Chapter 13

Reaction Equilibria In Systems Containing Components In Condensed Solution

13.1 Introduction

For the rxn, $\mathrm{SiO}_{2(s)} = \mathrm{Si}_{(s)} + \mathrm{O}_{2(g)}$

At equilibrium, $\overline{G}_{\mathrm{SiO}_2} = \overline{G}_{\mathrm{Si}} + \overline{G}_{\mathrm{O}_2}$

If SiO_2, Si are both pure, and the pure solids are chosen as the standard states,

13.1 Introduction

The calculation of the equilibrium state of any reaction system with condensed phase needs a knowledge of thermo property of various solutions in the system.

We will study the influence of solution thermos on rxn equilibria.

13.2 The Criteria For Reaction Equilibrium In Systems Containing Components In Condensed Solution

For the general reaction $aA + bB = cC + dD$

If none of the reactants or products of the reaction occurs in its standard state, then,

$$\Delta G = c\overline{G}_C + d\overline{G}_D - a\overline{G}_A - b\overline{G}_B \tag{13.1}$$

If, all of the reaction and products occur in their standard states, then, $\Delta G°$ is

$$\Delta G^\circ = cG_C^\circ + dG_D^\circ - aG_A^\circ - bG_B^\circ \tag{13.2}$$

13.2 The Criteria For Reaction Equilibrium In Systems Containing Components In Condensed Solution

Reaction equilibrium is established,

$$a\bar{G}_A + b\bar{G}_B = c\bar{G}_C + d\bar{G}_D$$

At equilibrium, $\Delta G = 0$, then. From (13.3)

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

where Q^{eq} is the value of the activity quotient at equilibrium. From Eq. (11.8),

$$\Delta G^\circ = -RT \ln K$$

And thus

$$Q^{eq} = K$$

At equilibrium the activity quotient = numerically the equilibrium constant K.

13.2 The Criteria For Reaction Equilibrium In Systems Containing Components In Condensed Solution

For the oxidation of the pure M and pure MO_2:

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

For this reaction

$$Q = \frac{a_{MO_2}}{a_M a_{O_2}}$$

As M, MO_2 are pure, and occur in their standard states, then , $a_M = a_{MO_2} = 1$, and, from the formal definition of activity, the activity of oxygen gas is given as

$$a_{O_2} = \frac{\text{the pressure of oxygen in the gas phase}}{\text{the pressure of oxygen in its standard state}}$$

then the activity of oxygen in the gas phase = its partial pressure (assuming ideal behavior of the gas).
Thus,

$$Q = \frac{1}{p_{O_2}} \quad \text{and} \quad Q^{eq} = \frac{1}{p_{O_2(eq,T)}} = K$$

13.2 The Criteria For Reaction Equilibrium In Systems Containing Components In Condensed Solution

if the pure metal M is in equilibrium with MO_2 occurring at the activity in solution and oxygen in a gas phase, then

$$Q^{eq} = \frac{a_{MO_2}}{p_{O_2(eq.T)}} = K$$

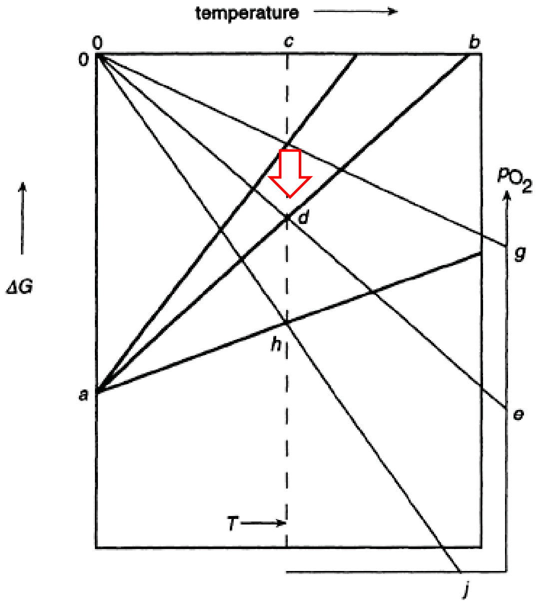

Figure 13.1 The influence of non-unit activities of the reactants and products of a reaction on the ΔG–T relationship for the reaction.

Then,

$P_{O_2(eq.T)}$ w/ pure M and solution MO_2 < $P_{O_2(eq.T)}$ w/ pure M and pure MO_2

the line $\overline{ab}$ is drawn as ΔG° changes,

$$M_{(s)} + O_{2(g,\,1\,atm)} = MO_{2(s)} \qquad \text{(i)}$$

At T, ΔG°=cd, and the oxygen pressure for equilibrium between pure solid M and pure solid MO_2 is drawn as the point e on the nomographic scale.

13.2 The Criteria For Reaction Equilibrium In Systems Containing Components In Condensed Solution

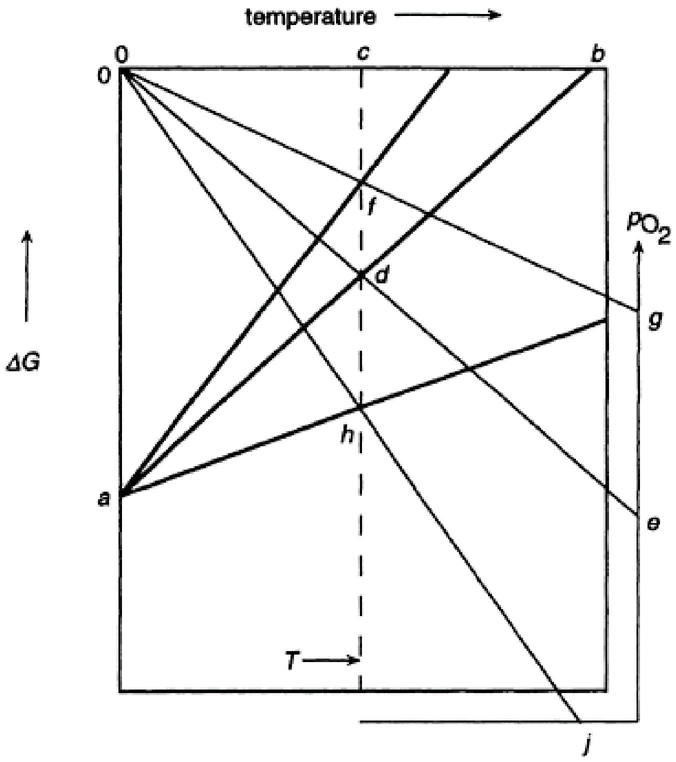

Figure 13.1 The influence of non-unit activities of the reactants and products of a reaction on the ΔG–T relationship for the reaction.

Thus

$$\begin{aligned}\Delta G_{(ii)} &= \Delta G_{(i)} + \Delta G_{(iii)} \\ &= \Delta G^\circ - RT \ln a_M\end{aligned}$$

13.2 The Criteria For Reaction Equilibrium In Systems Containing Components In Condensed Solution

Consider the reaction

$$M_{(s,\ \text{pure})} + O_{2(g,\ 1\ \text{atm})} = MO_{2(\text{in solid solution at } a_{MO_2})} \qquad \text{(iv)} \qquad \Delta G_{(\text{iv})} = \Delta G^\circ + RT \ln a_{MO_2}$$

for which Reaction (iv) can be written as the sum of reaction (v), i.e.,

$$MO_{2(s,\ \text{pure})} \rightarrow MO_{2(\text{in solution at } a_{MO_2})} \qquad \text{(v)}$$

and reaction (i), i.e.,

$$M_{(s)} + O_{2(g,\ 1\ \text{atm})} = MO_{2(s)} \qquad \text{(i)} \qquad \Delta G_{(\text{i})} = \Delta G^\circ \text{ at the temperature } T$$

13.2 The Criteria For Reaction Equilibrium In Systems Containing Components In Condensed Solution

In the general case,

$$\mathrm{M}_{(\text{in solution at } a_{\mathrm{M}})} + \mathrm{O}_{2(g,\ \text{at } p_{\mathrm{O}_2})} = \mathrm{MO}_{2(\text{in solution at } a_{\mathrm{MO}_2})} \qquad \text{(vi)}$$

13.3 Alternative Standard States

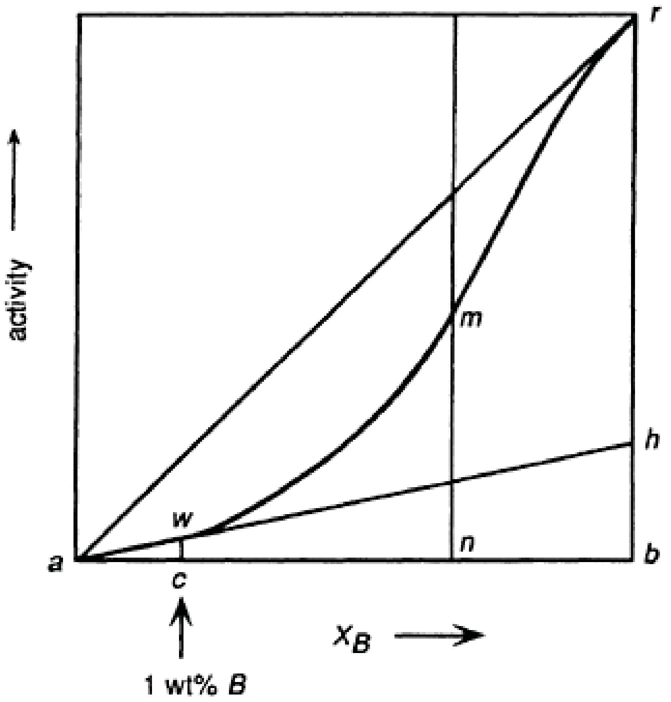

Figure 13.3 Illustration of the Raoultian, Henrian, and 1 weight percent standard states for component *B* in a binary *A–B* system.

Up to this point the standard state of a component of a system has been chosen as being the pure component in its stable state of existence at the temperature of interest. = called the Raoultian standard state;

The Raoultian standard state for the component B is located at point r.

The Henrian standard state is obtained from consideration of Henry's law, strictly being a limiting law obeyed by the solute B at infinite dilution,

$$\frac{a_B}{X_B} \rightarrow k_B \quad \text{as } X_B \rightarrow 0$$

where a_B is the activity of B in the solution with respect to the Raoultian standard state, and k_B is the Henry's law constant at T.

Alternatively, Henry's law can be written as

$$\frac{a_B}{X_B} \rightarrow \gamma_B^\circ \quad \text{as } X_B \rightarrow 0$$

where $\gamma_B^0 (= k_B)$ is the constant activity coefficient.

If the solute obeys Henry's law over a finite range of composition, then, over this range

$$a_B = \gamma_B^\circ X_B$$

13.3 Alternative Standard States

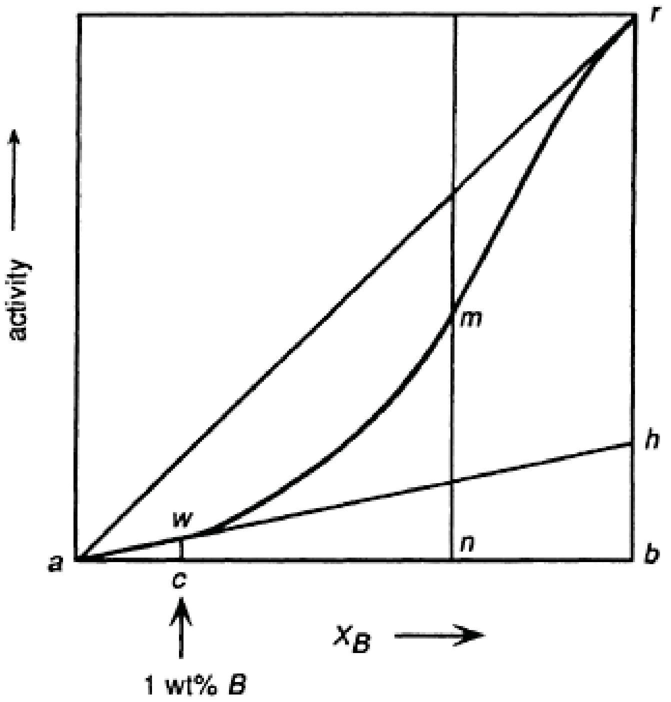

Figure 13.3 Illustration of the Raoultian, Henrian, and 1 weight percent standard states for component *B* in a binary *A*–*B* system.

The Henrian standard state is obtained by extrapolating the Henry's law line to X_B= 1.

The activity of B in the Henrian standard state with respect to the Raoultian standard state having unit activity is given by

$$a_B = \gamma_B^\circ$$

if the length rb is unity, then $hb = \gamma_B^0$.

Having defined the Henrian standard state thus, the activity of B in a solution, with respect to the Henrian standard state having unit activity, is given by

$$h_B = f_B X_B$$

where h_B is the Henrian activity and f_B is the Henrian activity coefficient.

In the range of Henrian region, f_B =1, and the solute exhibits Henrian ideality.

13.3 Alternative Standard States

(1) The mole fraction of *B* in an *A*–*B* solution

$$X_B = \frac{\dfrac{\text{wt\%}B}{MW_B}}{\dfrac{\text{wt\%}B}{MW_B} + \dfrac{(100 - \text{wt\%}B)}{MW_A}}$$

where *MWA* and *MWB* are, respectively, the molecular weights of *A* and *B.* Thus, in dilute solution,
as the mole fraction of *B* is virtually proportional to the weight percentage of *B,* i.e.,

$$X_B \sim \frac{\text{wt\%}B \times MW_A}{100 \times MW_B}$$

(2) the 1 weight percent standard state, which is defined as

$$\frac{h_{B(1\text{ wt\%})}}{\text{wt\%}B} \rightarrow 1 \text{ as wt\%}B \rightarrow 0$$

and is located at the point on the Henry's law line which corresponds to a concentration of 1 weight percent *B* (the point *w* in Fig. 13.3). With respect to the 1 weight percent standard state having unit activity, the activity of *B,* $h_{B(1\text{ wt\%})}$ is given by

$$h_{B(1\text{ wt\%})} = f_{B(1\text{ wt\%})}\text{wt\%}B$$

where $f_{B(1\text{ wt\%})}$ is the 1 weight percent activity coefficient, and in the range of composition in which the solute *B* obeys Henry's law, $f_{B(1\text{ wt\%})} = 1$.

$$h_{B(1\text{ wt\%})} = \text{wt\%}B$$

13.3 Alternative Standard States

From consideration of the similar triangles *awc* and *ahb* in Fig. 13.3, the activity of *B* in the 1 wt% SS with respect to the Henrian SS is

$$\frac{wc}{hb} = \frac{ac}{ab} = \frac{MW_A}{100MW_B}$$

with respect to the Raoultian SS having unit activity, is

$$\frac{\gamma_B^\circ MW_A}{100MW_B}$$

The value of the equilibrium constant for any reaction, being equal to the quotient of the activities of the reactants and products at reaction equilibrium, necessarily depends on the choice of standard states for the components.

The magnitude of ΔG° for the reaction depends on the choice of standard states.
And it is necessary that the differences between the Gibbs free energies of the standard states be known.

$$B_{(\text{in the Raoultian standard state})} \rightarrow B_{(\text{in the Henrian standard state})}$$

$$G_B^\circ(R \rightarrow H) = G_{B(H)}^\circ - G_{B(R)}^\circ = RT \ln \frac{a_{B(\text{in the Henrian standard state})}}{a_{B(\text{in the Raoultian standard state})}}$$

where both activities are measured on the same activity scale. On either the Raoultian or Henrian scales

$$\frac{a_{B(\text{in the Henrian standard state})}}{a_{B(\text{in the Raoultian standard state})}} = \frac{\frac{1}{hb}}{rb} = \frac{1}{\gamma_B^\circ} \quad \text{and thus} \quad \Delta G_{B(R\rightarrow H)}^\circ = RT \ln \frac{1}{\gamma_B^\circ} \qquad (13.9)$$

γ_B^0 is the Henrian activity coefficient at the temperature *T*.

13.3 Alternative Standard States

(3) For the change of standard state,

$$B_{(\text{in the Henrian standard state})} \rightarrow B_{(\text{in the 1 wt\% standard state})}$$

$$\Delta G^{\circ}_{B}(H \rightarrow 1\ \text{wt\%}) = G^{\circ}_{B(1\ \text{wt\%})} - G^{\circ}_{B(H)} = RT \ln \frac{a_{B(\text{in the 1 wt\% standard state})}}{a_{B(\text{in the Henrian standard state})}}$$

both activities are measured on the same scale:

$$\frac{a_{B(\text{in the 1 wt\% standard state})}}{a_{B(\text{in the Henrian standard state})}} = \cfrac{1}{\cfrac{wc}{hb}} = \cfrac{1}{\cfrac{ac}{ab}} = \cfrac{1}{\cfrac{MW_A}{100MW_B}}$$

and thus

$$\Delta G^{\circ}_{B(H \rightarrow 1\text{wt\%})} = RT \ln \cfrac{1}{\left(\cfrac{MW_A}{100MW_B} \right)} \qquad (13.10)$$

Combination of Eqs. (13.9) and (13.10) gives

$$\Delta G^{\circ}_{B(R \rightarrow 1\text{wt\%})} = RT \ln \left(\frac{\gamma^{\circ}_{B} MW_A}{100MW_B} \right)$$

for the change of standard state, Raoultian → 1 wt%. Using the subscript *(R)* to denote the Raoultian standard state, the subscript *(H)* to denote the Henrian standard state, and the subscript (wt%) to denote the 1 weight percent standard state,

13.3 Alternative Standard States

consider the oxidation of metal M to form the oxide MO_2 at the temperature *T:*

$$\mathrm{M}_{(R)} + \mathrm{O}_{2(g)} = \mathrm{MO}_{2(R)}$$

For this equilibrium

$$\Delta G^\circ_{(R)} = -RT \ln K_{(R)} = -RT \ln \frac{a_{\mathrm{MO}_2}}{a_{\mathrm{M}} p_{\mathrm{O}_2}}$$

If M occurs in dilute solution, in which case it may be more convenient to use the Henrian standard state for M, then

$$\mathrm{M}_{(H)} + \mathrm{O}_{2(g)} = \mathrm{MO}_{2(R)}$$

$$\Delta G^\circ_{(H)} = \Delta G^\circ_{(R)} - \Delta G^\circ_{\mathrm{M}(R\to H)}$$

i.e.,

$$-RT \ln K_{(H)} = -RT \ln K_{(R)} - RT \ln \gamma^\circ_{\mathrm{M}} \qquad \text{or} \qquad RT \ln \frac{a_{\mathrm{MO}_2}}{h_{\mathrm{M}} p_{\mathrm{O}_2}} = RT \ln \frac{a_{\mathrm{MO}_2}}{a_{\mathrm{M}} p_{\mathrm{O}_2}} + RT \ln \gamma^\circ_{\mathrm{M}}$$

Thus

$$a_{\mathrm{M}} = h_{\mathrm{M}} \gamma^\circ_{\mathrm{M}}$$

which relates the activity of M in solution with respect to the Raoultian standard state to the activity of M in solution with respect to the Henrian standard state.

13.3 Alternative Standard States

in the case of composition *m* in Fig. 13.3,

$$a_B = \frac{mn}{rb} = \frac{mn}{hb}\frac{hb}{rb} = h_B \gamma_B^\circ$$

Similarly, if it is convenient to use the 1 wt.% standard state for M, then

$$\mathrm{M}_{(1\ \mathrm{wt\%})} + \mathrm{O}_{2(g)} = \mathrm{MO}_{2(R)}$$

$$\Delta G^\circ_{(1\ \mathrm{wt\%})} = \Delta G^\circ_{(R)} - \Delta G^\circ_{\mathrm{M}(R\rightarrow 1\ wt\%)}$$

or

$$-RT\ln K_{(1\ \mathrm{wt\%})} = -RT\ln K_{(R)} - RT\ln\frac{\gamma_\mathrm{M}^\circ MW_\mathrm{solvent}}{100MW_\mathrm{M}}$$

or

$$-RT\ln\frac{a_{\mathrm{MO}_2}}{f_{\mathrm{M}(1\ \mathrm{wt\%})}\mathrm{wt\%\ M}\cdot p_{\mathrm{O}_2}} = -RT\ln\frac{a_{\mathrm{MO}_2}}{a_\mathrm{M}p_{\mathrm{O}_2}} - RT\ln\frac{\gamma_\mathrm{M}^\circ MW_\mathrm{solvent}}{100MW_\mathrm{M}}$$

or

$$a_\mathrm{M} = f_{\mathrm{M}(1\ \mathrm{wt\%})}\cdot\mathrm{wt\%\ M}\cdot\gamma_\mathrm{M}^\circ\cdot\frac{MW_\mathrm{solvent}}{100MW_\mathrm{M}}$$