Part 1: Equilibrium

9. Chemical equilibrium

Bilingual Program

9. Chemical equilibrium

Spontaneous chemical reactions

9.1 The Gibbs energy minimum ▶

The response of equilibria to the conditions

9.2 How equilibria respond to pressure

9.3 The response of equilibria to temperature

Applications to selected systems

9.4 The extraction of metals from their oxides

9.5 Acids and bases

9.6 Biological activity:the thermodynamics of ATP

9.1 The Gibbs energy minimum

1) The reaction Gibbs energy

For the simplest possible chemical equilibrium

$$\mathrm{A} \Leftrightarrow \mathrm{B}$$

Suppose an infinitesimal amount d ξ of A turns into B:
The change in the amount of A present is $\mathrm{d}n_\mathrm{A} = -\mathrm{d}\xi$
The change in the amount of B present is $\mathrm{d}n_\mathrm{B} = +\mathrm{d}\xi$.

The quantity ξ is called the extent of reaction;
The dimensions is amount of substance, (moles).

9.1 The Gibbs energy minimum

1) The reaction Gibbs energy

The reaction Gibbs energy, $\Delta_r G$, is defined as the slope of the graph of the Gibbs energy plotted against the extent of reaction, ξ

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$$

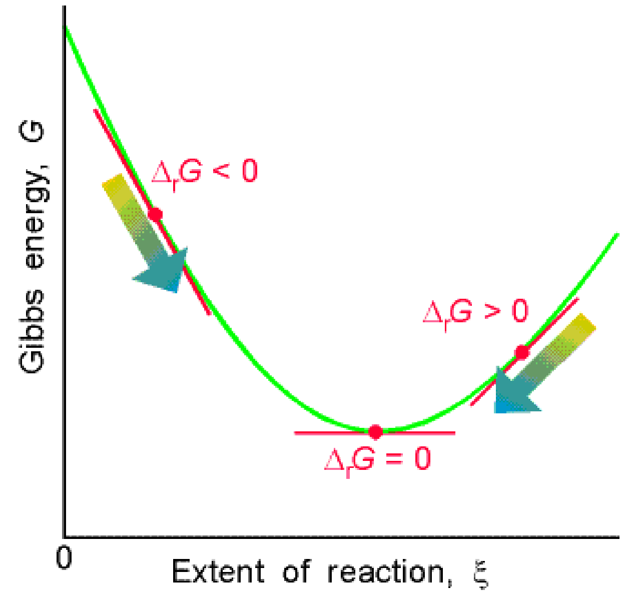
At constant T、p, the change in Gibbs energy is

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

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A$$

9.1 The Gibbs energy minimum

1) The reaction Gibbs energy



As the reaction advances the slope of the Gibbs energy changes. Equilibrium corresponds to zero slope, at the foot of the valley.

$$\Delta_r G = \mu_B - \mu_A$$

☐ when $\mu_A > \mu_B$, , $\Delta_r G<0$

the reaction A →B is spontaneous;

☐ when $\mu_A < \mu_B$, , $\Delta_r G>0$

the reaction B →A is spontaneous;

☐ when $\Delta_r G=0$: The slop is zero and the reaction is spontaneous in neither direction. The composition of the reaction mixture at equilibrium

9.1 The Gibbs energy minimum

2) Exergonic and endergonic reactions

The spontaneity of a reaction at constant temperature and pressure is expressed by the reaction Gibbs energy:

If $\Delta_r G < 0$, the forward reaction is spontaneous; it is called exergonic (work-producing)

If $\Delta_r G > 0$, the reverse reaction is spontaneous; it is called endergonic (work-consuming)

If $\Delta_r G = 0$, the reaction is at equilibrium; it is spontaneous in neither direction, and neither exergonic nor endergonic

9.1 The Gibbs energy minimum

3) Perfect gas equilibria

When A and B are perfect gases:

$$\Delta_r G = \mu_B - \mu_A$$

$$= (\mu_B^\ominus + RT \ln p_B) - (\mu_A^\ominus + RT \ln p_A)$$

$$= \Delta_r G^\ominus + RT \ln \frac{p_B}{p_A}$$

If denote the ratio of partial pressures by Q

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

9.1 The Gibbs energy minimum

3) Perfect gas equilibria

At equilibrium $\Delta_r G = 0$. When the ratio of partial pressures at equilibrium is denoted K

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

$$\Downarrow$$

$$\Delta_r G^\ominus = -RT \ln K \qquad K = \left[\frac{p_B}{p_A}\right]_{\text{equilibrium}}$$

9.1 The Gibbs energy minimum

3) Perfect gas equilibria

When $\Delta_r G^{\ominus} > 0$, $K < 1$: at equilibrium the partial pressure of A exceeds that of B, the reactant A is favoured in the equilibrium.

When $\Delta_r G^{\ominus} < 0$, $K > 1$: at equilibrium the partial pressure of B exceeds that of A, the product B is favoured in the equilibrium.

9.1 The Gibbs energy minimum

4) The general case of a reaction

For the reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \rightarrow c\,\mathrm{C} + d\,\mathrm{D}$$

When the reaction advances by d*ξ*, the amounts of reactants and products change as follows:

$$\mathrm{d}n_\mathrm{A} = -a\mathrm{d}\xi \qquad \mathrm{d}n_\mathrm{B} = -b\mathrm{d}\xi \qquad \mathrm{d}n_\mathrm{C} = +c\mathrm{d}\xi \qquad \mathrm{d}n_\mathrm{D} = +d\mathrm{d}\xi$$

In general $\mathrm{d}n_\mathrm{J} = v_\mathrm{J}\mathrm{d}\xi$, the change in the Gibbs energy at constant temperature and pressure is

$$\mathrm{d}G = (c\mu_\mathrm{C} + d\mu_\mathrm{D} - a\mu_\mathrm{A} - b\mu_\mathrm{B})\mathrm{d}\xi$$

$$= \left(\sum_\mathrm{J} v_\mathrm{J}\mu_\mathrm{J}\right)\mathrm{d}\xi$$

9.1 The Gibbs energy minimum

4) The general case of a reaction

It follows that

$$\Delta_r G = c\mu_C + d\mu_D - a\mu_A - b\mu_B$$

Since $\mu_J = \mu_J^\ominus + RT\ln a_J$

$$\Delta_r G = c\mu_C^\ominus + d\mu_D^\ominus - a\mu_A^\ominus - b\mu_B^\ominus + cRT\ln a_C + dRT\ln a_D - aRT\ln a_A - bRT\ln a_B$$

$$\Delta_r G = \Delta_r G^\ominus + RT\ln\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right) \Rightarrow Q = \left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)$$

9.1 The Gibbs energy minimum

4) The general case of a reaction

The general expression for *Q*

$$Q = \prod_{\mathrm{J}} a_{\mathrm{J}}^{\nu_{\mathrm{J}}}$$

At equilibrium, the slope of G is zero: $\Delta_r G = 0$

$$K = \left(\frac{a_{\mathrm{C}}^{c} a_{\mathrm{D}}^{d}}{a_{\mathrm{A}}^{a} a_{\mathrm{B}}^{b}} \right)_{\text{equilibrium}} \quad \Rightarrow \quad K = \left(\prod_{\mathrm{J}} a_{\mathrm{J}}^{\nu_{\mathrm{J}}} \right)_{\text{equilibrium}}$$

9.1 The Gibbs energy minimum

4) The general case of a reaction

An equilibrium constant K expressed in terms of activities is called a **thermodynamic equilibrium constant**. The thermodynamic equilibrium constant is also dimensionless because activities are dimensionless numbers.

At equilibrium, $\Delta_r G = 0$ $$RT\ln K = -\Delta_r G^{\ominus}$$

This important thermodynamic relation enables us to predict the equilibrium constant of any reaction from tables of thermodynamic data, and hence to predict the equilibrium composition of reaction mixtures.

Example

Estimating the degree of dissociation at equilibrium

The standard Gibbs energy of reaction for the decomposition

$$H_2O(g) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$$

is +118.08 $\mathrm{kJmol^{-1}}$ at 2300 K. What is the degree of dissociation of H_2O at 2300 K and 1.00 bar?

Example

Method: The equilibrium constant is obtained from the standard Gibbs energy of reaction, so we need to relate the degree of dissociation, α, to K and then to find its numerical value. Proceed by expressing the equilibrium compositions in terms of α, and solve for α in terms of K. Because the standard Gibbs energy of reaction is large and positive, we can anticipate that K will be small, and hence that $\alpha \ll 1$, which opens the way to making approximations to obtain its numerical value.

Example

Answer: The equilibrium constant is obtained from the equation that

$$\ln K = -\frac{\Delta_r G^\ominus}{RT}$$

$$= -\frac{118.08\,\mathrm{kJmol^{-1}}}{(8.3145\,\mathrm{JK^{-1}mol^{-1}})\times(2300\,\mathrm{K})} = -6.175$$

$$K = 2.08\times10^{-3}$$

Example

The equilibrium composition can be expressed in terms of α :

	H_2O	H_2	O_2
Initial amount	n	0	0
Changes to reach equil.	$-\alpha n$	$+\alpha n$	$+\frac{1}{2}\alpha n$
Amount at equili.	$(1-\alpha)n$	αn	$\frac{1}{2}an$
Mole fraction	$\frac{1-\alpha}{1+\frac{1}{2}\alpha}$	$\frac{\alpha}{1+\frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha}{1+\frac{1}{2}\alpha}$
Partial pressure	$\frac{(1-\alpha)p}{1+\frac{1}{2}\alpha}$	$\frac{\alpha p}{1+\frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha p}{1+\frac{1}{2}\alpha}$

Example

The equilibrium constant is

$$K = \frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}}$$

$$= \frac{\dfrac{\alpha p}{(1+\frac{1}{2}\alpha)} \left(\dfrac{\frac{1}{2}\alpha p}{(1+\frac{1}{2}\alpha)} \right)^{1/2}}{\dfrac{(1-\alpha)p}{(1+\frac{1}{2}\alpha)}}$$

$$= \frac{\alpha^{2/3} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$$

Example

$$K = \frac{\alpha^{2/3} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$$

In this expression, p in place of $p/p^{\ominus}$ to keep the notation simple. Now make the approximation that a << 1:

$$K \approx \frac{\alpha^{2/3} p^{1/2}}{\sqrt{2}}$$

Under the stated conditions, p=1.00 (that is, $p/p^{\ominus} = 1.00$), so

$$\alpha \approx (\sqrt{2}K)^{2/3} = 0.0205$$

That is, about 2 per cent of the water has decomposed.

9.1 The Gibbs energy minimum

5) The relation between equilibrium constants

Express the thermodynamic equilibrium constant in terms of the mole fractions, x_J, or molalities, b_J, of the species.

$$a_J = \gamma_J x_J \quad \text{or} \quad a_J = \gamma_J \frac{b_J}{b^{\ominus}}$$

For example, in the latter case, for an equilibrium of the form A + B →C + D, where all four species are solutes:

9.1 The Gibbs energy minimum

5) The relation between equilibrium constants

$$K=\frac{a_{\mathrm{C}}^{c}a_{\mathrm{D}}^{d}}{a_{\mathrm{A}}^{a}a_{\mathrm{B}}^{b}}=\frac{\gamma_{\mathrm{C}}^{\mathrm{c}}\gamma_{\mathrm{D}}^{\mathrm{d}}}{\gamma_{\mathrm{A}}^{\mathrm{a}}\gamma_{\mathrm{B}}^{\mathrm{b}}}\times\frac{b_{\mathrm{C}}^{\mathrm{c}}b_{\mathrm{D}}^{\mathrm{d}}}{b_{\mathrm{A}}^{\mathrm{a}}b_{\mathrm{B}}^{\mathrm{b}}}=K_{\gamma}K_{b}$$

$$\underline{K=K_{\gamma}K_{b}}$$

The activity coefficients must be evaluated at the equilibrium composition of the mixture. In elementary applications, the assumption is often made that the activity coefficients are all so close to 1 or they cancel so that $K_{\gamma}=1$. Then we obtain the result that $\underline{K\approx K_{\mathrm{b}}}$, and equilibria are discussed in terms of molalities.

9. Chemical equilibrium

Spontaneous chemical reactions

9.1 The Gibbs energy minimum

The response of equilibria to the conditions

9.2 How equilibria respond to pressure ▶

9.3 The response of equilibria to temperature

Applications to selected systems

9.4 The extraction of metals from their oxides

9.5 Acids and bases

9.6 Biological activity:the thermodynamics of ATP

版权所有：华东理工大学物理化学教研室

9.2 How equilibria respond to pressure

The equilibrium constant depends on the value of $\Delta_r G^\ominus$, which is defined at a single, standard pressure. The value of $\Delta_r G^\ominus$, and hence of K, is independent of the pressure at which the equilibrium is actually established.

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

The conclusion that K is independent of pressure does not necessarily mean that the equilibrium composition is independent of the pressure.

9.2 How equilibria respond to pressure

1) **To increase the pressure within a reaction vessel by injecting an inert gas into it.**

Provided the gases are perfect, this addition of gas leaves all the partial pressures of the reacting gases unchanged; and the addition of an inert gas leaves the molar concentrations of the original gases unchanged.

pressurization by the addition of an inert gas has no effect on the equilibrium composition of the system

9.2 How equilibria respond to pressure

2). Increase the pressure of the system by confining the gases to a smaller volume.

Now the partial pressures are changed; and their molar concentrations are modified because the volume the gases occupy is reduced. The compression can adjust the individual partial pressures of the reactants and products in such a way that, although each one changes, their ratio remains the same.

pressurization by confining the gases to a smaller volume has effect on the equilibrium composition of the system although it has no effect on the equilibrium constant .

9.2 How equilibria respond to pressure

When the two perfect gases are at equilibrium $\mathrm{A} \Leftrightarrow 2\mathrm{B}$, for which K is

$$K = p_{\mathrm{B}}^{2} \big/ p_{\mathrm{A}} p^{\ominus}$$

K remains constant only if an increase in p_{A} cancels an increase in the square of p_{B}. the number of A molecules will increase as the volume of the container is decreased and its partial pressure will rise more rapidly than can be ascribed to a simple change in volume alone.

9.2 How equilibria respond to pressure

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.

The principle implies that, if a system at equilibrium is compressed, then the reaction will adjust so as to minimize the increase in pressure. It can do by reducing the number of particles in the gas phase, which implies a shift A ← 2B.

9. Chemical equilibrium

Spontaneous chemical reactions

9.1 The Gibbs energy minimum

The response of equilibria to the conditions

9.2 How equilibria respond to pressure

9.3 The response of equilibria to temperature ▶

Applications to selected systems

9.4 The extraction of metals from their oxides

9.5 Acids and bases

9.6 Biological activity:the thermodynamics of ATP

版权所有：华东理工大学物理化学教研室
上一页 下一页 节首

9.3 How equilibria respond to temperature

Le Chatelier's principle predicts that a system at equilibrium will tend to shift in the endothermic direction if *T* is raised. Conversely, an equilibrium can be expected to shift in the exothermic direction if *T* is lowered.

That is

- Exothermic reactions: increased *T* favours the reactants.
- Endothermic reactions: increased *T* favours the products.

9.3 How equilibria respond to temperature

1) The van't Hoff equation

Since $\ln K = -\dfrac{\Delta_r G^\ominus}{RT}$ ⬇

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = -\frac{1}{R}\frac{\mathrm{d}(\Delta_r G^\ominus / T)}{\mathrm{d}T}$$

The differentials are complete because K and $\Delta_r G^\ominus$ depend only on T, not on p. From the Gibbs-Helmholtz equation:

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

where $\Delta_r H^\ominus$ is the standard reaction enthalpy at temperature T

9.3 How equilibria respond to temperature

1) The van't Hoff equation

the van't Hoff equation

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T}=\frac{\Delta_\mathrm{r}H^\ominus}{RT^2} \quad \text{and} \quad \frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)}=-\frac{\Delta_\mathrm{r}H^\ominus}{R}$$

The van't Hoff equation is an expression for the slope of a plot of the equilibrium constant (ln*K*) as a function of temperature; and d ln*K*<0 (d*K*/d*T* <0) for a reaction that is exothermic under standard conditions. A negative slope means that ln*K*, and *K* itself, decreases as *T* rises. in the case of an exothermic reaction the equilibrium shifts away from products.

9.3 How equilibria respond to temperature

2) The value of *K* at different temperatures

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

integrate this equation:

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

When $\Delta_r H^\ominus$ varies only slightly with temperature over the temperature range of interest

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

Example

Estimate the equilibrium constant for the synthesis of ammonia at 500 K from its value at 298 K (6.0×10^5 for the reaction) as written in the following:

$$N_2\,(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Example

Answer:

$$\mathrm{N_2\,(g) + 3H_2(g) \rightarrow 2NH_3(g)}$$

because $\Delta_r H^{\ominus} = 2\Delta_f H^{\ominus}(\mathrm{NH_3, g})$ **and assume that its value is constant over the range of *T*:**

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

$$= \ln(6.0\times 10^{5}) - \frac{-92.2\mathrm{kJmol^{-1}}}{8.314\mathrm{JK^{-1}mol^{-1}}}\left(\frac{1}{500\mathrm{K}} - \frac{1}{298\mathrm{K}}\right)$$

$$= -1.73$$

It follows that $K_2 = 0.18$

9. Chemical equilibrium

Spontaneous chemical reactions

9.1 The Gibbs energy minimum

The response of equilibria to the conditions

9.2 How equilibria respond to pressure

9.3 The response of equilibria to temperature

Applications to selected systems

9.4 The extraction of metals from their oxides ▶

9.5 Acids and bases

9.6 Biological activity:the thermodynamics of ATP

版权所有：华东理工大学物理化学教研室

9.4 The extraction of metals from their oxide

Metals can be obtained from their oxides by reduction with carbon or carbon monoxide if any of the equilibria lie to the right ($K > 1$).

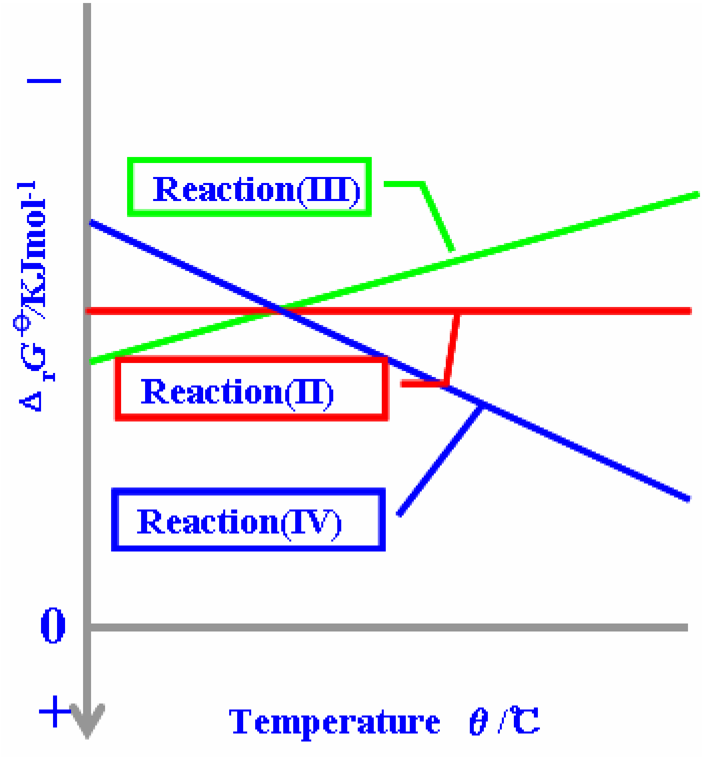
$$\mathrm{MO(s)} + \mathrm{C(s)} \Leftrightarrow \mathrm{M(s)} + \mathrm{CO(g)}$$

$$\mathrm{MO(s)} + \tfrac{1}{2}\mathrm{C(s)} \Leftrightarrow \mathrm{M(s)} + \tfrac{1}{2}\mathrm{CO_2(g)}$$

$$\mathrm{MO(s)} + \mathrm{CO(g)} \Leftrightarrow \mathrm{M(s)} + \mathrm{CO_2(g)}$$

These equilibria can be discussed in terms of the thermodynamic functions for the reactions

9.4 The extraction of metals from their oxide



An Ellingham diagram for the discussion of metal ore reduction. Note that $\Delta_r G$ is most negative at the top of the diagram.

(I) $M(s) + \frac{1}{2}O(g) \rightarrow MO(s)$

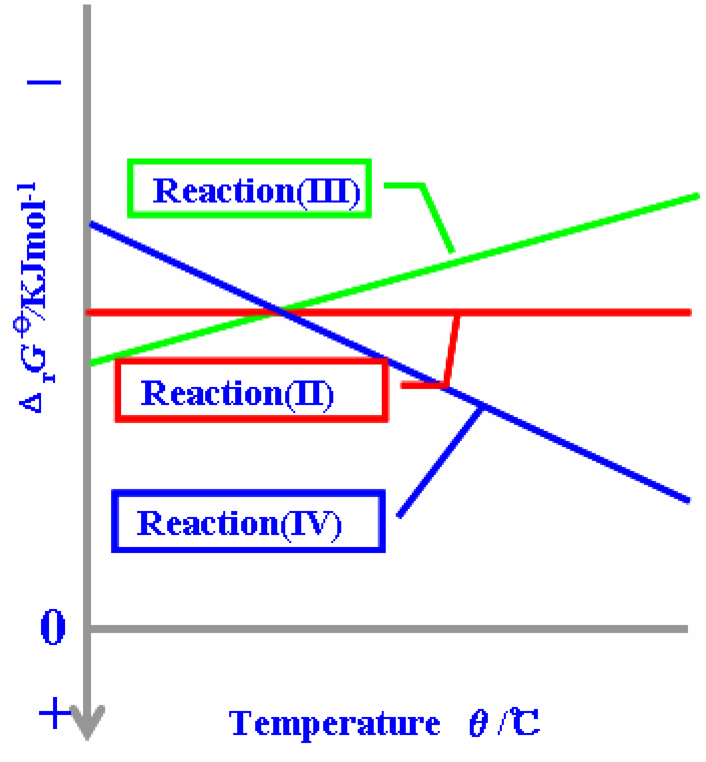
(II) $\frac{1}{2}C(s) + \frac{1}{2}O(g) \rightarrow \frac{1}{2}CO_2(g)$

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

(IV) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

In reaction (II), the amount of gas is constant, so the entropy change is small and $\Delta_r G^\ominus$ changes only slightly with T;

9.4 The extraction of metals from their oxide



An Ellingham diagram for the discussion of metal ore reduction. Note that $\Delta_r G$ is most negative at the top of the diagram.

(I) $M(s) + \frac{1}{2}O(g) \rightarrow MO(s)$

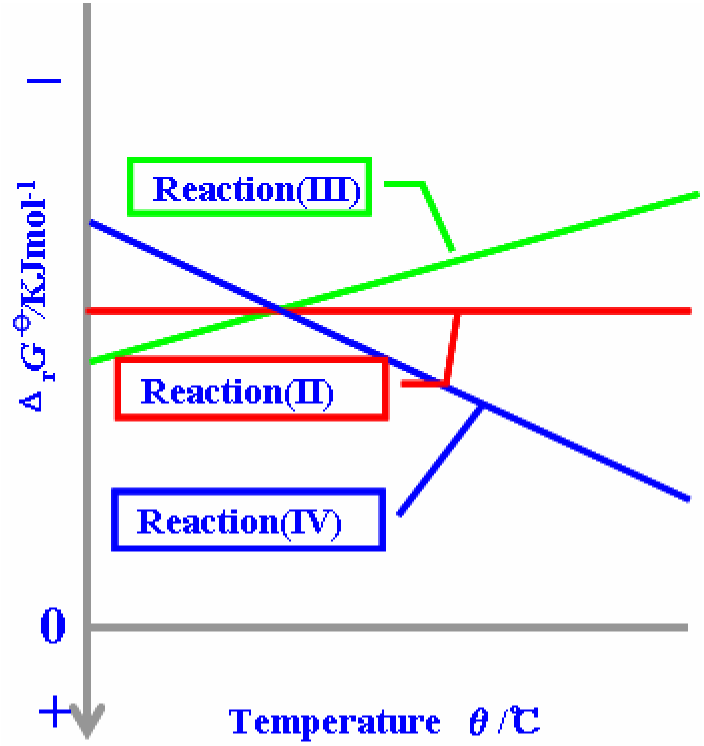
(II) $\frac{1}{2}C(s) + \frac{1}{2}O(g) \rightarrow \frac{1}{2}CO_2(g)$

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

(IV) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

In reaction (III) there is an increase in the amount of gas,the standard reaction entropy is large and positive; therefore, its $\Delta_r G^{\ominus}$ decreases sharply with increasing T;

9.4 The extraction of metals from their oxide



An Ellingham diagram for the discussion of metal ore reduction. Note that $\Delta_r G$ is most negative at the top of the diagram.

(I) $M(s) + \frac{1}{2}O(g) \rightarrow MO(s)$

(II) $\frac{1}{2}C(s) + \frac{1}{2}O(g) \rightarrow \frac{1}{2}CO_2(g)$

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

(IV) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

In reaction (IV), there is a similar net decrease in the amount of gas, so $\Delta_r G^\ominus$ increases sharply with increasing *T*.

9.4 The extraction of metals from their oxide

The standard Gibbs energies for the reductions can be expressed in terms of the standard Gibbs energies for the reactions :

(I) $M(s)+\frac{1}{2}O(g)\rightarrow MO(s)$

(II) $\frac{1}{2}C(s)+\frac{1}{2}O(g)\rightarrow \frac{1}{2}CO_2(s)$

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

(IV) $CO(g)+\frac{1}{2}O_2(g)\rightarrow CO_2(g)$

$$MO(s) + C(s) \rightarrow M(s) + CO(g)$$

$$\Delta_r G^\ominus = \Delta_r G^\ominus(III) - \Delta_r G^\ominus(I)$$

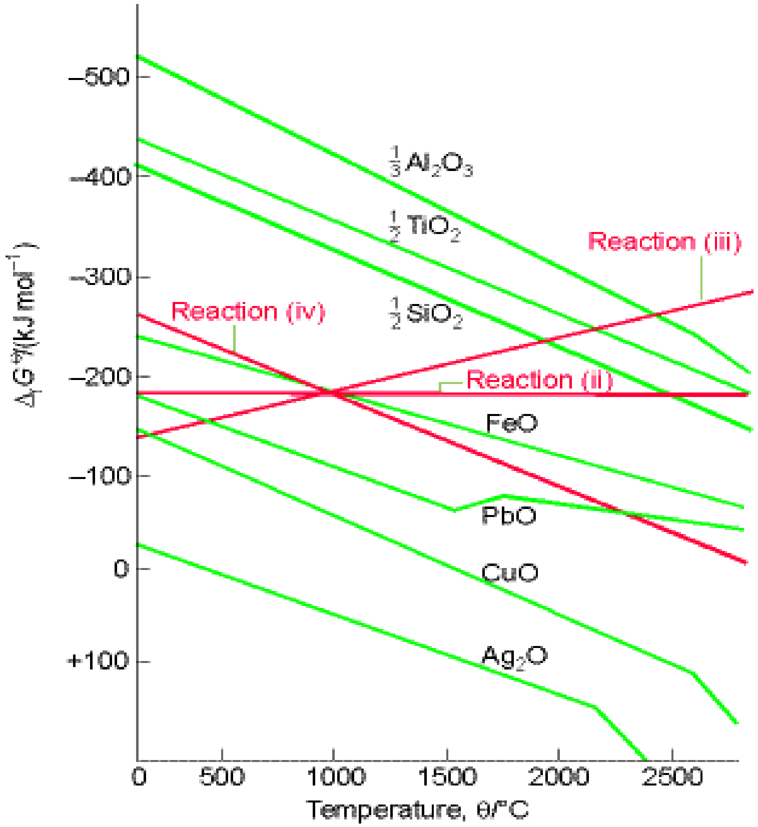
$$MO(s) + \frac{1}{2}C(s) \rightarrow M(s) + \frac{1}{2}CO_2(g)$$

$$\Delta_r G^\ominus = \Delta_r G^\ominus(II) - \Delta_r G^\ominus(I)$$

$$MO(s) + CO(g) \rightarrow M(s) + CO_2(g)$$

$$\Delta_r G^\ominus = \Delta_r G^\ominus(IV) - \Delta_r G^\ominus(I)$$

9.4 The extraction of metals from their oxide



An Ellingham diagram for the discussion of metal ore reduction. Note that $\Delta_r G$ is most negative at the top of the diagram.

The spontaneity at any temperature can be predict from the diagram.

The equilibrium of reduction lies to the right if $\Delta_r G^\ominus < 0$.

9. Chemical equilibrium

Spontaneous chemical reactions

9.1 The Gibbs energy minimum

The response of equilibria to the conditions

9.2 How equilibria respond to pressure

9.3 The response of equilibria to temperature

Applications to selected systems

9.4 The extraction of metals from their oxides

9.5 Acids and bases

9.6 Biological activity:the thermodynamics of ATP ▶

版权所有：华东理工大学物理化学教研室

9.6 Biological activity:the thermodynamics of ATP

1) Biological standard states

The conventional standard state of hydrogen ions (pH = 0) is not appropriate to normal biological conditions. In biochemistry it is common to adopt the biological standard state, in which pH = 7 (neutral solution).

Based on the biological standard state, the corresponding standard thermodynamic functions are labeled as $G^{\oplus}$, $H^{\oplus}$, and $S^{\oplus}$(some texts use $X^{\ominus\prime}$); and they are related to the standard thermodynamic functions.

9.6 Biological activity:the thermodynamics of ATP

1) Biological standard states

For a reaction of the form $A + \nu H^+ (aq) \rightarrow P$:

$$\Delta_r G = \mu_P - \mu_A - \nu\mu_{H^+}$$

If all the species other than H⁺ are in their standard states:

$$\Delta_r G = \mu_P^{\ominus} - \mu_A^{\ominus} - \nu\mu_{H^+}$$

since $\mu_{H^+} = \mu_{H^+}^{\ominus} + RT \ln a_{H^+}$ **and** $\ln a_{H^+} = \ln 10 \log a_{H^+}$

then $\mu_{H^+} = \mu_{H^+}^{\ominus} - (RT\ln 10) \times \text{pH}$

so $\Delta_r G = \mu_P^{\ominus} - \mu_A^{\ominus} - \nu\mu_{H^+}^{\ominus} + (\nu RT \ln 10) \times \text{pH}$

$$= \Delta_r G^{\ominus} + (\nu RT \ln 10) \times \text{pH}$$

9.6 Biological activity:the thermodynamics of ATP

1) Biological standard states

$$\Delta_r G = \Delta_r G^{\ominus} + (\nu RT \ \ln 10) \times \mathrm{pH}$$

When we set pH = 7, it follows that

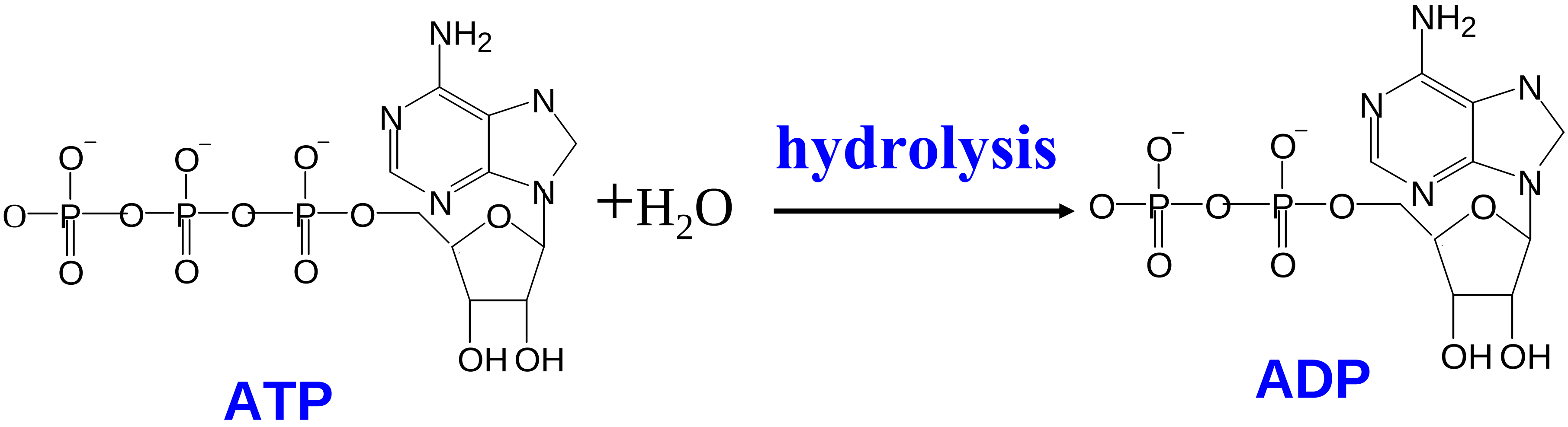
$$\Delta_r G^{\oplus} = \Delta_r G^{\ominus} + 7\nu RT \ \ln 10$$

This equation shows the relation between the thermodynamic and biological standard Gibbs energies of reaction.

9.6 Biological activity:the thermodynamics of ATP

1) Biological standard states

An important biochemical is adenosine triphosphate (ATP). The essence of ATP's action is its ability to lose its terminal phosphate group by hydrolysis and to form adenosine diphosphate (ADP):



9.6 Biological activity:the thermodynamics of ATP

1) Biological standard states

The standard values for ATP hydrolysis at 37 ℃ (310 K, blood temperature) are:

$$\Delta_r G^{\ominus} = -30\text{kJmol}^{-1} \qquad \Delta_r H^{\ominus} = -20\text{kJmol}^{-1} \qquad \Delta_r S^{\ominus} = +34\text{JK}^{-1}\text{mol}^{-1}$$

The hydrolysis is therefore exergonic ($\Delta_r G^{\ominus} < 0$) under these conditions. The action of ATP depends on it being intermediate in activity. Thus it acts as a phosphate donor to a number of acceptors (e.g. glucose), but is recharged by more powerful phosphate donors in the respiration cycle.

9.6 Biological activity:the thermodynamics of ATP

2) Anaerobic and aerobic metabolism

Anaerobic metabolism is a form in which inhaled oxygen plays no role. The energy source of anaerobic cells is glycolysis, the partial oxidation of glucose to lactic acid at blood temperature, $\Delta_r G^{\ominus} = -218\ \mathrm{kJmol^{-1}}$.

$$\mathrm{Glucose} + 2\mathrm{P_i^-} + 2\mathrm{ADP} \longrightarrow 2\mathrm{Lactate^-} + 2\mathrm{ATP} + 2\mathrm{H_2O}$$

$$\Delta_r G^{\ominus} = (-218) - 2 \times (-30) = -158\ \mathrm{kJmol^{-1}}$$

The reaction is exergonic, and therefore spontaneous. the metabolism of the food has been used to 'recharge' ATP

2) Anaerobic and aerobic metabolism

Aerobic metabolism is a series of reactions in which inhaled oxygen plays a role. Metabolism by aerobic respiration is much more efficient. The standard Gibbs energy of combustion of glucose is −2880 kJmol^{-1}.

Part 1: Equilibrium

1. The properties of gases
2. The First Law: the concepts
3. The First Law: the machinery
4. The Second Law: the concepts
5. The Second Law: the machinery
6. Physical transformations of pure substances
7. Simple mixtures
8. Phase diagrams
9. Chemical equilibrium
10. Electrochemistry