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7. Chemical equilibrium

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Spontaneous chemical reactions

7.1 The Gibbs energy minimum

The direction of spontaneous change at constant p & T is towards lower G ($\Delta G < 0$).

(a) The reaction Gibbs energy

Consider the equilibrium A (reactant) $\leftrightarrow$ B (product)

Suppose an infinitesimal amount of A ($d\xi$)turns into B

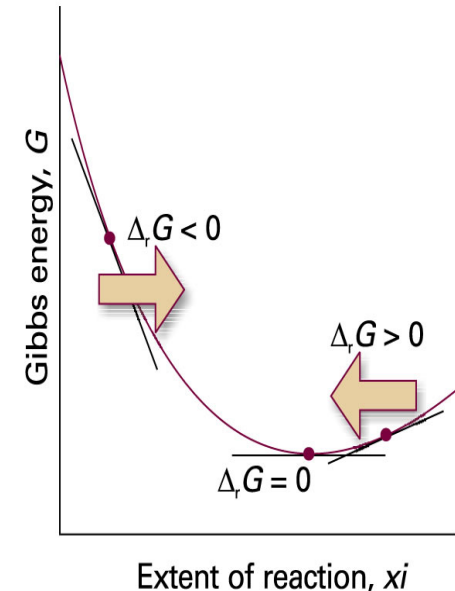Then $dn_A = -d\xi$ and $dn_B = +d\xi$ → ξ is called **the extent of reaction**

(unit: moles)

The reaction Gibbs energy is, $\Delta_r G = \left(\dfrac{\partial G}{\partial \xi}\right)_{p,T}$ ($\Delta_r G$: the slope of G vs ξ)

$$dG = \mu_A dn_A + \mu_B dn_B = -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A)d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A \quad \longrightarrow \quad \Delta_r G = \mu_B - \mu_A \text{ (at the composition of the reaction mixture)}$$

Fig. 7.1 As the reaction advances (represented by motion from left to right along the horizontal axis) the slope of the Gibbs energy changes. Equilibrium corresponds to zero slope, at the foot of the valley.

(b) Exergonic and endergonic reactions (see Fig. 7.1)

- $\mu_A > \mu_B$: $\Delta_r G < 0$, **exergonic** (work-producing, A→B : spontaneous)
- $\mu_A < \mu_B$: $\Delta_r G > 0$, **endergonic** (work-consuming, B→A: spontaneous)
- $\mu_A = \mu_B$: $\Delta_r G = 0$, equilibrium

7.2 The description of equilibrium

(a) Perfect gas equilibria

When A and B are perfect gases,

$$\Delta_r G = \mu_B - \mu_A = (\mu_B^\circ + RT \ln p_B) - (\mu_A^\circ + RT \ln p_A) \quad = \Delta_r G^\circ + RT \ln \frac{p_B}{p_A}$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q \qquad Q = \frac{p_B}{p_A} \quad (Q : \textbf{reaction quotient})$$

The standard reaction Gibbs energy :

$$\Delta_r G^\circ = G^\circ_{B,m} - G^\circ_{A,m} = \mu_B^\circ - \mu_A^\circ$$

$$\Delta_r G^\circ = \Delta_f G^\circ(B) - \Delta_f G^\circ(A) \quad \textbf{(See Section 3.6)}$$

At equilibrium, $\Delta_r G = 0$

$$0 = \Delta_r G^\circ + RT \ln K$$

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

$$K = \left(\frac{p_B}{p_A} \right)_{equilibrium} \quad (K : \textbf{equilibrium constant})$$
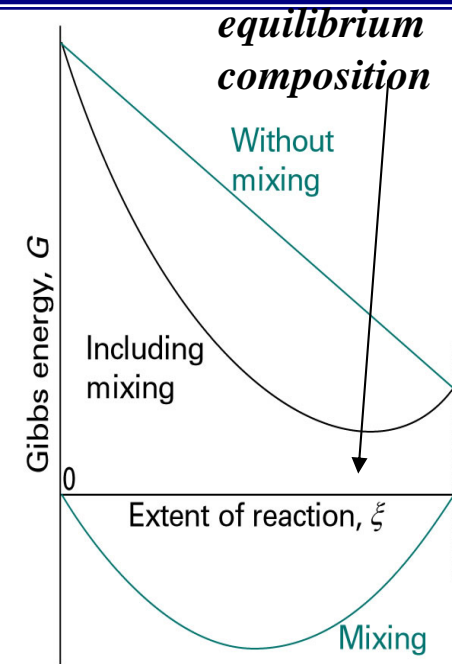
- If no mixing $\rightarrow$ a linear slope (see Fig. 7.3) : A $\rightarrow$ B
- If mixing $\rightarrow$ the change in G due to mixing
: $\Delta_{mix} G = nRT(x_A \ln x_A + x_B \ln x_B)$
$\rightarrow$ U-shaped curve of $G \rightarrow$ minimum in G : *equilibrium composition*

Fig. 7.3 If the mixing of reactants and products is ignored, then the Gibbs energy changes linearly from its initial value (pure reactants) to its final value (pure products) and the slope of the line is $\Delta_r G^\ominus$. However, as products are produced, there is a further contribution to the Gibbs energy arising from their mixing (lowest curve). The sum of the two contributions has a minimum. That minimum corresponds to the equilibrium composition of the system.

7.2 The description of equilibrium

$$K = \left(\frac{p_B}{p_A} \right)_{equilibrium}$$

- $\Delta_r G > 0 \rightarrow K < 1$ $(p_B < p_A)$: reactant A is favoured in the equilibrium
- $\Delta_r G < 0 \rightarrow K > 1$ $(p_B > p_A)$: product B is favoured in the equilibrium

(b) The general case of a reaction

In case of the reaction $2A + B \rightarrow 3C + D$,

$$\rightarrow 0 = 3C + D - 2A - B \rightarrow 0 = \sum_J v_J J \quad \text{(J : substances, } \textbf{\textit{v}}_\textbf{J} \text{ : stoichiometric numbers)}$$

: v_J is (+) for products and (–) for reactants $\rightarrow v_A = -2, v_B = -1, v_C = +3, v_D = +1$

$$\Delta_r G = \Delta_r G^o + RT \ln Q \quad \text{(see Justification 7.1)}$$

$$\Delta_r G^o = \sum_{Products} v\Delta_f G^o - \sum_{Reactants} v\Delta_f G^o \quad \text{or, more formally} \quad \Delta_r G^o = \sum_J v_J \Delta_f G^o(J)$$

reaction quotient $Q = \dfrac{\text{activities of products}}{\text{activities of reactants}} \quad \longrightarrow \quad Q = \prod_J a_J^{v_J}$

ex) $2A + 3B \rightarrow C + 2D \rightarrow v_A = -2, v_B = -3, v_C = +1, v_D = +2 \quad \longrightarrow \quad Q = \dfrac{a_C a_D^{\,2}}{a_A^{\,2} a_B^{\,3}}$

7.2 The description of equilibrium

By $\quad dn_J = v_J d\xi \qquad dG = \sum_J \mu_J dn_J = \left(\sum_J v_J \mu_J\right) d\xi$

$\longrightarrow \quad \Delta_r G = \left(\dfrac{\partial G}{\partial \xi}\right)_{p,T} = \sum_J v_J \mu_J$

Using the chemical potential of a species J, $\quad \mu_J = \mu_J^{\,o} + RT \ln a_J$

$$\Delta_r G = \sum_J v_J \mu_J^{\,o} + RT \sum_J v_J \ln a_J = \overbrace{\Delta_r G^{\circ}}^{\Delta_r G^{o}} + RT \sum_J \ln a_J^{v_J} = \Delta_r G^{\circ} + RT \ln \overbrace{\prod_J a_J^{v_J}}^{Q} = \Delta_r G^{\circ} + RT \ln Q$$

At equilibrium $\Delta_r G = 0$,

$K = \left(\displaystyle\prod_J a_J^{v_J}\right)_{\text{equilibrium}}$ **K : thermodynamic equilibrium constant**
(the same form as Q)

By replacing Q by K at $\Delta_r G = 0$,

$RT \ln K = -\Delta_r G^{\circ} \;\rightarrow$ enable to predict K and the composition of mixture at the equilibrium

7.2 The description of equilibrium

(c) The relation between equilibrium constants

By $a_J = \gamma_J x_J$ or $a_J = \gamma_J b_J / b^o$,

$A + B \leftrightarrow C + D$ $\qquad K = \dfrac{a_C a_D}{a_A a_B} = \dfrac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \times \dfrac{b_C b_D}{b_A b_B} = K_\gamma K_b$

Molecular interpretation 7.2

Consider Boltzmann distribution of molecules over the available states of a system (A and B)
1) the dominant species by the lower set of energy levels→ A is dominant at equilibrium (see Fig. 7.4)
2) more closely spaced energy level → higher entropy → B is dominant at equilibrium (see Fig. 7.5) (entropy effects dominate adverse energy effects)

Using $\quad \Delta_r G^o = \Delta_r H^o - T \Delta_r S^o$,

$\qquad RT \ln K = -\Delta_r G^o \quad \rightarrow \quad K = e^{-\Delta_r H^o / RT} e^{\Delta_r S^o / R}$

- positive reaction enthalpy : $K \downarrow \rightarrow$ reactant is favoured
- positive reaction entropy : $K \uparrow \rightarrow$ product is favoured

Boltzmann distribution

Boltzmann distribution
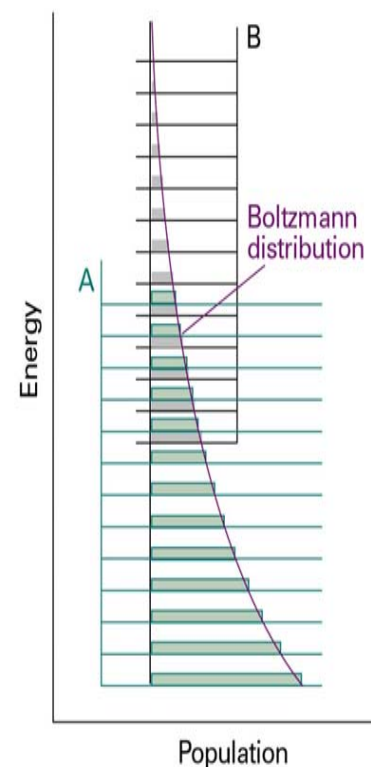
Fig. 7.4 The Boltzmann distribution of populations over the energy levels of two species A and B with similar densities of energy levels; the reaction A → B is endothermic in this example. The bulk of the population is associated with the species A, so that species is dominant at equilibrium.
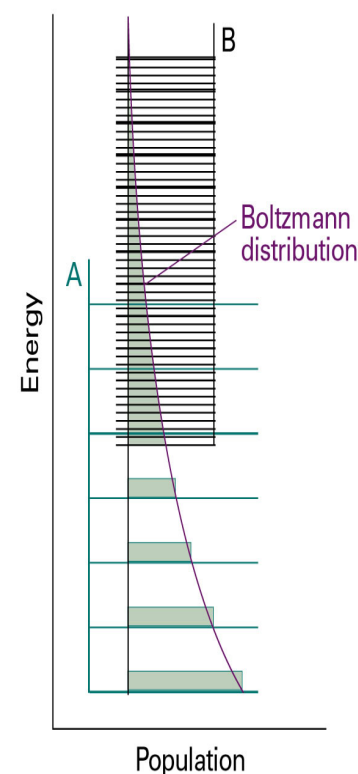
Fig. 7.5 Even though the reaction A → B is endothermic, the density of energy levels in B is so much greater than that in A that the population associated with B is greater than that associated with A, so B is dominant at equilibrium.
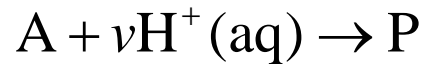
7.2 The description of equilibrium

(d) Equilibria in biological systems

For biological systems (pH = 7),

$$A + vH^+(aq) \rightarrow P$$

By eqn 5.56, $\qquad \mu_{H^+}^{\oplus} = \mu_{H^+}^{\,o} - 7RT \ln 10$

$$\Delta_r G^{\oplus} = \Delta_r G^{\,o} + 7vRT \ln 10$$

: no difference between the two standard values

if hydrogen ions are not involved in the reaction ($v = 0$)

The response of equilibria to the conditions

7.3 How equilibria respond to pressure

Where $\Delta_r G$ is the standard Gibbs function defined for species at a specific pressure and therefore K is independent of pressure.

$$\left(\frac{\partial K}{\partial p}\right)_T = 0$$

: This does not imply that the composition of the species at equilibrium do not change.

Two ways in which pressure may be applied

- injecting an inert gas in a reaction vessel

 → if it's a perfect gas, all the partial p of the reacting gases are unchanged

- compression (confining the gases to a smaller volume)

 → the partial p of the reacting gases are changed

For the perfect gas equilibrium A ↔ 2B,

$$K = \frac{p_B^2}{p_A p^o}$$

: If the equilibrium composition shifts (A↑), p_A↑ (compared to p_B) **(see Fig. 7.6)**

(a)   (b)
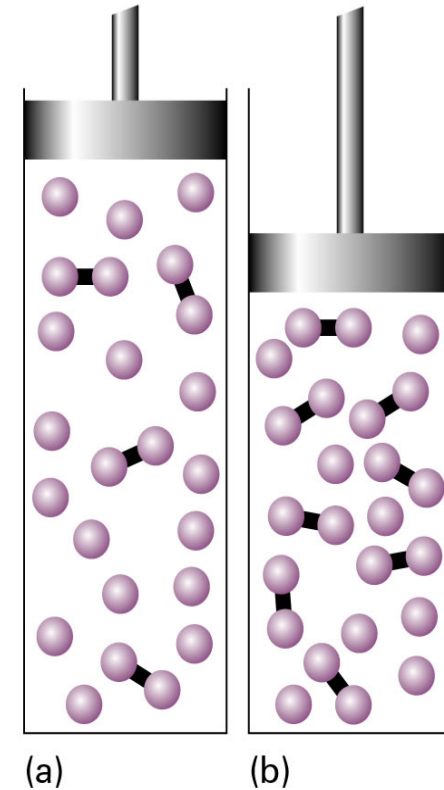
Fig. 7.6 When a reaction at equilibrium is compressed (from *a* to *b*), the reaction responds by reducing the number of molecules in the gas phase (in this case by producing the dimers represented by the linked spheres).

# 7.3 How equilibria respond to pressure

A molecules ↑ → B molecules ↓ by compression

→ **Le Chatelier's principle**

: A system at equilibrium, when subjected to a disturbance, responds
in a way that tends to minimize the effect of the disturbance

- if a system at equilibrium is compressed, then the reaction will adjus
so as to minimize the increase in pressure (A ← 2B)

$$\alpha = \left(\frac{1}{1+4p/K_p^{\circ}} \right)^{1/2} \quad (\alpha : \text{the extent of dissociation})$$

→ the amounts of A and B depend on pressure & $p\uparrow \rightarrow \alpha\downarrow$
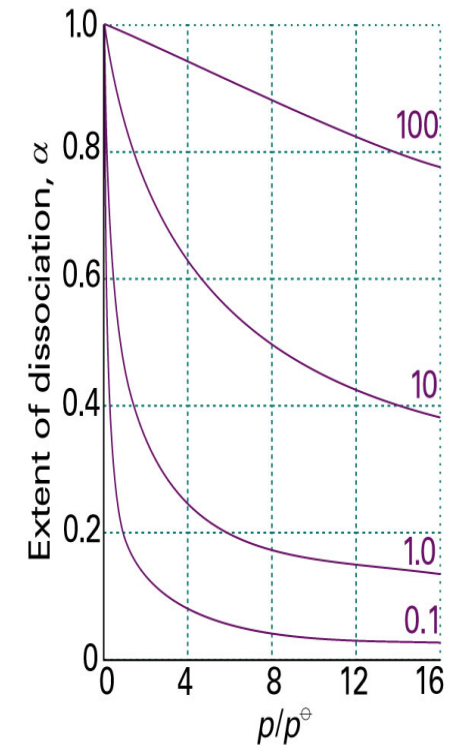
Fig. 7.7 The pressure dependence of the
degree of dissociation, α, at equilibrium for
an $A(g) \rightleftharpoons 2 B(g)$ reaction for different
values of the equilibrium constant K. The
value $\alpha = 0$ corresponds to pure A; $\alpha = 1$
corresponds to pure B.

7.4 The response of equilibria to temperature

Le Chatelier's principle

- if $T \uparrow$: endothermic direction (until energy is absorbed as heat)
  endothermic reactions : As $T \uparrow$, the products are favoured.
- if $T \downarrow$: exothermic direction (until energy is released as heat)
  exothermic reactions : As $T \uparrow$, the reactants are favoured.

(a) The van't Hoff equation

$$(a) \frac{d \ln K}{dT} = \frac{\Delta_r H^o}{RT^2} \qquad (b) \frac{d \ln K}{d(1/T)} = -\frac{\Delta_r H^o}{R}$$

: **The van't Hoff equation**
the slope of a plot of the equilibrium
constant (specially ln$K$) vs temperature

Justification 7.2 *(The van't Hoff equation)*

$$\ln K = -\frac{\Delta_r G^o}{RT}$$ Differentiation of ln$K$ with respect to T : $$\frac{d \ln K}{dT} = -\frac{1}{R} \frac{d(\Delta_r G^o / T)}{dT}$$

Using the Gibbs-Helmholtz equation

$$\frac{d(\Delta_r G^o / T)}{dT} = -\frac{\Delta_r H^o}{T^2}$$

$$\frac{d(1/T)}{dT} = -\frac{1}{T^2} \longrightarrow dT = -T^2 d(1/T) \qquad \therefore \frac{d \ln K}{d(1/T)} = -\frac{\Delta_r H^o}{R}$$

7.4 The response of equilibria to temperature

(a) $\dfrac{d \ln K}{dT} = \dfrac{\Delta_r H^{\circ}}{RT^2}$

- $d\ln K/dT < 0 \rightarrow$ exothermic reaction at $\Delta_r H^{\circ} < 0$
- negative slope, As $T \uparrow$, $K \downarrow$
- reactants are favoured in the exothermic reaction

$\Delta_r G = \Delta_r H - T\Delta_r S \quad \longrightarrow \quad -\Delta_r G/T = -\Delta_r H/T + \Delta_r S$

- Exothermic, $\Delta_r H < 0 \rightarrow \Delta_r G < 0$: products $\uparrow$

  As $T \uparrow$, $-\Delta_r H/T \downarrow$ & $\Delta_r S$ is not important

  : equilibrium lies less to the right (products)

- Endothermic, $\Delta_r S$ is important

  As $T \uparrow$, products are favoured

Molecular interpretation 7.3

1) endothermic reaction - As $T \uparrow$, B molecules
   to higher energy state become populated
   (see Fig. 7.8a)

2) exothermic reaction - As $T \uparrow$, A molecules
   to higher energy state become populated
   (see Fig. 7.8b)

Fig. 7.8 The effect of temperature on a chemical equilibrium can be interpreted in terms of the change in the Boltzmann distribution with temperature and the effect of that change in the population of the species. (a) In an endothermic reaction, the population of B increases at the expense of A as the temperature is raised. (b) In an exothermic reaction, the opposite happens.
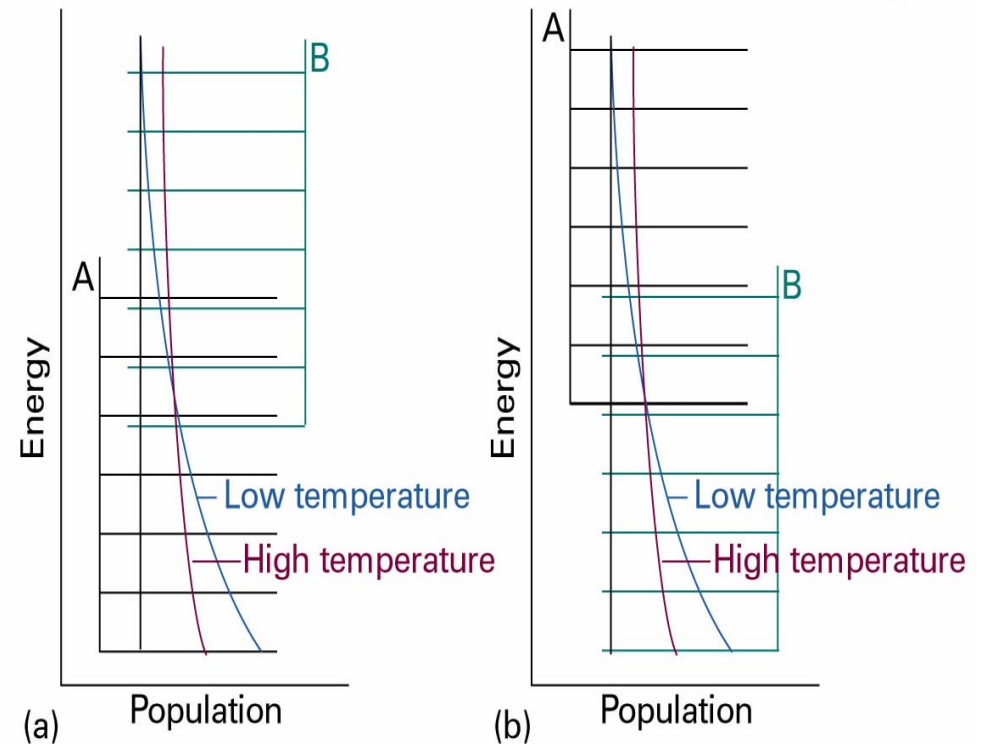
7.4 The response of equilibria to temperature

(b) The value of K at different temperatures

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta_r H^o}{R}$$

the values of K at T_1 and T_2 :

$$\ln K_2 - \ln K_1 = -\frac{1}{R} \int_{1/T_1}^{1/T_2} \Delta_r H^o d(1/T)$$

If $\Delta_r H^o$ varies only slightly,

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

: useful in the design of laboratory and industrial processes
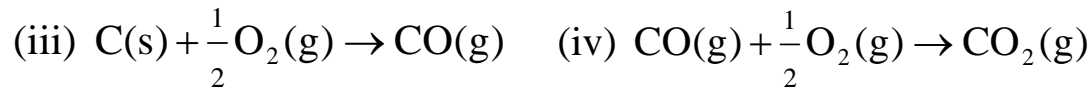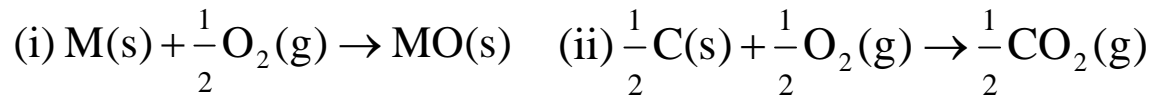 ex) - improving the yield of a reaction by changing T of the reaction mixture
      - reduction of a metal oxide with carbon or carbon monoxide $\rightarrow$ extraction of metal

7.4 The response of equilibria to temperature

I7.1 The extraction of metals from their oxides

Ellingham diagram : a plot of $\Delta_r G^o$ vs temperature $\rightarrow \Delta_r G^o$ decreases upwards *!!*

(i) $M(s) + \frac{1}{2} O_2(g) \rightarrow MO(s)$ (ii) $\frac{1}{2} C(s) + \frac{1}{2} O_2(g) \rightarrow \frac{1}{2} CO_2(g)$

(iii) $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ (iv) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$

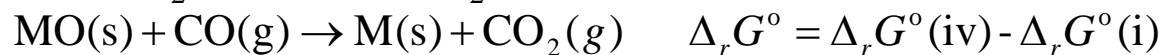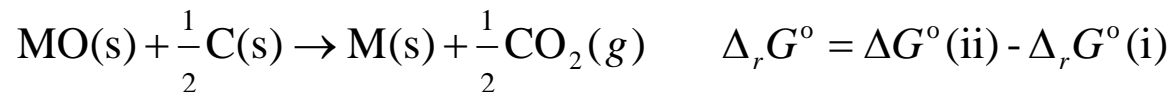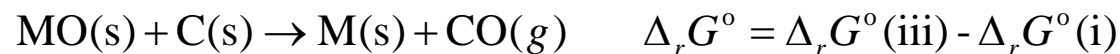- reaction (iii) : gas(net) $\uparrow \rightarrow \Delta S \uparrow \rightarrow \Delta_r G^o \downarrow$ as $T \uparrow$
- reaction (iv) : gas(net) $\downarrow \rightarrow \Delta S \downarrow \rightarrow \Delta_r G^o \uparrow$ as $T \uparrow$
- reaction (ii) : gas is constant $\rightarrow \Delta_r G^o$ changes slightly as $T \uparrow$

At room temperature $\rightarrow \Delta_r H^o$ dominates $\Delta_r G^o$
- the entropy of reaction is approximately the same for all metals
$\rightarrow \Delta_r G^o$ as T should be similar slopes of the lines in the diagram

$MO(s) + C(s) \rightarrow M(s) + CO(g)$ $\Delta_r G^\circ = \Delta_r G^\circ(iii) - \Delta_r G^\circ(i)$

$MO(s) + \frac{1}{2} C(s) \rightarrow M(s) + \frac{1}{2} CO_2(g)$ $\Delta_r G^\circ = \Delta G^\circ(ii) - \Delta_r G^\circ(i)$

$MO(s) + CO(g) \rightarrow M(s) + CO_2(g)$ $\Delta_r G^\circ = \Delta_r G^\circ(iv) - \Delta_r G^\circ(i)$

$\rightarrow \Delta_r G^o < 0$ **:** the equilibrium lies to the right, which is the case
when the line for $\Delta_r G^o(i)$ lies below the line for one of the carbon
reactions (ii)~(iv)
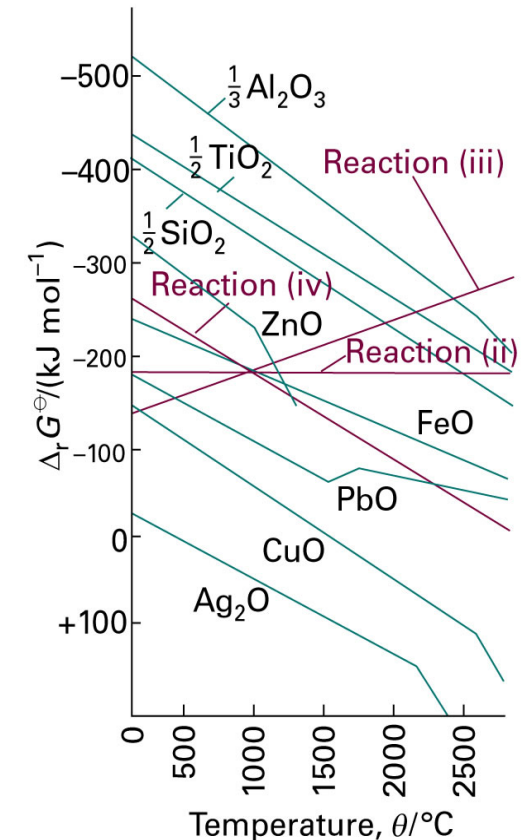
Fig. 7.10 An Ellingham diagram for the discussion of the reduction of metal ores.