delta G_1^o = -177800 - 111.2\,T$

Q –1 : Reaction (1) : T = 1223 K , P = 1atm , final composition of gas phase p_i =?

Sol–1: $T = 1223$ K , $\Delta G_1^o = 41800$

$$\because \quad \Delta G_1^o = -RT \ln K_1 = -RT \ln\left(\frac{p_{CO_2} \cdot p_{Zn}}{p_{CO}}\right)$$

$$\therefore \quad \left(\frac{p_{CO_2} \cdot p_{Zn}}{p_{CO}}\right) = \exp\left(-\frac{\Delta G_1^o}{RT}\right) = 0.0164$$

$P = p_{Zn} + p_{CO_2} + p_{CO}$ but $p_{Zn} = p_{CO_2}$

$\therefore\ p_{CO} = 1 - 2\,p_{Zn}$

$$\therefore \quad \frac{p_{Zn}^2}{1-2p_{Zn}} = 0.0164$$

$$\therefore \quad \begin{cases} p_{Zn} = 0.113 \text{ atm} \\ p_{CO_2} = 0.113 \text{ atm} \\ p_{CO} = 0.774 \text{ atm} \end{cases}$$

Q-2 : When P ↑ (p_{Zn}) increases , condensation of $Zn_{(g)}$ occurs .

T = 1223 K , p_{Zn} = ? P_C = ?

Given : $Zn_{(l)} = Zn_{(g)}$

$$\ln p^{o}_{Zn(l)} = \frac{-15250}{T} - 1.255 \ln T + 21.58 \text{ (atm)}$$

Sol –2 : $T=1223$ K , $p^{o}_{Zn(l)} = 1.49$ atm

$$\because\ K_1 = \left(\frac{p_{CO_2} \cdot p_{Zn}}{p_{CO}}\right) = 0.0164 \quad , \quad p_{Zn} = p_{CO_2} = 1.49 \text{ atm}$$

$$\therefore\ 0.0164 = \frac{1.49 \times 1.49}{P_c - (2 \times 1.49)}$$

$$\therefore\ P_C = 138.35 \text{ atm} \quad , \quad p_{CO} = 135.37 \text{ atm}$$

Q-3 : $T=1223$ K , $P = 150$ atm equilibrium $p_i = ?$

Sol –3 : $\because\ Zn_{(l)} = Zn_{(g)}$ equilibrium must be maintained.

$$\therefore\ p_{Zn} = 1.49 \text{ atm}$$

But $p_{CO_2} \neq p_{Zn}$ ($\because\ P > 138$ atm)

$$\therefore\ K_1 = \left(\frac{p_{CO_2} \cdot 1.49}{p_{CO}}\right) = 0.0164 \quad \ldots\ldots.(I)$$

$$P = 150 = 1.49 + p_{CO_2} + p_{CO} \quad \ldots\ldots..(II)$$

Solve (I) (II)

$$\therefore\ p_{CO_2} = 1.61 \text{ atm} \quad , \quad p_{CO} = 146.9 \text{ atm}$$

Example 4 :

Given , $CO_{2(g)} + H_{2(g)} = CO_{(g)} + H_2O_{(g)}$ …(1) $\Delta G^o_1 = 36000 - 32\,T$

$CO - CO_2 - H_2 - H_2O$ gas mixture produced by mixing with

$CO_{2(g)}$ + $H_{2(g)}$ 1:1 moles , $T = 1000$ K, $P = 1$ atm

Q-1 $p_{i(eq)} = ?$

Sol : $\Delta G^o_1 = -RT \ln K_{P1}$ $\quad K_{P1} = \exp(-\frac{\Delta G^o_1}{RT}) = 0.618$

$$K_{P1} = \left(\frac{p_{H_2O} \cdot p_{CO}}{p_{CO_2} \cdot p_{H_2}} \right)$$

$\because \; p_{CO} = p_{H_2O} \;, \quad p_{CO_2} = p_{H_2}$

$\therefore \; P = 1 = p_{H_2O} + p_{CO} + p_{CO_2} + p_{H_2} = 2\,(p_{H_2} + p_{H_2O})$

$\therefore \; p_{H_2O} + p_{H_2} = 0.5 \qquad \therefore \; p_{H_2O} = 0.5 - p_{H_2}$

$\therefore \; p_{CO} = p_{H_2O} = 0.5 - p_{H_2}$

$p_{CO_2} = p_{H_2}$

$$\therefore \; K_{P1} = \left(\frac{(0.5 - p_{H_2}) \cdot (0.5 - p_{H_2})}{p_{H_2} \cdot p_{H_2}} \right) = \left(\frac{(0.5 - p_{H_2})^2}{{p_{H_2}}^2} \right)$$

$$\therefore \quad \begin{cases} p_{H_2} = p_{CO_2} = 0.28 \text{ atm} \\ p_{H_2O} = 0.5 - p_{H_2} = 0.22 \text{ atm} = p_{CO} \end{cases}$$

Q-2 : Equilibrium gas mixture at initial P = 1 atm , T = 1000 K

Contained in a constant volume vessel . What are final p_i' if $CaO_{(s)}$

is introduced ?

$$\begin{cases} CaO_{(s)} + 5CO_{(g)} = CaC_{2(s)} + 3\,CO_{2(g)} \quad \text{.....(2)} \\ CaO_{(s)} + H_2O_{(g)} = Ca(OH)_{2(s)} \quad \text{...................(3)} \\ CaO_{(s)} + CO_{2(g)} = CaCO_{3(s)} \quad \text{......................(4)} \end{cases}$$

$$\begin{cases} \Delta G_2^o = -37480 + 300.7\,T \\ \Delta G_3^o = -117600 + 145\,T \\ \Delta G_4^o = -168400 + 144\,T \end{cases}$$

Sol : T = 1000 K

If : Equilibrium (I) $K_2 = \exp(-\frac{\Delta G_2^o}{RT}) = \frac{{p'_{CO_2}}^3}{{p'_{CO}}^5} = 1.78 \times 10^{-14}$

substitute $\begin{cases} p'_{CO_2} = 0.053 \text{ atm} \\ p'_{CO} = 152.9. \text{ atm} \quad \text{impossible !!} \end{cases}$

(II) $K_3 = 0.037 = \frac{1}{p'_{H_2O}}$

$\begin{cases} p'_{H_2O} = 27.027 \text{ atm} \\ P \leq 1 \text{ atm} \qquad \text{impossible !!} \end{cases}$

(III) $K_4 = 18.82 = \frac{1}{p'_{CO_2}}$

$p'_{CO_2} = 0.053 \text{ atm} < p_{CO_2} = 0.28 \text{ atm}$ Yes !!

$\therefore$ only reaction (4) is equilibriated .

$\therefore$ $p'_{CO_2} = 0.053$ atm ($< p_{CO_2} = 0.28$ atm)

$\therefore$ $CO_{2(g)}$ is consumed and (1) P ↓ , (2) reaction (1) ←

at new equilibrium $p'_{CO} = p'_{H_2O}$

$p'_{H_2O} + p'_{H_2} = 0.5$ atm (not changed)

$\therefore$ $K_{P1} = 0.618 = \left(\frac{p'_{H_2O} \cdot p'_{CO}}{p'_{CO_2} \cdot p'_{H_2}}\right) = \left(\frac{{p'_{H_2O}}^2}{(0.5 - p'_{H_2O}) \cdot 0.053}\right)$

$\therefore$ $\begin{cases} p'_{H_2O} = 0.113 \text{ atm} = p'_{CO} \\ p'_{H_2} = (0.5 - 0.113) = 0.387 \text{ atm} \\ p'_{CO_2} = 0.053 \text{ atm} \\ P' = 0.666 \text{ atm} \end{cases}$

Q-3 : If $C_{(s)}$, graphite is introduced , what is the final p_i'' ?

Given , $C_{(s)} + CO_{2(g)} = 2CO_{(g)}$ …………(5)

$$\Delta G_5^o = 170700 - 174.5\ T$$

Sol-3 : $K_5 = \exp(-\frac{\Delta G_5^o}{RT}) = 1.579 = \left(\frac{p''_{CO}{}^2}{p''_{CO_2}}\right)$

In order to maintain equilibrium of (4)

$\therefore\ p''_{CO_2} = p'_{CO_2} = 0.053$ atm

$\therefore\ p''_{CO} = (K_5\ p''_{CO_2})^{\frac{1}{2}} = (1.579 \times 0.053)^{\frac{1}{2}} = 0.289$ atm

However , $p''_{H_2O} + p''_{H_2} = 0.5$ atm (not changed !!)

$$\therefore\ K_{P1} = 0.618 = \left(\frac{p''_{H_2O} \cdot p''_{CO}}{p''_{CO_2} \cdot p''_{H_2}}\right) = \left(\frac{(0.5 - p''_{H_2}) \cdot 0.289}{p''_{H_2} \cdot 0.053}\right)$$

$$\therefore \begin{cases} p''_{H_2} = 0.449 \text{ atm} \\ p''_{H_2O} = (0.5 - 0.449) = 0.051 \text{ atm} \\ p''_{CO_2} = 0.053 \text{ atm} \\ p''_{CO} = 0.289 \text{ atm} \\ P = 0.842 \text{ atm} \end{cases}$$

Note : If process 2 , 3 , Q2 , Q3 are reversed , the final equilibrium p_i'' is the same .