Chapter 12A

Reactions Involving Pure Condensed Phases and A Gaseous Phase

12. 1 Introduction

- Reaction of pure metal to form oxide, sulfide and halides.
- Possibility of oxidation and reduction.
- T, P condition for the decomposition of carbonate ($CaCO_3$).
- Equil'm between the gas phase and individual condensed phases, between various species in the gas phases.
- T sensitivity of the saturated vapor P of pure condensed phases
  + P insensitivity of F. E. of species in the condensed phase
  ⇒ make our life easier.

12. 2 Reaction Equilibrium in A System Containing Pure Condensed Phases and A Gas Phase

12. 2 Reaction Equilibrium in A System Containing Pure Condensed Phases and A Gas Phase

As has been stated, phase equilibrium in the system requires that

$$\overline{G}_{M}\ (\text{in the gas}) = G_{M}\ (\text{in the solid metal phase}) \tag{12.2}$$

$$\overline{G}_{MO}\ (\text{in the gas phase}) = G_{MO}\ (\text{in the solid oxide phase}) \tag{12.3}$$

12. 2 Reaction Equilibrium in A System Containing Pure Condensed Phases and A Gas Phase

$$G^{\circ}_{MO(g)} + RT \ln p_{MO(g)} = G^{\circ}_{MO(s)} + \int_{P=1}^{P=p_{MO(g)}} V_{MO} dP \qquad (12.5)$$

Eq. (12.4) can be written as

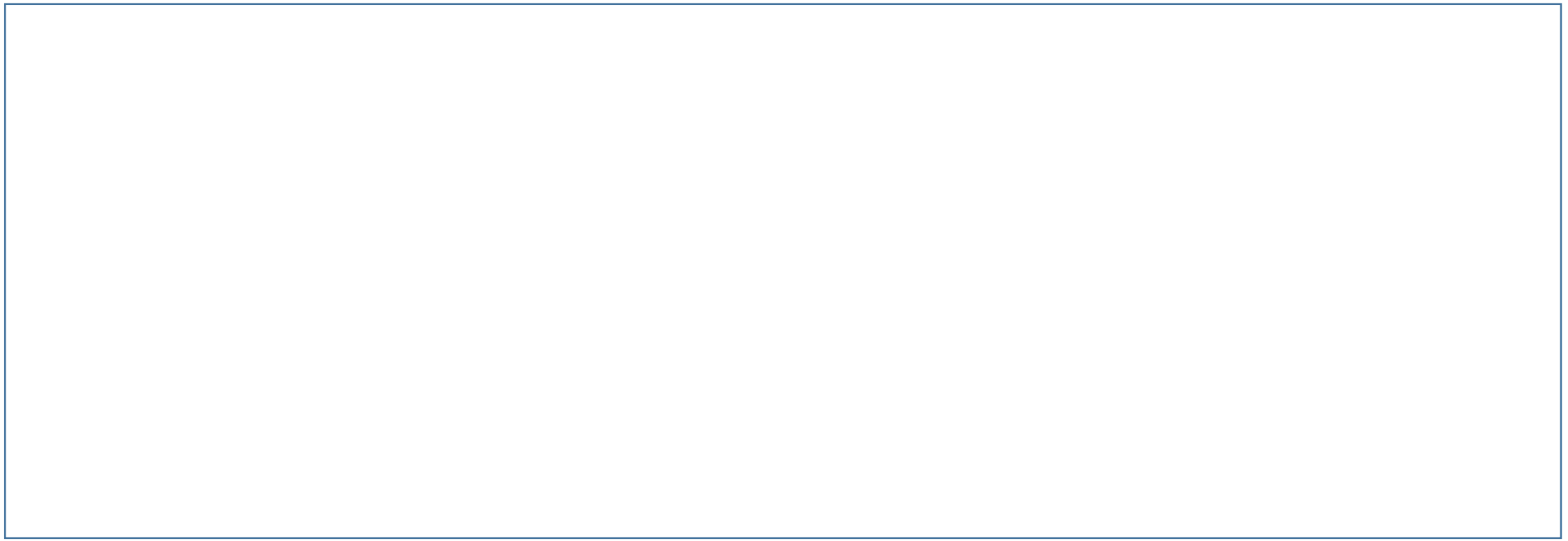
$$G^{\circ}_{M(g)} + RT \ln p_{M(g)} = G^{\circ}_{M(s)}$$

The standard state of a species occurring as a condensed phase can be defined as the pure species at T.
There is no need to include P=1 atm as a condition

Similarly, Eq. (12.5)

$$G^{\circ}_{MO(g)} + RT \ln p_{MO(g)} = G^{\circ}_{MO(s)}$$

12. 2 Reaction Equilibrium in A System Containing Pure Condensed Phases and A Gas Phase



12. 2 Reaction Equilibrium in A System Containing Pure Condensed Phases and A Gas Phase

$$\Delta G^\circ = -RT \ln K \qquad (12.6)$$

For such system as gas + solid:

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

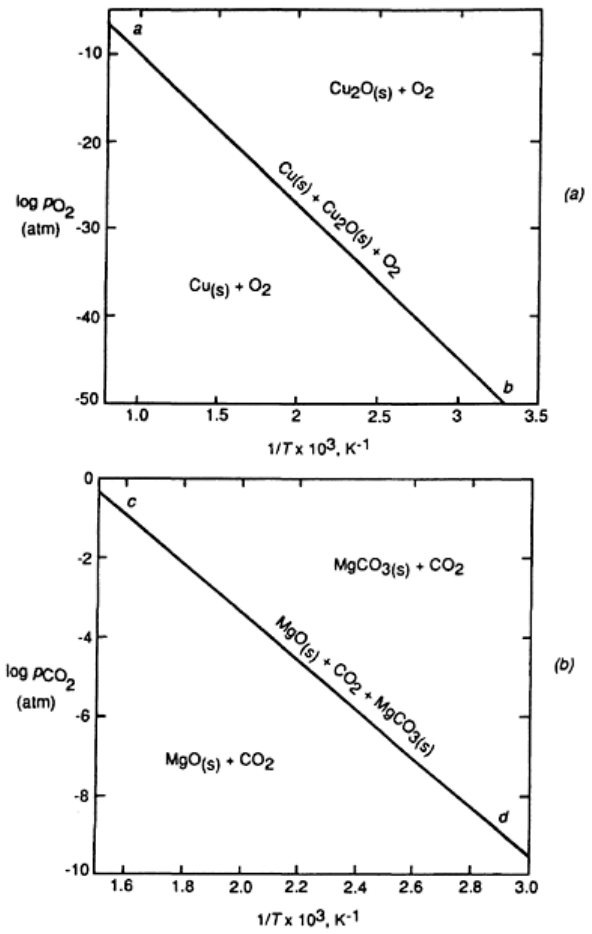
K can be written only with gas species.

ΔG° = f(T) only and K= f(T) only i.e., at a fixed T, rxn equil'm fixed: i.e., $P_{O_2} = P_{O_{2(eq.T)}}$
From the phase rule P = 3 (MO, M, O2), C = (M, O): F = C- P + 2 = 2 – 3 + 2 = 1 (temp.)

At T, reduction of ores controlled by

If $P_{O_2} > P_{O_{2(eq.T)}}$ ⇒ spontaneous oxidation to reduce P_{O_2}
If $P_{O_2} < P_{O_{2(eq.T)}}$ ⇒ spontaneous reduction to increase P_{O_2}

12. 2 Reaction Equilibrium in A System Containing Pure Condensed Phases and A Gas Phase



The standard Gibbs free energy change for the reaction between Cu and O_2

$4Cu_{(s)} + O_{2(g)} = 2Cu_2O_{(s)}$ is $\Delta G^\circ = -324{,}400 + 138.5T\ \text{J}$

In the temperature range 298-1200K. Thus,

$$-\ln K = \ln p_{O_2(\text{eq.}T)} = \frac{\Delta G^\circ}{RT} \quad \text{or} \quad \log p_{O_2(\text{eq.}T)} = -\frac{324{,}400}{2.303 \times 8.3144T} + \frac{138.5}{2.303 \times 8.3144}$$

$$= -\frac{16{,}940}{T} + 7.23$$

The standard Gibbs free energy change for the reaction between MgO and CO_2

$MgO_{(s)} + CO_{2(g)} = MgCO_{3(s)}$

$\Delta G^\circ = -117{,}600 + 170T\ \text{J}$

$$\log p_{CO_2(\text{eq.}T)} = -\frac{117{,}600}{2.303 \times 8.3144T} + \frac{170}{2.303 \times 8.3133}$$

$$= -\frac{6141}{T} + 8.88$$

Figure 12.1 *(a)* the variation, with temperature, of the oxygen pressure required for maintenance of the equilibrium 4Cu*(s)* +O2=2Cu2O. *(b)* The variation, with temperature, of the carbon dioxide pressure required for maintenance of the equilibrium MgO*(s)*+CO2=MgCO3*(s)*.

12. 3 The Variation of The Standard Gibbs Free Energy Change With Temperature

12. 3 The Variation of The Standard Gibbs Free Energy Change With Temperature

For the reaction, the Gibbs-Helmholtz equation is

$$\frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial T} = -\frac{\Delta H^\circ}{T^2} = -\frac{\Delta H_0}{T^2} - \frac{\Delta a}{T} - \frac{\Delta b}{2} + \frac{\Delta c}{T^3} \qquad \text{Eq (12.9)}$$

12. 3 The Variation of The Standard Gibbs Free Energy Change With Temperature

For the exemplary reaction

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

$$\Delta H^\circ_{298} = -324{,}400 \text{ J}$$

$$\Delta S^\circ_{298} = -138.5 \text{ J/K}$$

and thus $\Delta G^\circ_{298} = -324{,}400 + (298 \times 138.5) = -283{,}100$ J

$$c_{p,Cu(s)} = 22.6 + 6.3 \times 10^{-3} T \text{ J/K}$$ in 298 <T< 1356 K

$$c_{p,Cu_2O(s)} = 62.34 + 24 \times 10^{-3} T \text{ J/K}$$ in 298 <T< 1200 K

$$c_{p,O_2(g)} = 30 + 4.2 \times 10^{-3} T - 1.7 \times 10^{5} T^{-2} \text{ J/K}$$ and in 298 <T< 3000 K,

such that in 298 <T< 1200 K

$$\Delta c_p = 2c_{p,Cu_2O(s)} - 4c_{p,Cu(s)} - c_{p,O_2(g)}$$
$$= 4.28 + 18.6 \times 10^{-3} T + 1.7 \times 10^{5} T^{-2} \text{ J/K}$$

Thus

$$\Delta H^\circ_T = \Delta H_0 + 4.28T + 9.3 \times 10^{-3} T^2 - 1.7 \times 10^{5} T^{-1} \text{ J}$$

12. 3 The Variation of The Standard Gibbs Free Energy Change With Temperature

$$\Delta H_T^\circ = \Delta H_0 + 4.28T + 9.3 \times 10^{-3}T^2 - 1.7 \times 10^5 T^{-1}\ \text{J}$$

Substitution of $\Delta H_{298}^0 = -324{,}400\text{J}$ gives $\Delta H_0 = -325{,}900\text{J}$. Dividing by $-T^2$, integrating with respect to T, and multiplying through by T gives

$$\frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial T} = -\frac{\Delta H^\circ}{T^2} = -\frac{\Delta H_0}{T^2} - \frac{\Delta a}{T} - \frac{\Delta b}{2} + \frac{\Delta c}{T^3}$$

$$\Delta G_T^\circ = -325{,}900 - 4.28T \ln T - 9.3 \times 10^{-3}T^2 - 0.85 \times 10^5 T^{-1} + IT$$

Substitution of gives $\Delta G_{298}^0 = -283{,}100J$ gives I = 171.7, and hence

$$\Delta G_T^\circ = -325{,}900 - 4.28T \ln T - 9.3 \times 10^{-3}T^2 - 0.85 \times 10^5 T^{-1} + 171.7\ \text{J} \quad \text{(i)}$$

and

$$-\ln K = \frac{\Delta G_T^\circ}{RT} = \ln p_{O_2(\text{eq.}T)}$$

$$= -\frac{39{,}200}{T} - 0.515 \ln T - 1.1 \times 10^{-3}T - \frac{10^4}{T^3} + 20.65$$

12. 3 The Variation of The Standard Gibbs Free Energy Change With Temperature

The variation of ΔG_T^0, as calculated from the experimentally measured variation of $P_{O_2(eq.T)}$ with temperature, can be fitted to an equation of the form:

$$\Delta G^\circ = A + BT \ln T + CT$$

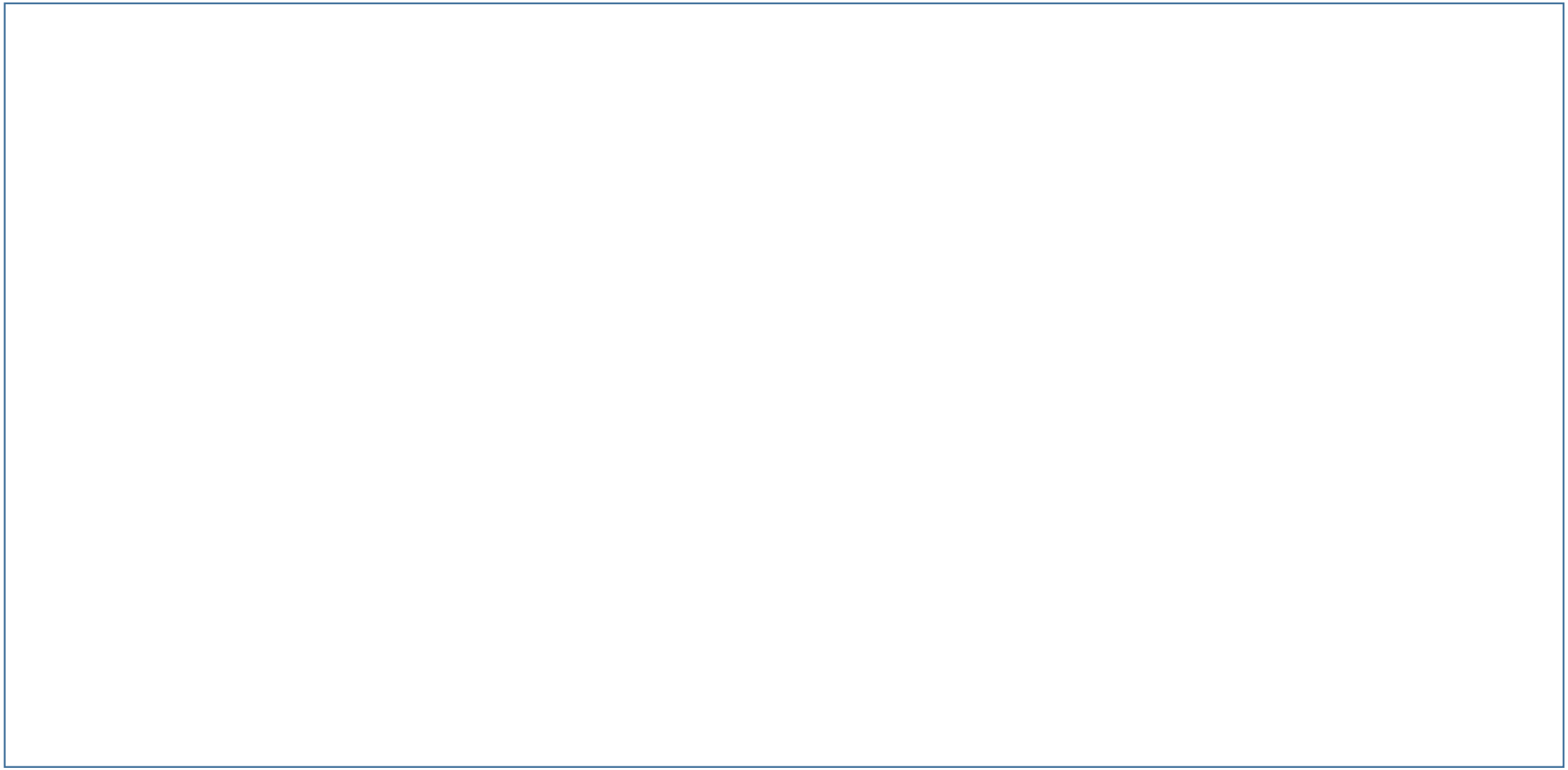
For the oxidation of 4Cu*(s)* to $2Cu_2O$*(s)*, this gives

$$\Delta G^\circ = -338{,}900 - 14.2T \ln T + 247T \text{ J} \quad \text{(ii)}$$

It can be changed in a

$$\Delta G^\circ = -333{,}000 + 141.3T \text{ J} \quad \text{(iii)}$$

12. 3 The Variation of The Standard Gibbs Free Energy Change With Temperature



(7.8)

12. 3 The Variation of The Standard Gibbs Free Energy Change With Temperature

If the vapor behaves ideally, then, at constant T, $H_{(v)}$ is independent of P, and thus

$$\ln P = -\frac{\Delta H}{RT} + \text{constant} \qquad (7.7)$$

The constant in Eq. (7.7) thus has the value $\Delta S_{evap}/R + \ln P_A$, and Eq. (7.7) becomes

$$\ln p_A = -\frac{\Delta H_{evap}}{RT} + \frac{\Delta S_{evap}}{R} + \ln p_A$$

$$\ln p_A = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

when the vapor is in equilibrium with the liquid at T,

$$\Delta S_{evap} = \frac{\Delta H_{evap}}{T} \qquad \text{or, as is required,} \qquad \Delta G_{evap} = 0$$

12. 4 Ellingham Diagrams

(i) Ellingham* plotted the experimentally determined variations of $\Delta G°$ with T for the oxidation and sulfidation simply as below:

$$\Delta G° = A + BT \qquad (12.11)$$

$$\Delta G° = IT + \Delta H° - \Delta aT \ln T - \frac{\Delta bT^2}{2} - \frac{\Delta c}{2T}$$

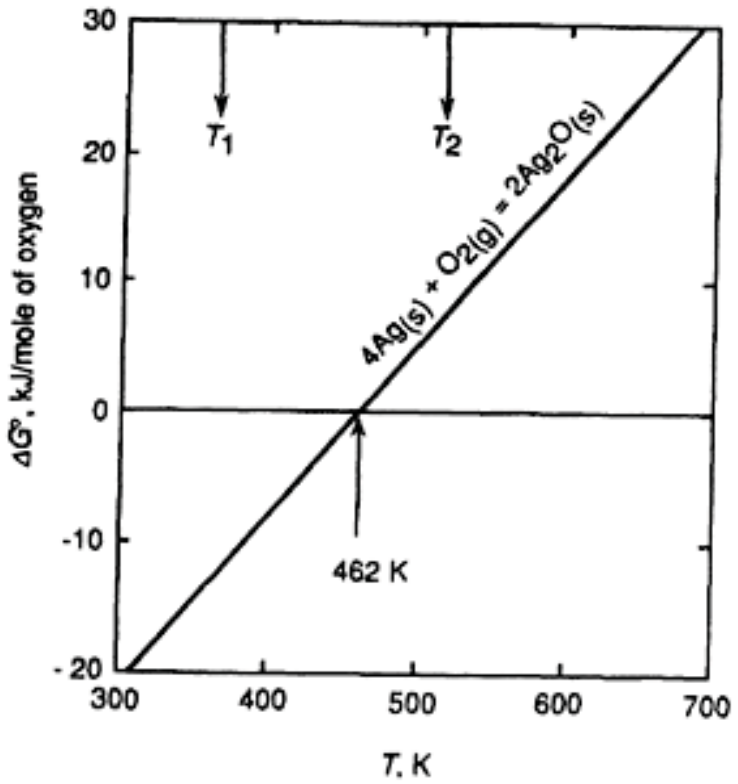


Figure 12.2 The Ellingham line for the oxidation of silver.

in which the constant A is identified with the T-independent $\Delta H°$ for the reaction, and the constant B is identified with T-independent $-\Delta S°$ for the reaction.

$$\Delta G° = \Delta H° - T\Delta S°$$

(ii) The variation of $\Delta G°$ with T for the oxidation reaction is shown in Fig. 12. 2

$$\boldsymbol{4Ag_{(s)} + O_{2(g)} = 2Ag_2O_{(s)}}$$

12. 4 Ellingham Diagrams

(iii) About ΔS° for the reaction $A + O_{2(g)} = AO_{2(s)}$

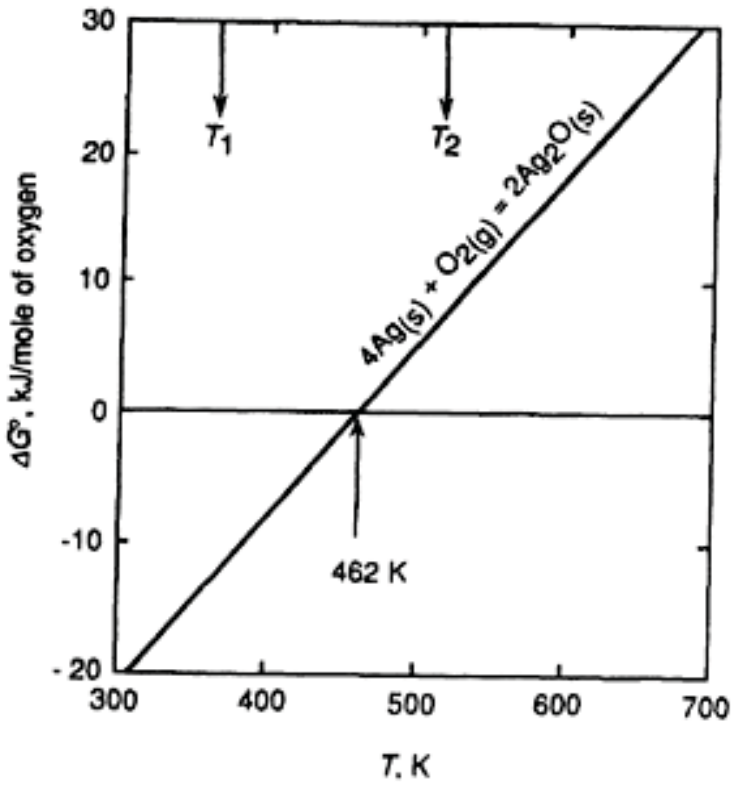


Figure 12.2 The Ellingham line for the oxidation of silver.

$$\Delta S^\circ = S^\circ_{AO2} - S^\circ_{O2} - S^\circ_{A} \fallingdotseq - S^\circ_{O2}$$

ΔS° of the oxidation involving solid phases are almost the same : parallel each other for the oxidation

(iv) about ΔH° of the oxidation: $\Delta H^\circ < 0$ most oxidation process

12. 4 Ellingham Diagrams

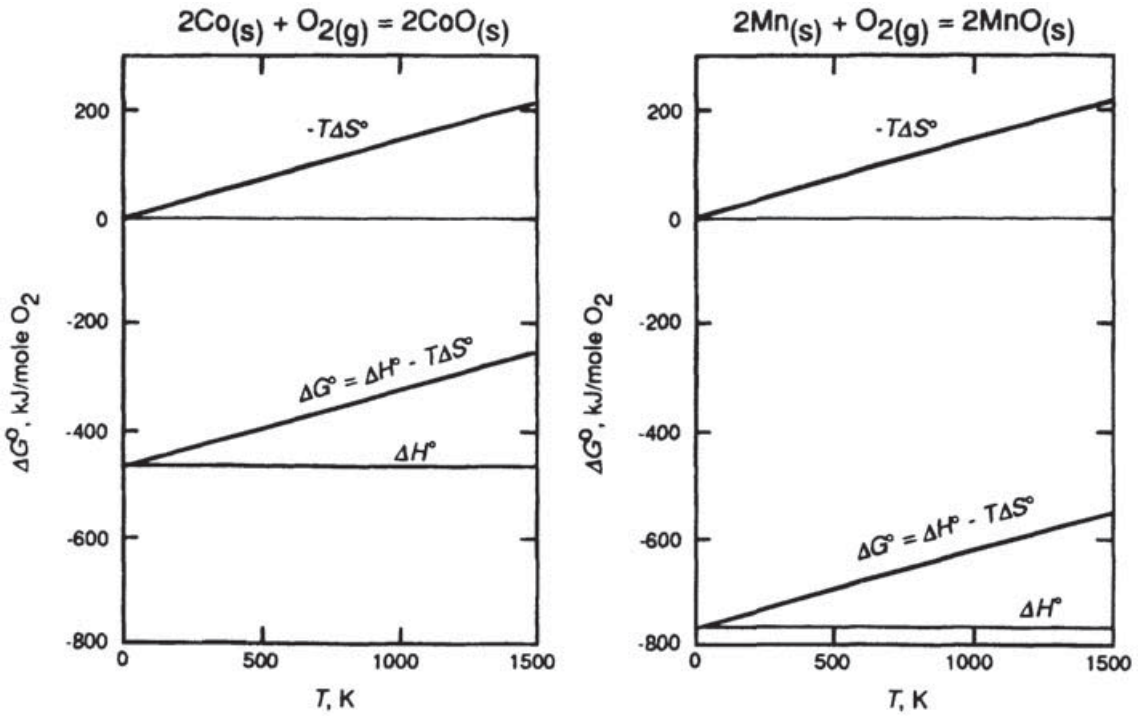


Figure 12.3 Illustration of the effect of the magnitude of $\Delta H°$ on the $\Delta G°$—T relationships for reactions of the type 2M*(s)*+O2*(g)*=2MO*(s)*.

$\Delta G°$ at any T = the sum of $\Delta H°$ contribution (which is independent of T if $\Delta C_p = 0$) and $-T\Delta S$ contribution (which, if $\Delta C_p = 0$, is a linear function of temperature).

The two contributions are illustrated in Fig. 12.3 for the oxidation reactions,

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

for which

$$\Delta G° = -467{,}800 + 143.7T \text{ J}$$

in 298 < T < 1763 K, and

$$2Mn_{(s)} + O_{2(g)} = 2MnO_{(s)}$$

for which

$$\Delta G° = -769{,}400 + 145.6T \text{ J}$$

in 298 < T < 1500 K.

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} = \ln\left(\frac{1}{p_{O_2(\text{eq.}T)}}\right)$$

$$p_{O_2(\text{eq.}T)} = \exp\frac{\Delta H°}{RT}\exp\frac{-\Delta S°}{R} = \text{constant} \times \exp\frac{\Delta H°}{RT} \qquad (12.12)$$

12. 4 Ellingham Diagrams

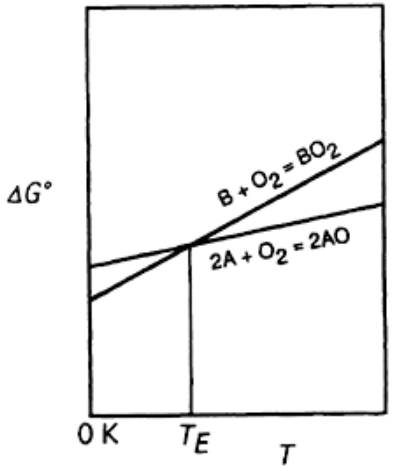


Figure 12.4 Intersecting Ellingham lines for two hypothetical oxidation reactions.

Two oxidation reactions, the Ellingham lines of which intersect one another, e.g.,

$$2A + O_2 = 2AO \qquad \text{(i)}$$

and

$$B + O_2 = BO_2 \qquad \text{(ii)}$$

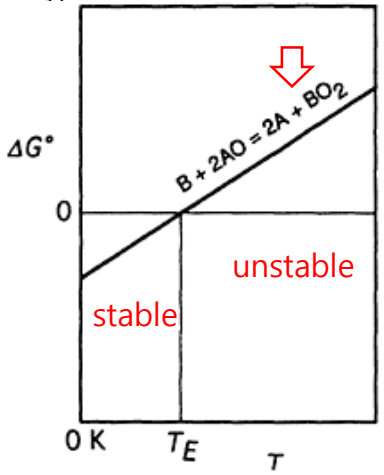


Figure 12.5 The variation of $\Delta G°$ with T for B+2AO=2 A+BO2 from Fig. 12.4.

12. 4 Ellingham Diagrams

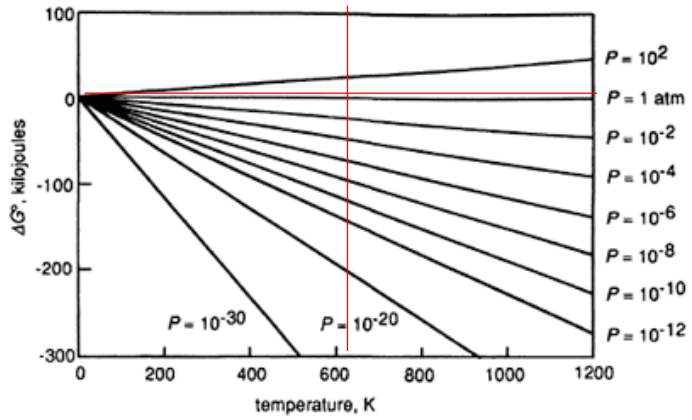


Figure 12.6 The variation, with temperature, of the difference between the Gibbs free energy of 1 mole of ideal gas in the state (P=P atm, T) and the Gibbs free energy of 1 mole of ideal gas in the state (P=1 atm, T).

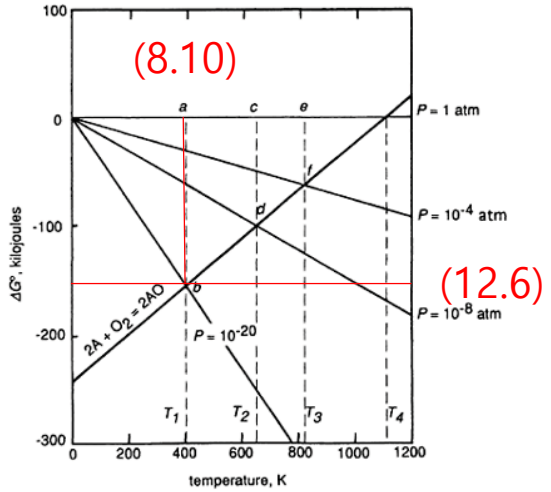


Figure 12.7 The superimposition of an Ellingham line on Fig. 12.6.

At T_1, $\Delta G^0_{T_1} = ab$= the decrease in ΔG when $P_{O_2}$is decreased from 1 atm to 10^{-20} atm at T_1.

At T_2, $\Delta G^0_{T_2} = cd$= the decrease in ΔG when $P_{O_2}$is decreased from 1 atm to 10^{-8} atm at T_2.

At T_3, $\Delta G^0_{T_3} = ef$= the decrease in ΔG when $P_{O_2}$is decreased from 1 atm to 10^{-4} atm at T_3.

At T_4, $\Delta G = 0$ = the decrease in ΔG when $P_{O_2}$is decreased from 1 atm. Thus $P_{O_2} = 1$ atm.

12. 4 Ellingham Diagrams

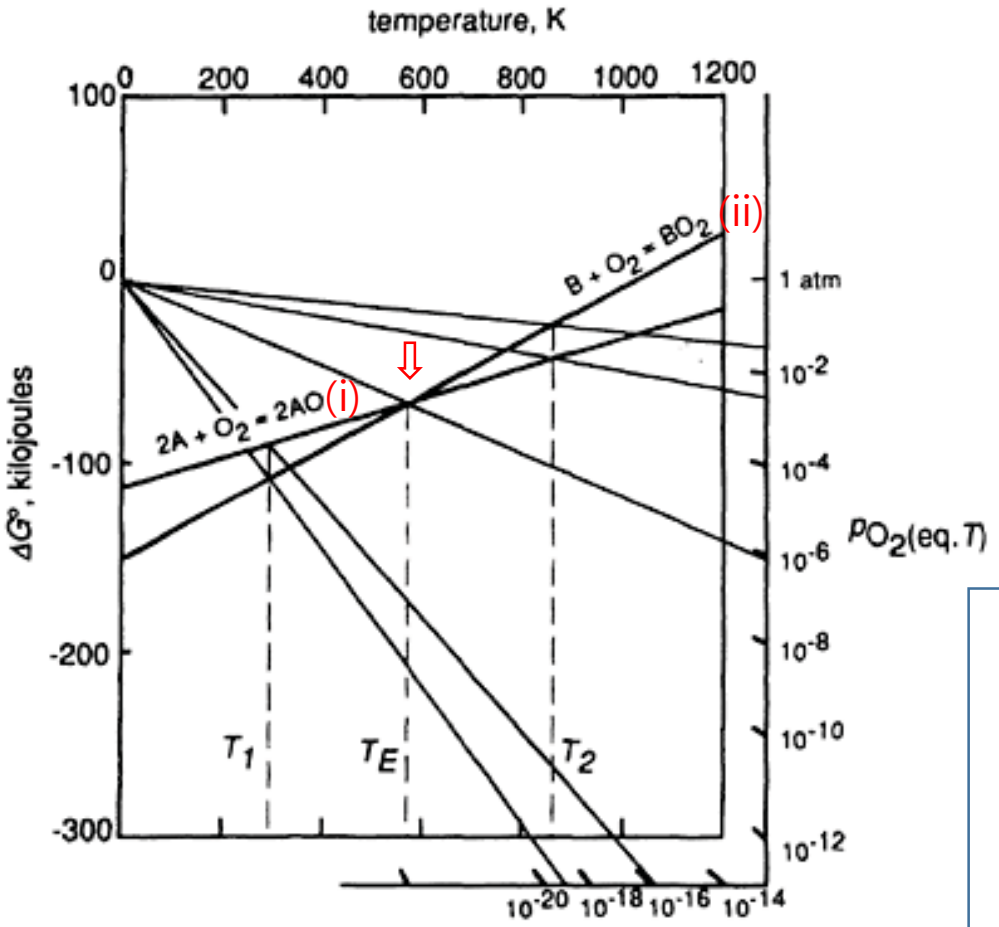


Figure 12.8 Illustration of the addition of the Richardson oxygen pressure nomographic scale to an Ellingham diagram.

At any temperature lower than $T_E^0(say, T_1)$, it is seen that

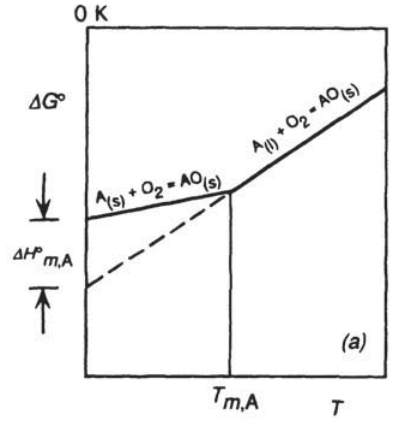
$$p_{O_2}\text{ [eq. for reaction (ii) at } T_1] < p_{O_2}\text{ [eq. for reaction (i) at } T_1]$$

At equilibrium, the state of the closed system containing, initially $A+B+O_2$ at 1 atm, is $A+BO_2+O_2$ at [eq. for reaction (ii) at T_1]. At $T > T_E$ (say, T_2),

$$p_{O_2}\text{ [eq. for reaction (i) at } T_2] < p_{O_2}\text{ [eq. for reaction (ii) at } T_2]$$

12. 5 The Effect of Phase Transformations

(i)



(ii)

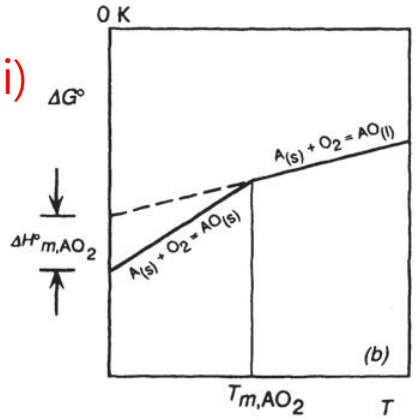


Figure 12.9 *(a)* The effect of melting of the metal on the Ellingham line for oxidation of the metal, *(b)* The effect of melting of the metal oxide on the Ellingham line for the oxidation of the metal.

(i) Consider the reaction

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

(1) $\Delta H°$, $\Delta S°$

At $T_{m(A)}$,

$$A_{(s)} \rightarrow A_{(l)}$$

(2) $\Delta H^0_{m(A)}$ (endo) , $\Delta S^0_{m(A)}$.

Thus for the reaction

$$A_{(l)} + O_{2(g)} = AO_{2(s)}$$

$\Delta H°$-$\Delta H^0_{m(A)}$,$\Delta S°$- $\Delta S^0_{m(A)}$

more negative

(ii) If $T_{m(AO_2)} < T_{m(A)}$, then, at $T_{m(AO_2)}$,

$$AO_{2(s)} \rightarrow AO_{2(l)}$$

(3) $\Delta H^0_{m(AO_2)}$, $\Delta S^0_{m(AO_2)}$

Thus, for the reaction

$$A_{(s)} + O_{2(g)} = AO_{2(l)}$$

(4)$\Delta H° + \Delta H^0_{m(AO_2)}$,$\Delta S° + \Delta S^0_{m(AO_2)}$

12. 5 The Effect of Phase Transformations

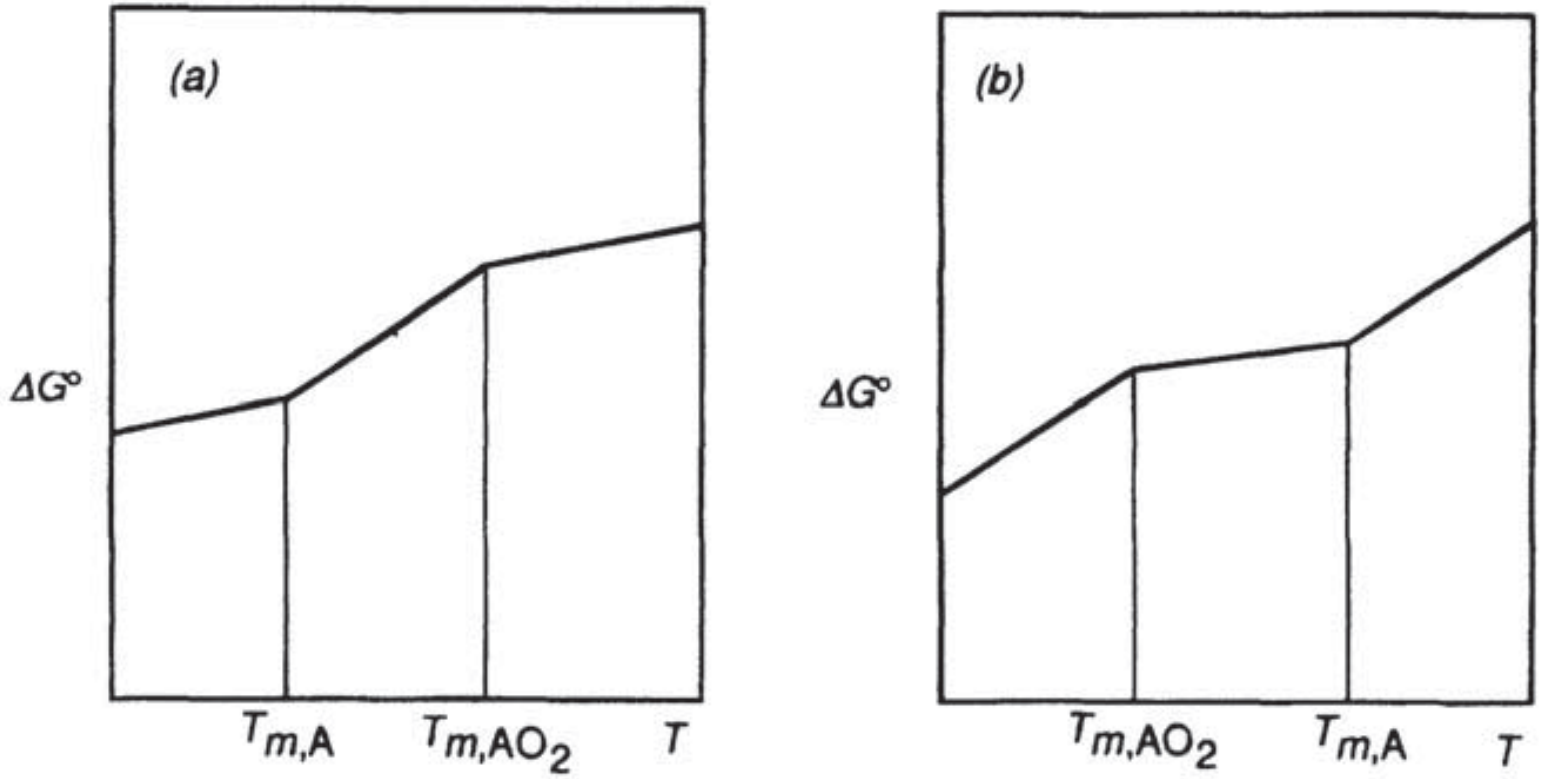


Figure 12.10 Illustration of the effects of phase changes of the reactants and products of a reaction on the Ellingham line for the reaction.

If $T_{m(A)} < T_{m(AO_2)}$, the Ellingham line is as shown in Fig. 12.10a, and,
if $T_{m(A)} > T_{m(AO_2)}$ the line is as shown in Fig. 12.10b

12. 5 The Effect of Phase Transformations

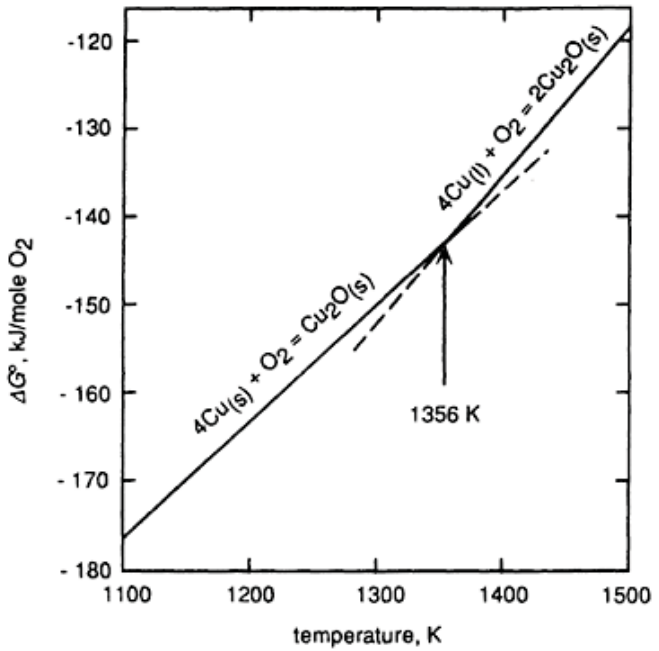


Figure 12.11 The Ellingham line for the oxidation of copper.

Copper is a metal which melts at a lower temperature than its lowest oxide Cu2O. The standard Gibbs free energy change for the oxidation of solid copper to form solid cuprous oxide in the range of temperature 298 K to $T_{m,Cu}$ is

$$\Delta G^\circ = -338{,}900 - 14.2T \ln T + 247T \text{ J} \qquad \text{(i)}$$

and, for the oxidation of liquid copper to form solid cuprous oxide in the range of temperature $T_{m,\text{Cu}}$ to 1503 K is

$$\Delta G^\circ = -390{,}800 - 14.2T \ln T + 285.3T \text{ J} \qquad \text{(ii)}$$

These two lines, which are drawn in Fig. 12.11, intersect at 1356 K, which is thus the melting temperature of copper. gives

$$\Delta G = 51{,}900 - 38.3T \text{ J}$$

for the phase change

$$4\text{Cu}_{(s)} = 4\text{Cu}_{(l)}$$

or, for the melting of 1 mole of Cu,

$$\Delta G^\circ_{m,\text{Cu}} = 12{,}970 - 9.58T \text{ J}$$

from which

$$\Delta H^\circ_{m,\text{Cu}} = 12{,}970 \text{ J} \qquad \text{and} \qquad \Delta S^\circ_{m,\text{Cu}} = 9.58 \text{ J/K}$$

12. 5 The Effect of Phase Transformations

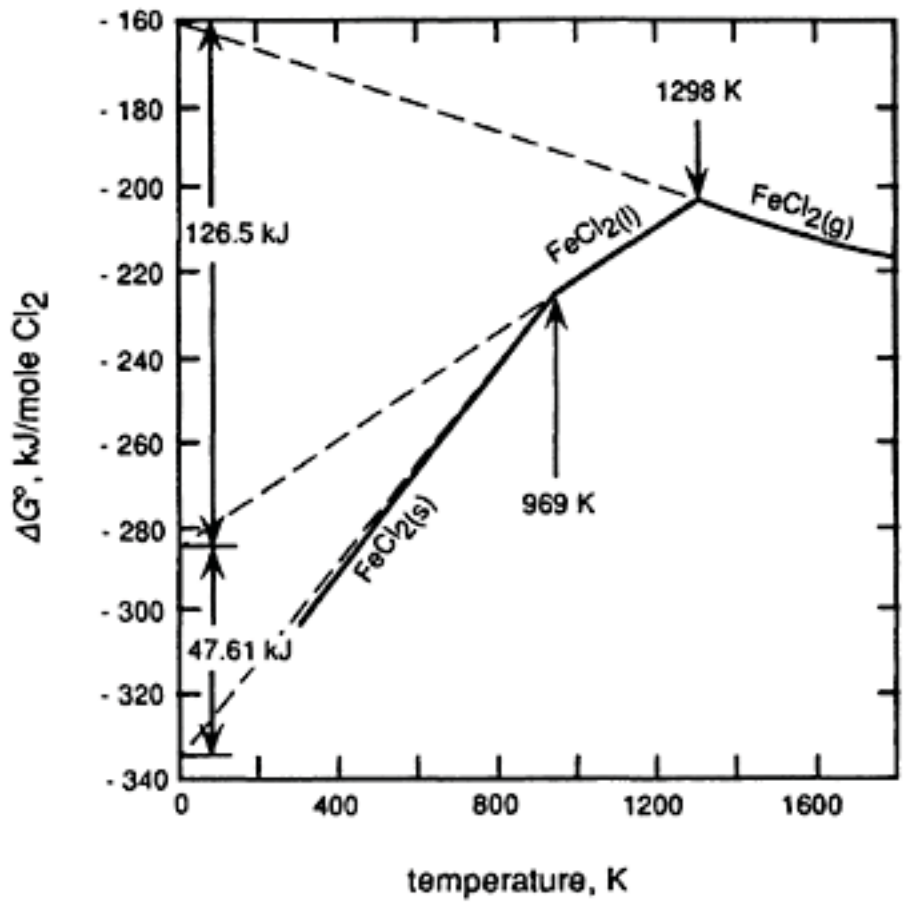


Figure 12.12 The Ellingham diagram for the chlorination of iron.

As $FeCl_2$ boils at a lower temperature than the melting temperature of Fe, the Ellingham diagram for the chlorination of Fe shows "elbows downwards" at the melting temperature of $FeCl_2$ and at the boiling temperature of $FeCl_2$. For

$$Fe_{(s)} + Cl_{2(g)} = FeCl_{2(s)}$$

$$\Delta G^\circ = -346{,}300 - 12.68T \ln T + 212.9T \text{ J} \qquad \text{(iii)}$$

in the range 298 K to $T_{m(FeCl_2)}$. For

$$Fe_{(s)} + Cl_{2(g)} = FeCl_{2(l)}$$

$$\Delta G^\circ = -286{,}400 + 63.68T \text{ J} \qquad \text{(iv)}$$

in the range $T_{m(FeCl_2)}$ to $T_{b,(FeCl_2)}$ and for

$$Fe_{(s)} + Cl_{2(g)} = FeCl_{2(g)}$$

$$\Delta G^\circ = -105{,}600 + 41.8T \ln T - 375.1T \text{ J} \qquad \text{(v)}$$

in the range $T_{b,(Cl_2)}$ to $T_{m(Fe)}$. Lines (iii), (iv), and (v) are shown in Fig. 12.12, which shows that

$$T_{m,FeCl_2} = 969 \text{ K} \quad \text{and} \quad T_{b,FeCl_2} = 1298 \text{ K}$$

For $FeCl_{2(s)} \rightarrow FeCl_{2(l)}, \Delta G^0_{(iv)} - \Delta G^0_{(iii)}$ gives

$$\Delta G^\circ_{m,FeCl_2} = 59{,}900 + 12.68T \ln T - 149.0T \text{ J}$$