Chapter 6. Chemical Reaction (toward Equilibrium)

$aA + bB \rightleftharpoons cC + dD$

Reactants *Products*

Reactants & Products: **Same Atomic Composition**

G(aA+bB) > G(cC+dD): the reaction will have a tendency to roll from left to right.

G(aA+bB) < G(cC+dD): a natural tendency to roll from right to left.

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

At low temperatures, $T\Delta S$ becomes very small.

$\therefore \Delta G \cong \Delta H$ If the reaction is **exothermic**, the reaction proceeds from left to right.

At high temperatures, ΔH becomes very small ($< T\Delta S$).

$\therefore \Delta G \cong -T\Delta S$ The reaction tends to occur in the direction that maximizes the **entropy** of the reaction mixture.

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

$$4Li + O_2 \rightleftharpoons 2Li_2O$$

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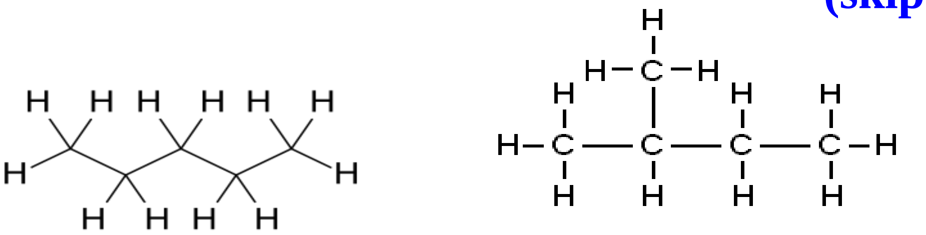
Which Way Is Down-Hill?

$\alpha \rightleftharpoons \beta$ $(A \rightleftharpoons B)$

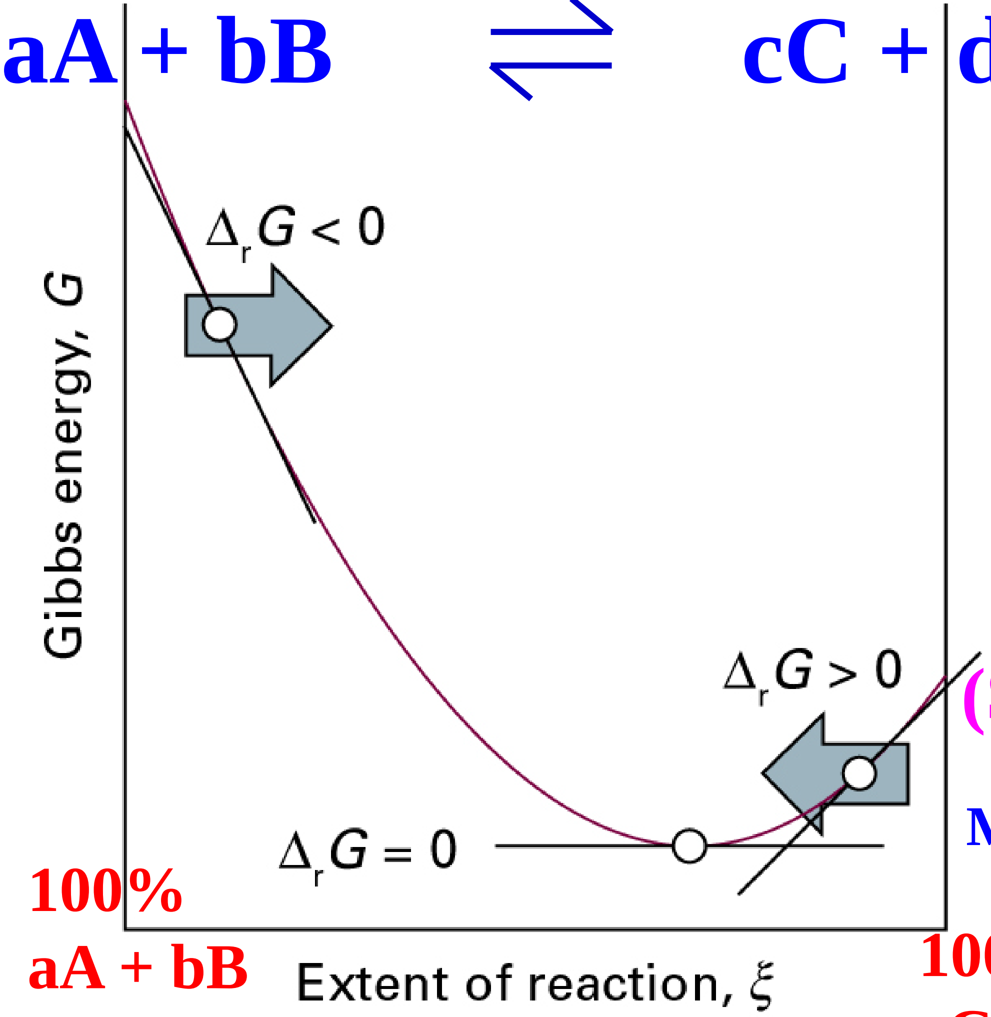


Pentane to 2-methylbutane (C_5H_{12})

Suppose an infinitesimal amount $d\xi$ of α turns into β:

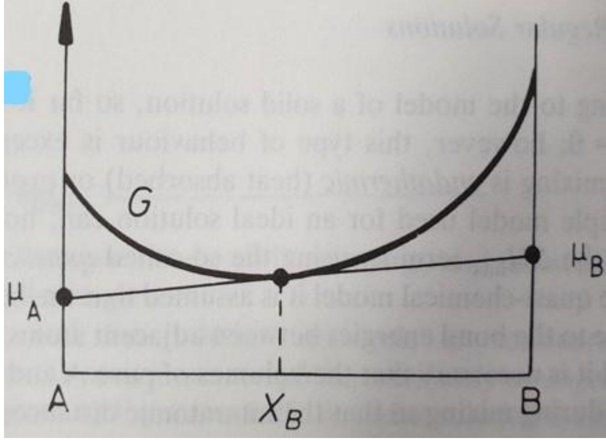
change in the amount of A present = $-\,d\xi$
change in the amount of B present = $+\,d\xi$

$aA + bB \rightleftharpoons cC + dD$



100%
$aA + bB$

100%
$cC + dD$



Binary Alloy

(Same Atomic Composition)

Minimum Total Gibbs Free Energy *G*

Figure 6A.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.

$aA + bB \rightleftharpoons cC + dD$

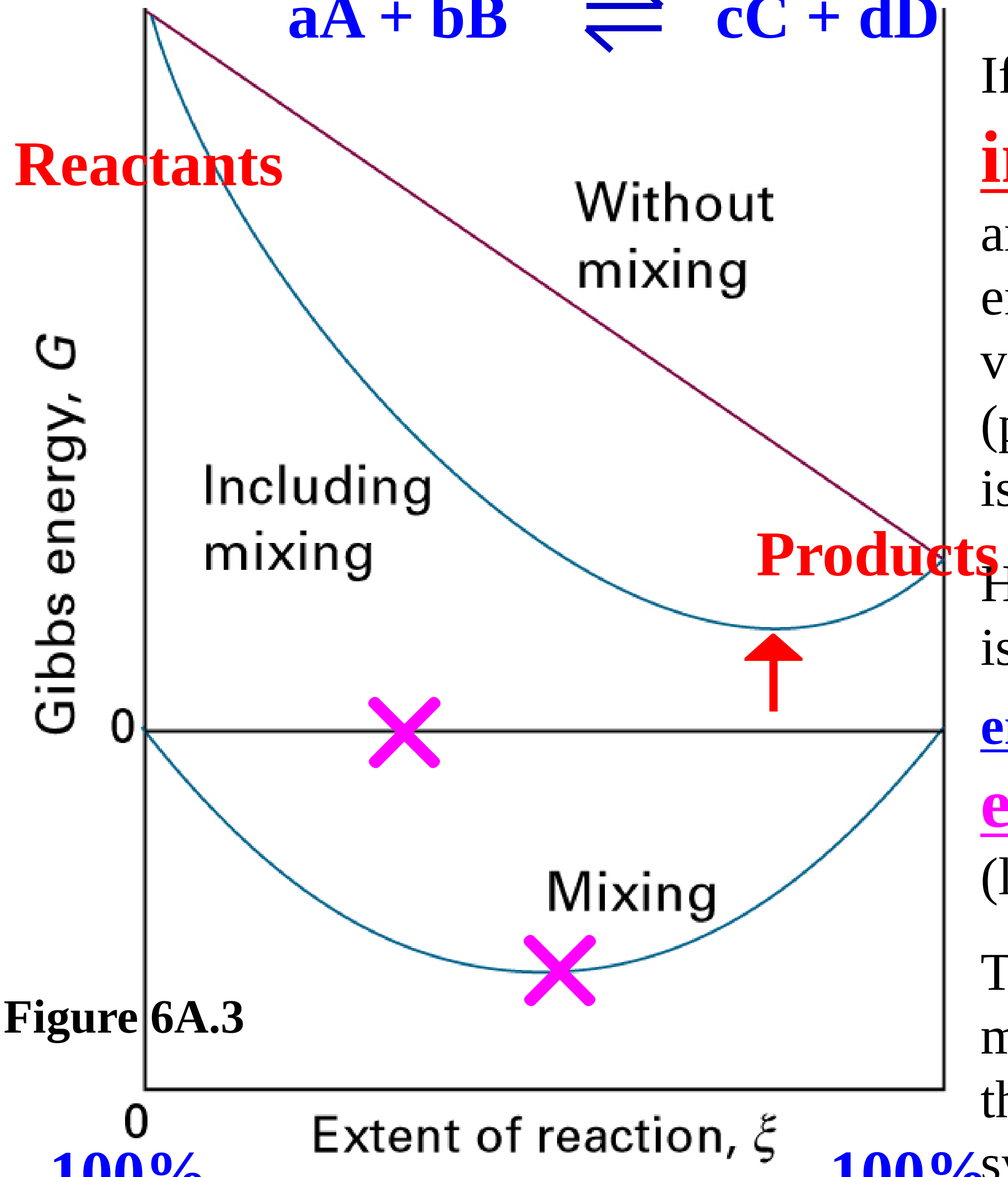


Figure 6A.3

100%
$aA + bB$

100%
$cC + dD$

(Same Atomic Composition)

If the **mixing entropy + interaction energy** of reactants and products are ignored, the Gibbs energy changes linearly from its initial value (pure reactants) to its final value (pure products), and the slope of the line is ΔG.

However, as products are produced, there is a further **contribution to the Gibbs energy arising from their mixing entropy + interaction energy** (lowest curve).

The sum of the two contributions has a minimum. That minimum corresponds to the equilibrium composition of the system.

6A.2(a) Pefect Gas Equilibrium

$$\mathrm{A} \rightleftharpoons \mathrm{B}$$

$$\alpha\text{-}C_5H_{12} \rightleftharpoons \beta\text{-}C_5H_{12}$$

For ideal gases

$$\overline{G}_i = G_i^\circ + RT \ln p_i \qquad i = \mathrm{A \ or \ B}$$

The condition of equilibrium then leads

$$G_A^\circ + RT\ln(p_\mathrm{A})_e = G_B^\circ + RT\ln(p_\mathrm{B})_e$$

$$\text{or} \quad RT\ln\left(\frac{p_\mathrm{B}}{p_\mathrm{A}}\right)_e = -\left(G_B^\circ - G_A^\circ\right)$$

The molar **standard Gibbs function for the reaction**

$$\underline{\Delta G_m^\circ = G_B^\circ - G_A^\circ}$$

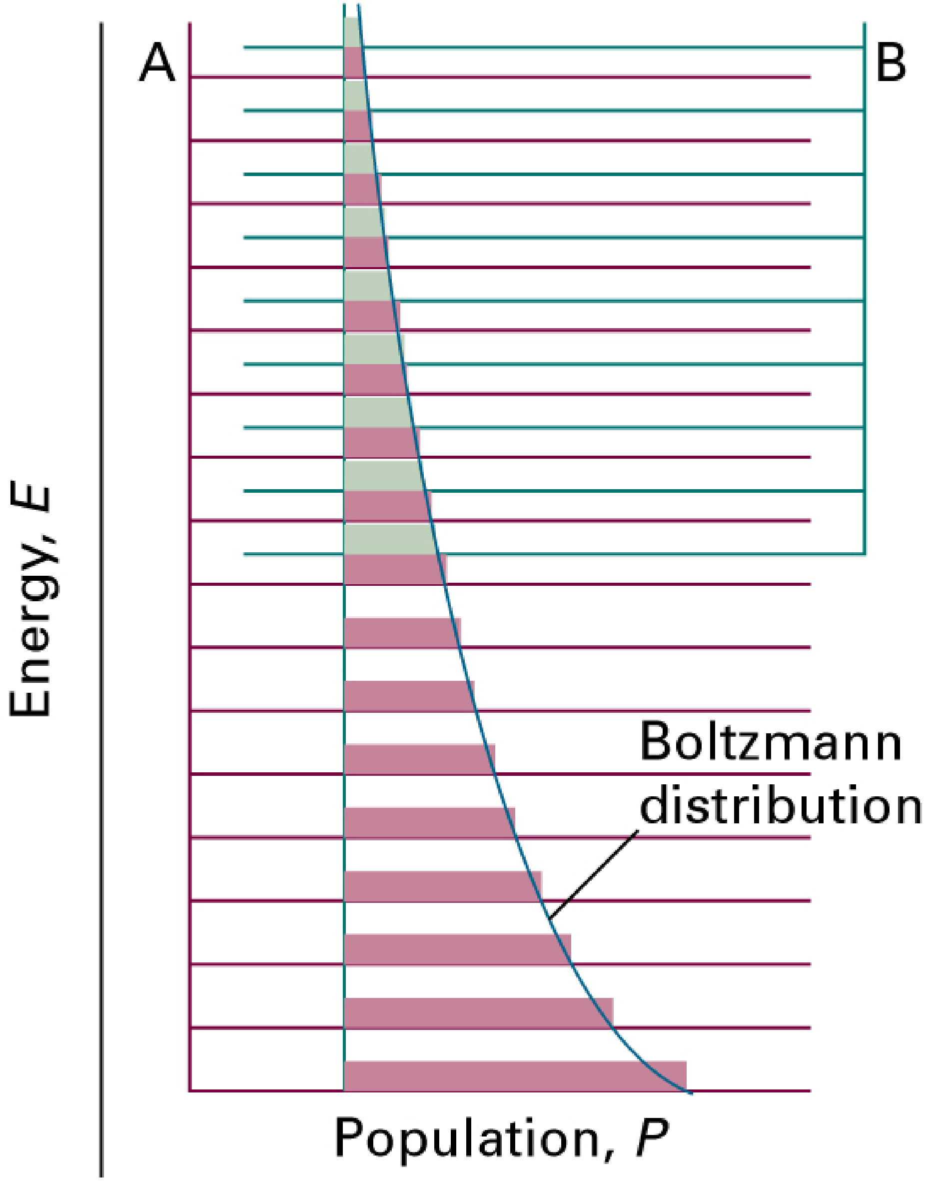
$$\therefore \ln\left(\frac{p_\mathrm{B}}{p_\mathrm{A}}\right)_e = -\frac{\Delta G_m^\circ}{RT} \qquad \therefore \left(\frac{p_\mathrm{B}}{p_\mathrm{A}}\right)_e = \exp\left(-\frac{\Delta G_m^\circ}{RT}\right)$$

(ideal gas)

All we need to know are the tabulated **standard molar Gibbs functions for the reactants and products** at the temperature of interest.

$$\Delta G_m^\circ > 0 \Rightarrow \frac{p_\mathrm{B}}{p_\mathrm{A}} < 1, \quad \text{i.e.,} \quad p_\mathrm{B} < p_\mathrm{A}$$

Molecular Interpretation of the Equilibrium Constant



$$A \rightleftharpoons B$$

Figure 6.4
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.

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6.2(b) Description of Equilibrium: General Case of Reaction

Consider the reaction

A + B ⇌ C

Change in amount of A = $-d\xi$
Change in amount of B = $-d\xi$
Change in amount of C = $+d\xi$

The Gibbs function changes by the amount

$$dG = \overline{G}_A dn_\mathrm{A} + \overline{G}_B dn_\mathrm{B} + \overline{G}_C dn_\mathrm{C} = -\overline{G}_A d\xi - \overline{G}_B d\xi + \overline{G}_C d\xi$$
$$= \left(-\overline{G}_A - \overline{G}_B + \overline{G}_C\right) d\xi$$

General: Considering
mixing entropy + interaction energy

At constant temperature and pressure,

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \overline{G}_C - \overline{G}_A - \overline{G}_B = 0$$ at equilibrium

Minimum *G*

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If A, B and C are all **ideal gases**, at equilibrium

$$\left\{G_C^\circ + RT\ln(p_c)_e\right\} - \left\{G_A^\circ + RT(p_A)_e\right\}$$
$$-\left\{G_B^\circ + RT\ln(p_B)_e\right\} = 0$$

$$\therefore RT\ln\left\{\frac{(p_C)}{(p_A)(p_B)}\right\}_e = -\left(G_C^\circ - G_A^\circ - G_B^\circ\right)$$

The standard molar Gibbs function for the reaction

$$\underline{\Delta G_m^\circ = G_m^\circ(\text{prod}) - G_m^\circ(\text{react}) = G_C^\circ - G_A^\circ - G_B^\circ}$$

Let $K_p = \dfrac{(p_C)}{(p_A)(p_B)}$, where K_p : the equilibrium constant.

$$RT\ln K_p = -\Delta G_m^\circ$$

$$K_p = \underline{\frac{(p_C)}{(p_A)(p_B)} = \exp\left(-\frac{\Delta G_m^\circ}{RT}\right)}$$

(ideal gas)

Consider the general reaction:

$$\nu_A \mathrm{A} + \nu_B \mathrm{B} + \cdots \rightleftharpoons \nu_Q \mathrm{Q} + \nu_R \mathrm{R} + \cdots$$

change in amount of A = $-n_\mathrm{A} d\xi$ change in amount of B = $-n_\mathrm{B} d\xi$

change in amount of Q = $+n_\mathrm{Q} d\xi$ change in amount of R = $+n_\mathrm{R} d\xi$

At constant temperature and pressure,

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \nu_Q \overline{G}_Q + \nu_R \overline{G}_R + \cdots - \nu_A \overline{G}_A - \nu_B \overline{G}_B - \cdots = 0 \ \text{ at equilibrium}$$

The standard Gibbs function

$$\Delta G_m^\circ = \nu_Q G_Q^\circ + \nu_R G_R^\circ + \cdots - \nu_A G_A^\circ - \nu_B G_B^\circ - \cdots$$

The equilibrium constant

$$K_p = \left\{ \frac{(p_Q / atm)^{\nu_Q} (p_R / atm)^{\nu_R} \cdots}{(p_A / atm)^{\nu_A} (p_B / atm)^{\nu_B} \cdots} \right\}_e$$

$$\therefore RT \ln K_p = -\Delta G_m^\circ$$

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A recipe for equilibrium constant: real gases

A ⇌ B

$$RT\ln\left(\frac{f_B}{f_A}\right)_e = -\Delta G_m^\circ \qquad \left(\frac{p_B}{p_A}\right)_e = \exp\left(-\frac{\Delta G_m^\circ}{RT}\right) \text{ for ideal gases}$$

$$f_i = \gamma_i p_i$$

where p_i and g_i are the pressure of component *i* and its fugacity coefficient, respectively.

$$RT\ln\left(\frac{\gamma_B p_B}{\gamma_A p_A}\right)_e = -\Delta G_m^\circ$$

$$RT\left\{\ln\left(\frac{p_B}{p_A}\right)_e + \ln\left(\frac{\gamma_B}{\gamma_A}\right)_e\right\} = -\Delta G_m^\circ$$

$$K_p = \left(\frac{p_B}{p_A}\right)_e, \quad K = \left(\frac{f_B}{f_A}\right)_e \qquad \text{thermodynamic equilibrium constant}$$

Example 6.1:

Calculate the equilibrium constant for the ammonia synthesis reaction at 298 *K*:

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

The molar Gibbs free energy of formation of NH_3 is –16.5 *kJ/mol*.

Solution:

The standard Gibbs energy of the reaction is

$$\begin{aligned}\Delta G_r^\circ &= 2G^\circ\left(\mathrm{NH_3}, g\right) - G^\circ\left(\mathrm{N_2}, g\right) - 3G^\circ\left(\mathrm{H_2}, g\right)\\ &= 2\Delta G_f^\circ\left(\mathrm{NH_3}, g\right) - \Delta G_f^\circ\left(\mathrm{N_2}, g\right) - 3\Delta G_f^\circ\left(\mathrm{H_2}, g\right)\\ &= 2\Delta G_f^\circ\left(\mathrm{NH_3}, g\right) = 2\times\left(-16.5 kJ/mol\right)\end{aligned}$$

Then, because $RT = 2.48 kJ/mol$,

$$\ln K = \frac{2\times\left(-16.5 kJ/mol\right)}{2.48 kJ/mol} = 13.3 \qquad \therefore K = 6.0\times 10^5$$

Note: In Chapter 3, we saw that the difference in standard molar Gibbs energies of the products and reactants is equal to the difference in their standard Gibbs energies of formation

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$

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

$$\therefore K = e^{-\Delta H^\circ / RT} e^{\Delta S^\circ / R}$$

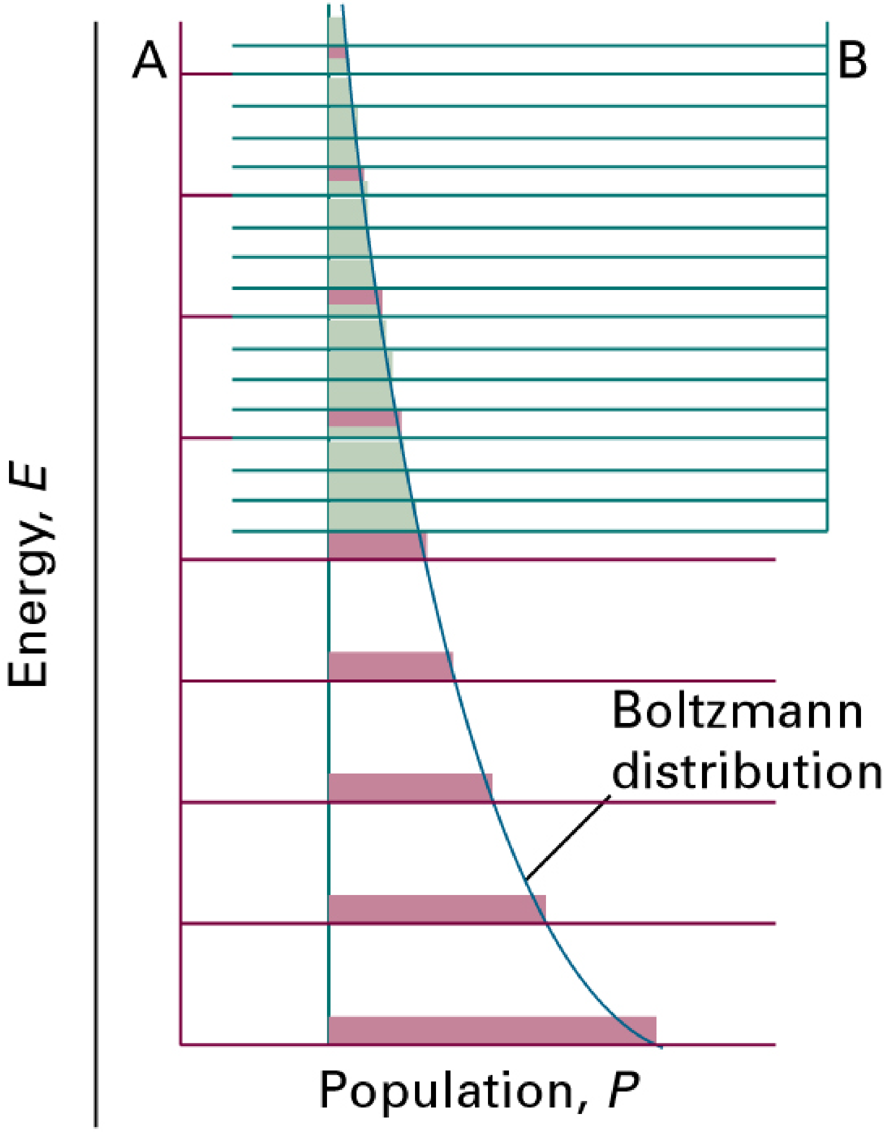


Figure 6.5
Even though the reaction A→B is endothermic, the density of energy levels in B is so much greater than that in A that the population associated with B is greater than that associated with A, so B is dominant at equilibrium.

Another recipe: real reactions

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{0} + RT \ln a_{\mathrm{A}}$$

$$\mathrm{A} + \mathrm{B} \leftrightarrow \mathrm{C} + \mathrm{D}$$

$$RT \ln K = -\Delta G_m^0$$

where $\Delta G_m^0 = \mu_{\mathrm{C}}^0 + \mu_{\mathrm{D}}^0 - \mu_{\mathrm{A}}^0 - \mu_{\mathrm{B}}^0,\ K = \left(\dfrac{a_{\mathrm{C}} a_{\mathrm{D}}}{a_{\mathrm{A}} a_{\mathrm{B}}}\right)_e$

Since $a_i = \gamma_i x_i$, where γ_i and x_i are the activity coefficient and mole fraction of component *i*, respectively, the equilibrium constant for the above reaction is expressed as

$$K = \left(\frac{\gamma_{\mathrm{C}} x_{\mathrm{C}} \gamma_{\mathrm{D}} x_{\mathrm{D}}}{\gamma_{\mathrm{A}} x_{\mathrm{A}} \gamma_{\mathrm{B}} x_{\mathrm{B}}}\right)_e = \left(\frac{\gamma_{\mathrm{C}} \gamma_{\mathrm{D}}}{\gamma_{\mathrm{A}} \gamma_{\mathrm{B}}}\right)\left(\frac{x_{\mathrm{C}} x_{\mathrm{D}}}{x_{\mathrm{A}} x_{\mathrm{B}}}\right) = K_\gamma K_x$$

In general case of a reaction

$$\left(\frac{\partial G}{\partial \xi}\right)_e = \nu_\mathrm{Q}\mu_\mathrm{Q} + \nu_\mathrm{R}\mu_\mathrm{R} + \cdots - \nu_\mathrm{A}\mu_\mathrm{A} - \nu_\mathrm{B}\mu_\mathrm{B} - \cdots = 0$$

$$\Delta G_m^0 = -RT\ln K$$

where $K = \left(\dfrac{a_\mathrm{Q}^{\nu_\mathrm{Q}} a_\mathrm{R}^{\nu_\mathrm{R}} \cdots}{a_\mathrm{A}^{\nu_\mathrm{A}} a_\mathrm{B}^{\nu_\mathrm{B}} \cdots}\right)_e$.

The standard Gibbs function for the reaction

$$\Delta G_m^0 = \nu_\mathrm{Q}\mu_\mathrm{Q}^0 + \nu_\mathrm{R}\mu_\mathrm{R}^0 + \cdots - \nu_\mathrm{A}\mu_\mathrm{A}^0 - \nu_\mathrm{B}\mu_\mathrm{B}^0 - \cdots$$

Example:

The standard Gibbs energy of reaction for the decomposition $\mathrm{H_2O}(g) \rightarrow \mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g)$ is +118.08 *kJ/mol* at 2300 *K*. What is the degree of dissociation of $\mathrm{H_2O}$ at 2300 *K* and 1.00 *bar*?

Solution:

The equilibrium constant is in the form

$$\ln K = -\frac{\Delta G_r}{RT} = \frac{118.08\times 10^3 J/mol}{\left(8.3145 JK^{-1}mol^{-1}\right)\times\left(2300K\right)} = -6.175$$

It follows that $K=2.08\times 10^{-3}$. The equilibrium composition can be expressed in terms of α by drawing up the following table:

	H_2O	H_2	O_2
Initial amount	n	0	0
Change to reach equilibrium	$-\alpha n$	$+\alpha n$	$+\frac{1}{2}\alpha n$
Amount at equilibirum	$(1-\alpha)n$	αn	$\frac{1}{2}\alpha n$
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	$\frac{(1-\alpha)p}{1+\frac{1}{2}\alpha}$	$\frac{\alpha p}{1+\frac{1}{2}\alpha}$	$\frac{\frac{1}{2}\alpha p}{1+\frac{1}{2}\alpha}$

The equilibrium constant is therefore

$$K = \frac{p_{H_2} p_{O_2}^{\frac{1}{2}}}{p_{H_2O}} = \frac{\alpha^{\frac{3}{2}} p^{\frac{1}{2}}}{(1-\alpha)(2+\alpha)^{\frac{1}{2}}}$$

In this expression, we have written *p* in place of *p*/p^0, to keep the notation simple. Now make the approximation that $\alpha \ll 1$, and hence obtain

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

Under the stated conditions, p=1.00 (that is, p/p^0=1.00), so

$$\alpha \approx \left(\sqrt{2}K\right)^{\frac{2}{3}} = 0.0205$$

That is, about 2 percent of the water has decomposed.

The pressure effect on the equilibrium constant K

$$\boldsymbol{RT \ln K_p = -\Delta G_m^0}$$

where ΔG_m^0 is the standard Gibbs function defined for species at a specific pressure and therefore K_p is independent of pressure.

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

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

Consider the gas-phase equilibrium.

$$\mathbf{A \rightleftharpoons 2B}$$

If an amount n of A was present initially, then at equilibrium its abundance will have fallen to an amount of B will have risen from zero to $2n\alpha$:

$$x_{\mathrm{A},e} = \frac{n(1-\alpha)}{n(1-\alpha)+2n\alpha} = \frac{1-\alpha}{1+\alpha} \qquad x_{\mathrm{B},e} = \frac{2\alpha}{1+\alpha}$$

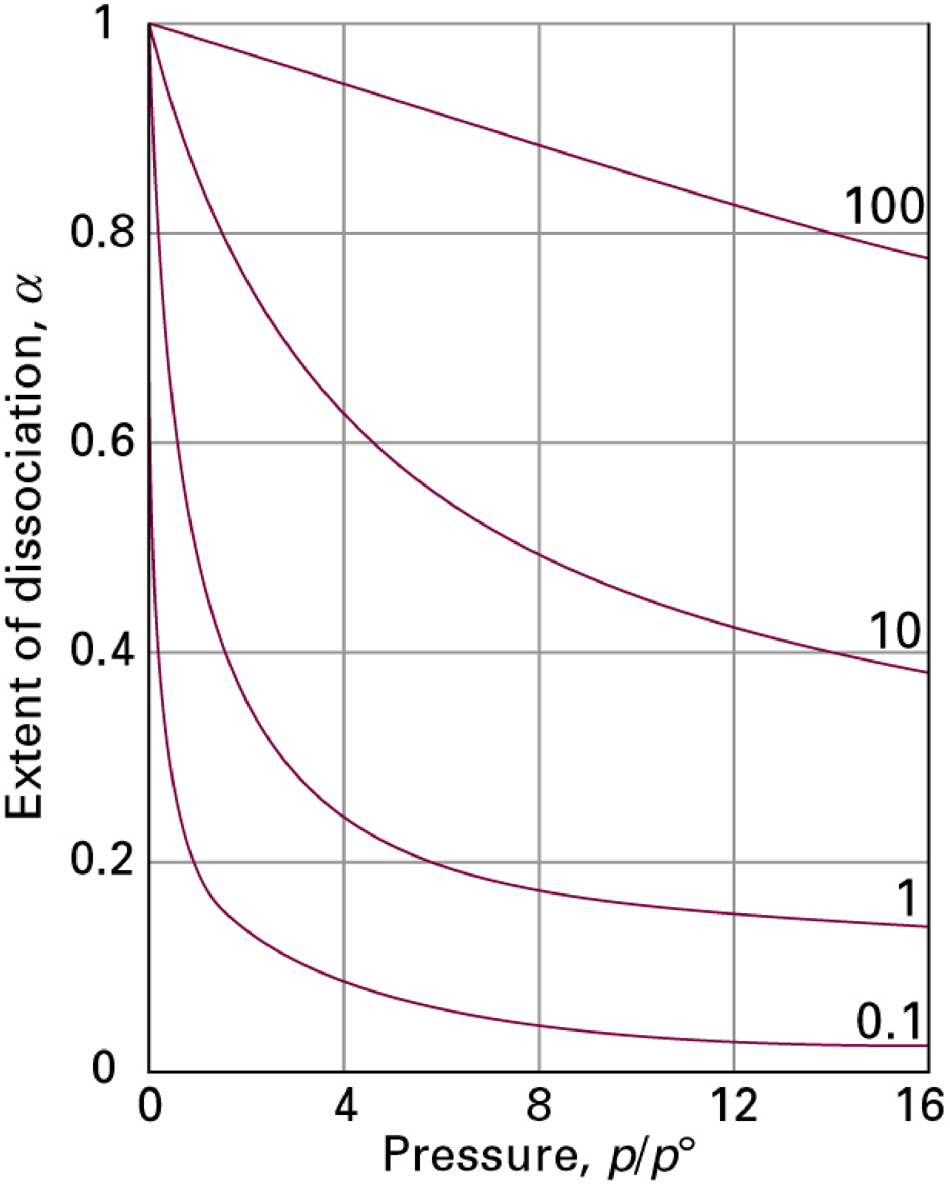
$$K_P = \left\{ \frac{\left(p_{\mathrm{B}}/atm\right)^2}{\left(p_{\mathrm{A}}/atm\right)} \right\}_e = \left\{ \frac{\left(x_{\mathrm{B}}p/atm\right)^2}{\left(x_{\mathrm{A}}p/atm\right)} \right\}_e = \left(\frac{x_{\mathrm{B}}^2}{x_{\mathrm{A}}} \right)\left(p/atm\right)$$

$$= \left\{ \frac{\dfrac{4\alpha^2}{(1+\alpha)^2}}{\dfrac{1-\alpha}{1+\alpha}} \right\}\left(p/atm\right) = \left(\frac{4\alpha^2}{1-\alpha^2} \right)\left(p/atm\right)$$

Since K_p is independent of pressure, α must depend on pressure in such a way that the r.h.s. of this expression does not depend on p.

$$\alpha = \left(\frac{K_p}{K_p + 4p/atm} \right)^{\frac{1}{2}} \qquad \text{(See Figure 6.6)}$$

As the pressure increase, α decreases, i.e., the reaction shifts in the direction of the reactant A.



$$\alpha = \left(\frac{K_p}{K_p + 4p/atm} \right)^{\frac{1}{2}}$$

Figure 6.6
The pressure dependence of the degree of dissociation, α, at equilibrium for an $\mathrm{A}(g) \rightleftharpoons 2\mathrm{B}(g)$ reaction for different values of the equilibrium constant K. The value α=0 corresponds to pure A; α=1 corresponds to pure B.

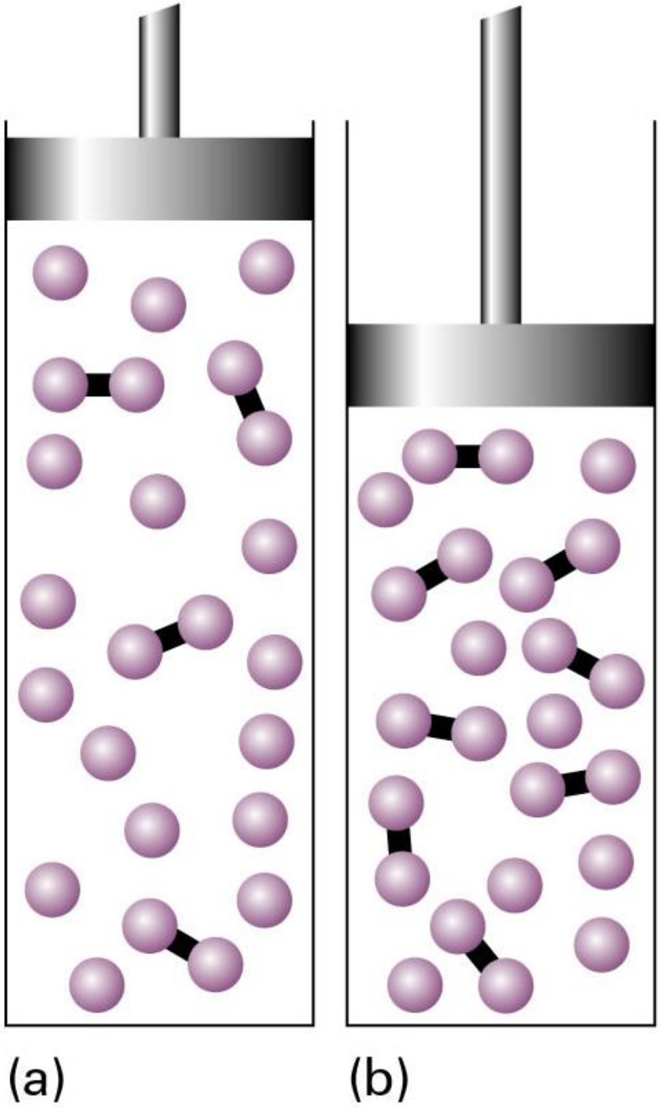


Figure 6.5
When a reaction at equilibrium is compressed (from *a* to *b*), the reaction responds by reducing the number of molecules in the gas phase (in this case by producing the dimers represented by the linked spheres).

More generally,

$$\nu_{\mathrm{A}}\mathrm{A}+\nu_{\mathrm{B}}\mathrm{B} \leftrightarrow \nu_{\mathrm{C}}\mathrm{C}+\nu_{\mathrm{D}}\mathrm{D}$$

$$K_p=\left\{\frac{\left(p_{\mathrm{C}}/atm\right)^{\nu_{\mathrm{C}}}\left(p_{\mathrm{D}}/atm\right)^{\nu_{\mathrm{D}}}}{\left(p_{\mathrm{A}}/atm\right)^{\nu_{\mathrm{A}}}\left(p_{\mathrm{B}}/atm\right)^{\nu_{\mathrm{B}}}}\right\}_e=\left(\frac{x_{\mathrm{C}}^{\nu_{\mathrm{C}}}x_{\mathrm{D}}^{\nu_{\mathrm{D}}}}{x_{\mathrm{A}}^{\nu_{\mathrm{A}}}x_{\mathrm{B}}^{\nu_{\mathrm{B}}}}\right)\left(p/atm\right)^{\nu_{\mathrm{C}}+\nu_{\mathrm{D}}-\nu_{\mathrm{A}}-\nu_{\mathrm{B}}}$$

where $\Delta\nu=\nu_{\mathrm{C}}+\nu_{\mathrm{D}}-\left(\nu_{\mathrm{A}}+\nu_{\mathrm{B}}\right)$

$$0=\left(\frac{\partial K_p}{\partial p}\right)_T=\left(\frac{\partial K_x}{\partial p}\right)_T\left(p/atm\right)^{\Delta\nu}+\Delta\nu K_x\left(p/atm\right)^{\Delta\nu-1}$$

$$\therefore\left(\frac{\partial\ln K_x}{\partial\ln p}\right)_T=-\Delta\nu$$

$\Delta\nu<0\rightarrow p\uparrow\rightarrow K_x\uparrow$ (larger amount of products)

$\Delta\nu>0\rightarrow p\uparrow\rightarrow K_x\downarrow$

$\Delta\nu=0\rightarrow$ the pressure will not affect the value of K_x.

The temperature dependence of equilibrium

$$T_1 \rightarrow K_1 \qquad \ln K_1 = -\frac{\Delta G_m^0(T_1)}{RT_1}$$

$$T_2 \rightarrow K_2 \qquad \ln K_2 = -\frac{\Delta G_m^0(T_2)}{RT_2}$$

On subtracting

$$\ln K_2 - \ln K_1 = -\left\{\frac{\Delta G_m^0(T_2)}{RT_2} - \frac{\Delta G_m^0(T_1)}{RT_1}\right\} \qquad \Delta G = \Delta H - T\Delta S$$

Assumption: Neither ΔH nor ΔS changes significantly over the temperature range of interest.

$$\Delta H_m^0(T_2) \approx \Delta H_m^0(T_1); \quad \Delta S_m^0(T_2) \approx \Delta S_m^0(T_1)$$

$$\ln K_2 = \ln K_1 - \left\{\frac{\Delta H_m^0(T_2)}{RT_2} - \frac{\Delta H_m^0(T_1)}{RT_1} - \cancel{\frac{\Delta S_m^0(T_2)}{R}} + \cancel{\frac{\Delta S_m^0(T_1)}{R}}\right\}$$

$$\approx \ln K_1 - \left(\frac{\Delta H_m^0}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Some approximation

Gibbs-Helmholtz equation

$$\left\{\frac{\partial\left(\Delta G/T\right)}{\partial T}\right\}_p = -\frac{\Delta H}{T^2}$$

$$\ln K = -\frac{\Delta G^0}{RT}$$

$$\frac{d\ln K}{dT} = -\frac{1}{R}\left\{\frac{d\left(\Delta G^0/T\right)}{dT}\right\}$$

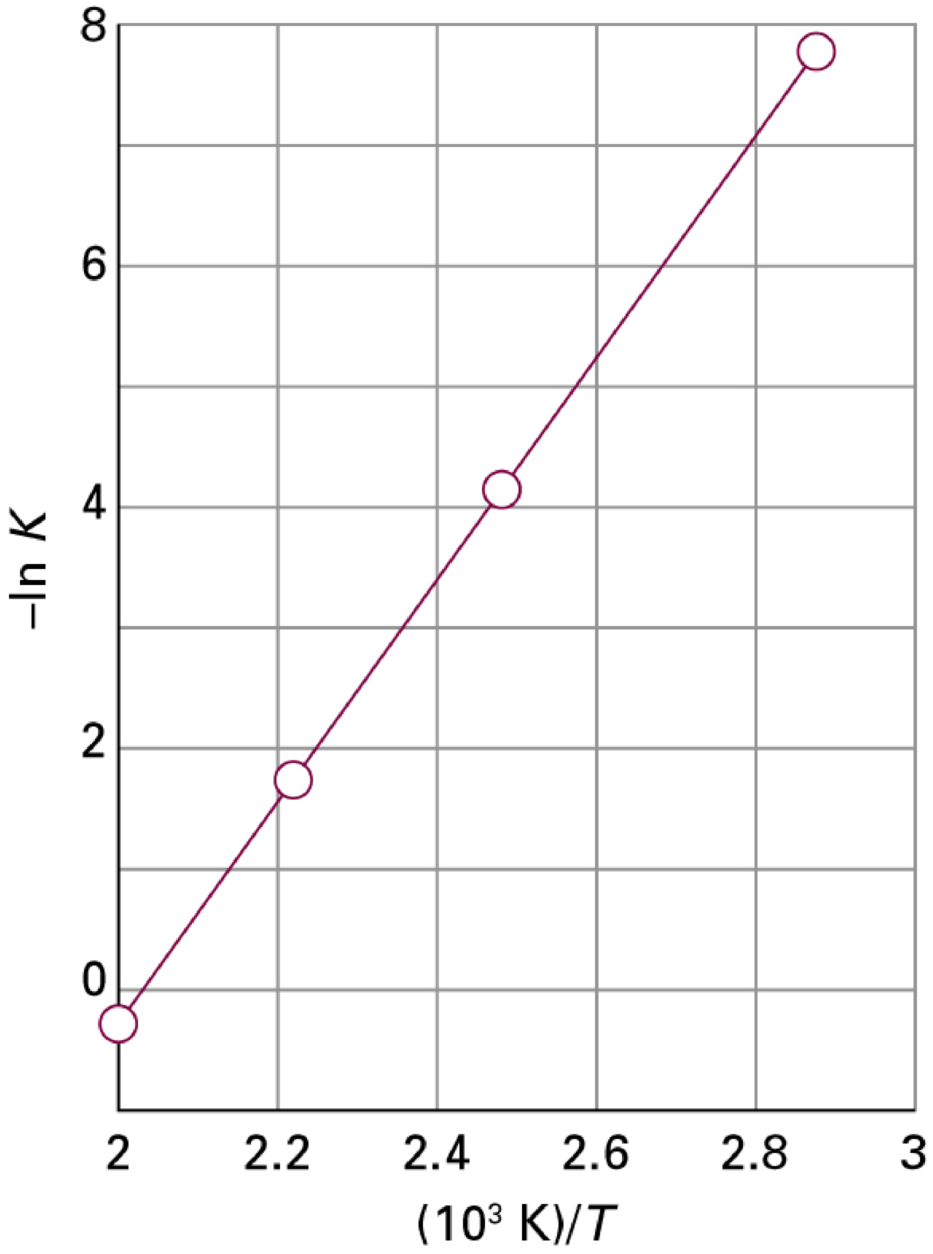
Combining the above two equations,

$$\frac{d\ln K}{dT} = \frac{\Delta H_m^0\left(T\right)}{RT^2}$$

van't Hoff equation

$$\frac{d\ln K}{d\left(1/T\right)} = -\frac{\Delta H_m^0\left(T\right)}{R}$$

ΔH^0 depends only weakly on the temperature, and so the line is almost straight. The van't Hoff equation provides a good way of measuring the enthalpy of a reaction without using a calorimeter. (See Figure 6.8)



$$\frac{d\ln K}{d\left(1/T\right)} = -\frac{\Delta H_m^0\left(T\right)}{R}$$

Figure 6.8
When –ln *K* is plotted against l/*T*, a straight line is expected with slope equal to $\Delta H^\circ/R$. This is a non-calorimetric method for the measurement of reaction enthalpies.

From van't Hoff equation,

$$\frac{d\ln K}{dT} = \frac{\Delta H_m^0(T)}{RT^2} < 0 \text{ for exothermic reaction}$$

$$\frac{d\ln K}{dT} = \frac{\Delta H_m^0(T)}{RT^2} > 0 \text{ for endothermic reaction}$$

A negative gradient (downhill from left to right) means that ln *K*, and therefore *K* itself, gets smaller as the temperature rises, i.e., the equilibrium shifts away from products.

Exothermic reaction: a rise in temperature favors the reactants.
Endothermic reaction: a rise in temperature favors the products.

Molecular interpretation for temperature dependence of the equilibrium constant is given in Figure 6.7.

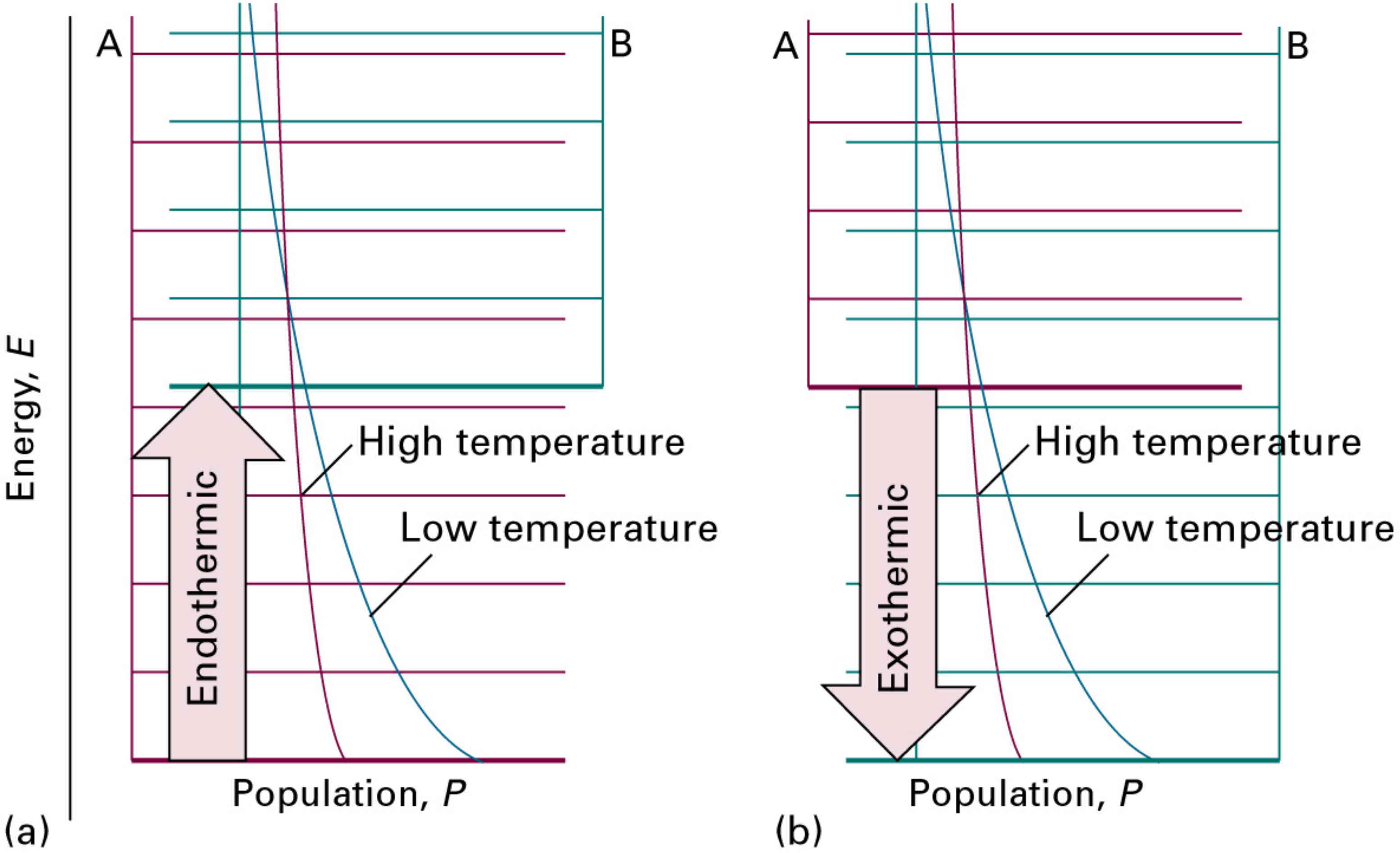


Figure 6.7
The effect of temperature on a chemical equilibrium can be interpreted in terms of the change in the Boltzmann distribution with temperature and the effect of that change in the population of the species. (a) In an endothermic reaction, the population of B increases at the expense of A as the temperature is raised. (b) In an exothermic reaction, the opposite happens.

Example: Estimate the chemical equilibrium constant at 500 K for the synthesis of ammonia: $N_2(g)+3H_2(g)\rightarrow 2NH_3(g)$ The chemical equilibrium constant at 298 K is 6.15×10^5 and $\Delta H_r=-92.2\ kJ/mol.$

Solution:

$$\ln K_2=\ln(6.1\times10^5)-\frac{(-92.2\times10^3\ J/mol)}{8.3145\,J/K\cdot mol}\left(\frac{1}{500K}-\frac{1}{298K}\right)$$

$$=-1.71$$

$$\therefore K_2=0.18$$

A lower value than 2998 K, as expected for this exothermic reaction.

Applications to selected systems

Extraction of metals from their oxides

(i) $M+\frac{1}{2}O_2 \leftrightarrow MO$

$MO+C \leftrightarrow M+CO$

or

(ii) $\frac{1}{2}C+\frac{1}{2}O_2 \leftrightarrow \frac{1}{2}CO_2$

$MO+\frac{1}{2}C \leftrightarrow M+\frac{1}{2}CO_2$

(iii) $C+\frac{1}{2}O_2 \leftrightarrow CO$

(iv) $CO+\frac{1}{2}O_2 \leftrightarrow CO_2$

$$\left(\frac{\partial \Delta G_m}{\partial T}\right)_p = -\Delta S_m$$

$\Delta S_m^0(\mathrm{ii}) << \Delta S_m^0(\mathrm{iii}) \longrightarrow$ generates the gas

The Gibbs function of the reaction (ii) is not very sensitive to the temperature, but for reaction (iii) it decreases sharply with increasing temperature. (See Figure 6.9)

The Gibbs function for reaction (i) indicates the metal's affinity for oxygen. At room temperature $\Delta H_m{}^0$ dominates $\Delta S_m{}^0$ and so $\Delta G_m{}^0$ is governed by the enthalpy of formation of the oxide. The entropy of reaction is approximately the same for all metals, because the reactions correspond to the elimination of gaseous oxygen to form a compact, solid oxide. As a result, the temperature dependence of the standard Gibbs energy of oxidation should be similar slopes of the lines in the diagram. (See Figure 6.9)

$$\mathrm{MO}+\mathrm{C} \leftrightarrow \mathrm{M}+\mathrm{CO} \qquad \Delta G_m^0 = \Delta G_m^0(\mathrm{iii}) - \Delta G_m^0(\mathrm{i})$$

$$\mathrm{MO}+\tfrac{1}{2}\mathrm{C} \leftrightarrow \mathrm{M}+\tfrac{1}{2}\mathrm{CO_2} \qquad \Delta G_m^0 = \Delta G_m^0(\mathrm{ii}) - \Delta G_m^0(\mathrm{i})$$

$$\mathrm{MO}+\mathrm{CO} \leftrightarrow \mathrm{M}+\mathrm{CO_2} \qquad \Delta G_m^0 = \Delta G_m^0(\mathrm{iv}) - \Delta G_m^0(\mathrm{i})$$

$\Delta G_m^0 < 0$: The equilibrium lies to the right, which is the case when the line for $\Delta G_m^0(\mathrm{i})$ lies below the line for one of the carbon reactions (ii) ~ (iv).

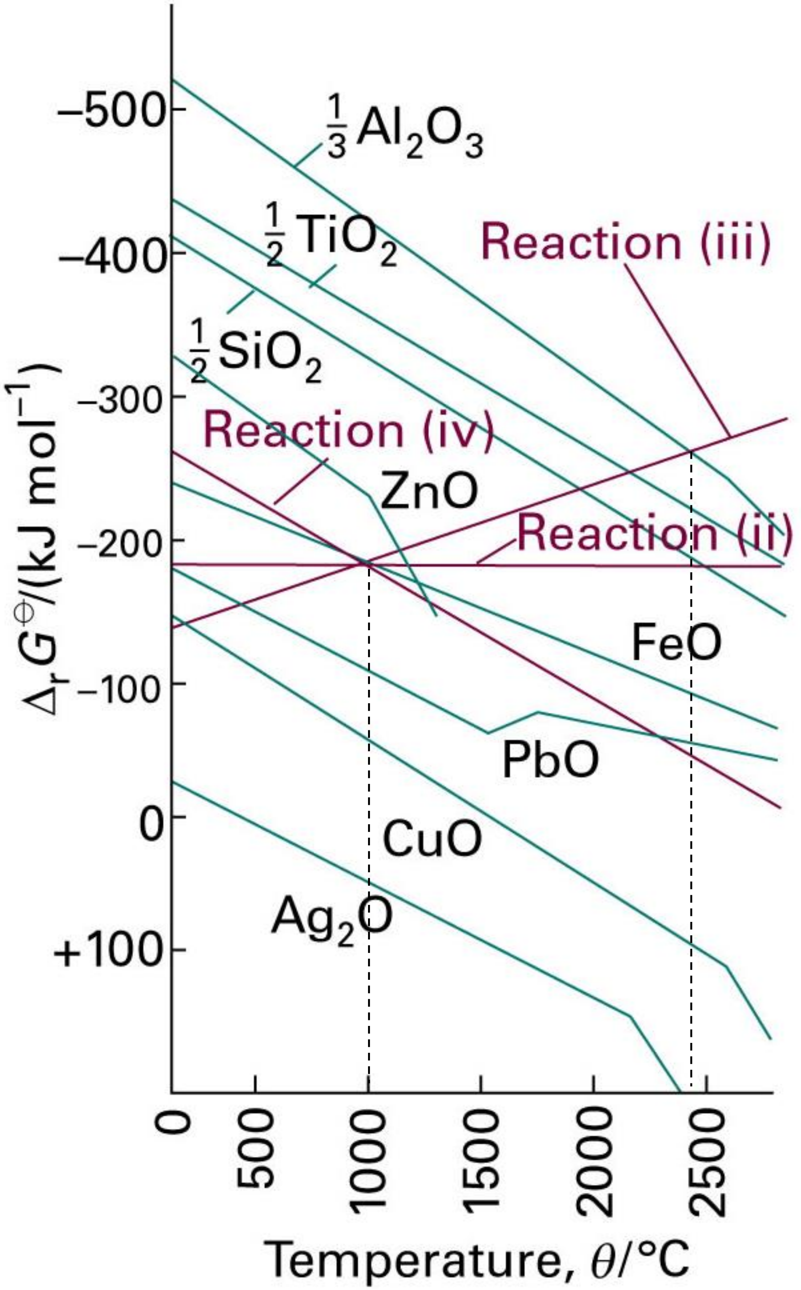


Figure 6.9

An Ellingham diagram for the discussion of metal ore reduction. Note that ΔG_r° is most negative at the top of the diagram.

Acids and Bases

An acid is a proton donor; a base is a proton acceptor.

$$\mathrm{pH} = -\log a_{\mathrm{H_3O^+}}$$

where H_3O^+ is the hydronium ion, a representation of the state of the proton in aqueous solution.

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \leftrightarrow \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \qquad K = \frac{a_{\mathrm{H_3O^+}} a_{\mathrm{A^-}}}{a_{\mathrm{HA}} a_{\mathrm{H_2O}}}$$

A^-: the conjugated base of the acid

$a_{\mathrm{H_2O}} \approx 1$ (the value for pure water)

Acidity constant K_a

$$K_a = \frac{a_{\mathrm{H_3O^+}} a_{\mathrm{A^-}}}{a_{\mathrm{HA}}}$$

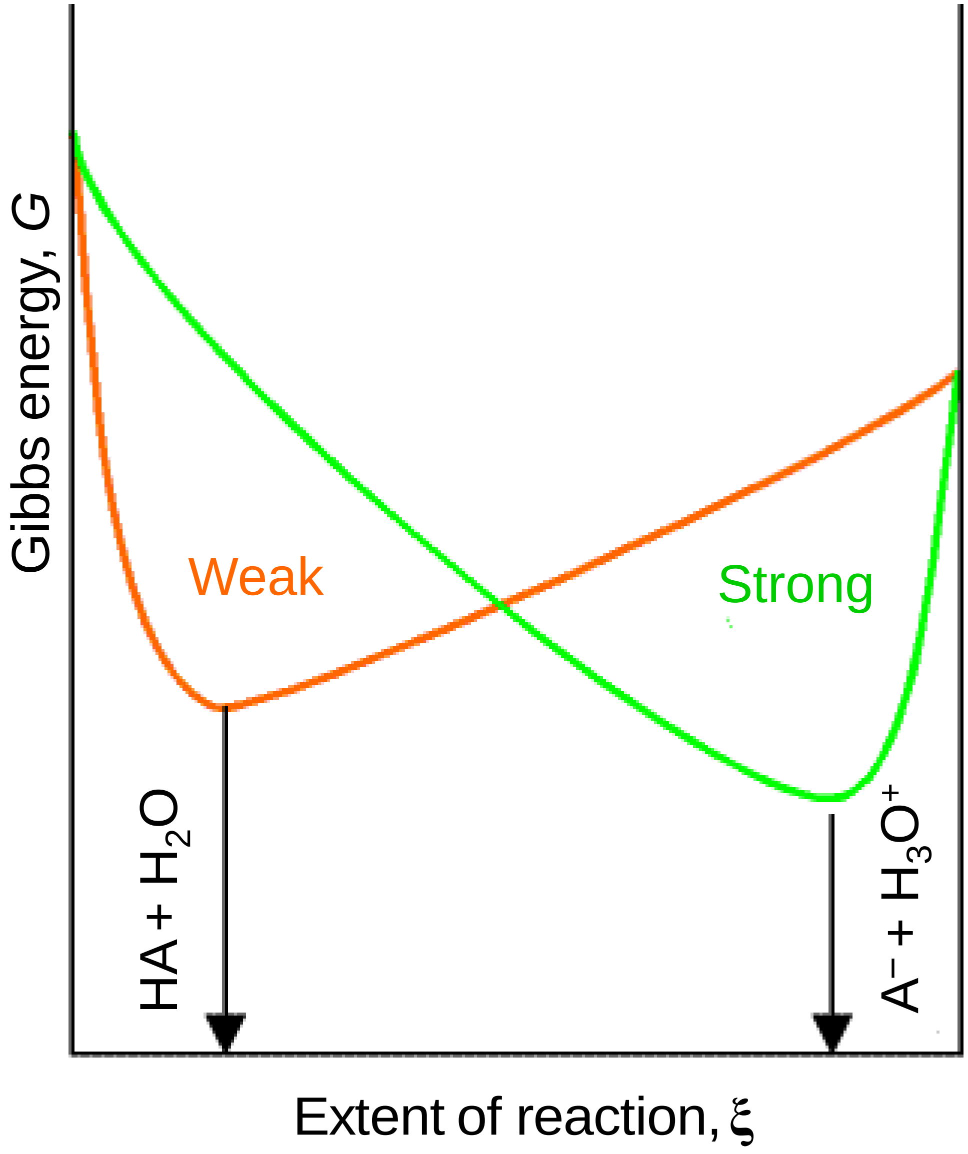


Figure 6.10
The Gibbs energy for a solution of a weak acid has a minimum that lies close to HA, and little deprotonation occurs at equilibrium. For a strong acid, the minimum lies close to products and deprotonation is almost complete.

Approximation: $a_J \sim [J]$ if all the ions are present at low concentration.

$$K_a \approx \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{A^-}\right]}{\left[\mathrm{HA}\right]} \qquad \mathrm{p}K_a = -\log K_a$$

A high value of pK_a signifies a very small value of K_a. $\left(\because K_a = 10^{-\mathrm{p}K_a}\right)$ and hence a very weak acid.

$$\Delta G = -RT\ln K_a = \left(RT\ln 10\right)\times \mathrm{p}K_a$$

For a base B in water,

$$\mathrm{B}(aq) + \mathrm{H_2 0}(l) \leftrightarrow \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq) \qquad K = \frac{a_{\mathrm{HB}}a_{\mathrm{OH^-}}}{a_{\mathrm{B}}a_{\mathrm{H_2O}}}$$

The basicity constant K_b

$$K_b = \frac{a_{\mathrm{HB^+}}a_{\mathrm{OH^-}}}{a_{\mathrm{B}}}$$

Although the basicity constant can be used to access the strength of a base, it is common to express proton transfer equilibria involving a base in terms of its conjugate acid:

$$\mathrm{HB^+}(aq) + \mathrm{H_2O}(l) \leftrightarrow \mathrm{H_3O^+}(aq) + \mathrm{B}(aq) \qquad K_a = \frac{a_{\mathrm{H_3O^+}} a_{\mathrm{B}}}{a_{\mathrm{HB^+}}}$$

$$K_a K_b = K_w$$

where K_w is the autoprotolysis of water.

$$2\mathrm{H_2O}(l) \leftrightarrow \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq) \qquad K_w = a_{\mathrm{H_3O^+}} a_{\mathrm{OH^-}}$$

At 25℃, $K_w = 1.008 \times 10^{-14}$ ($\mathrm{p}K_w = 14.00$)

$$\mathrm{pOH} = -\log a_{\mathrm{OH^-}}$$

$$\mathrm{p}K_w = \mathrm{pH} + \mathrm{pOH}$$

Since $[\mathrm{H_3O^+}] \approx [\mathrm{OH^-}]$ in pure water,

$$\mathrm{pH} = \frac{1}{2}\mathrm{p}K_w \approx 7.00$$

pH calculations

For a strong acid (one that is fully ionized in solution), the molar concentration of hydronium ions is the same as the nominal molar concentration of the acid, as each HA molecule generates one H_3O^+ ion.

For a weak acid or base, we need to take the partial ionization into account by considering the proton transfer equilibrium. Because the extent of ionization is so small (for typical solutions), an approximation is that the molar concentration of HA or B is unchanged from its nominal value. Moreover, because the molar concentrations of the species produced by the proton transfer are equal (to a good approximation), the expression for K_a simplifies to

$$K_a \approx \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{A^-}\right]}{[\mathrm{HA}]} \approx \frac{\left[\mathrm{H_3O^+}\right]^2}{[\mathrm{HA}]} \qquad \text{or} \qquad \left[\mathrm{H_3O^+}\right] \approx \left(K_a[\mathrm{HA}]\right)^{\frac{1}{2}}$$

$$\mathrm{pH} \approx \frac{1}{2}\mathrm{p}K_a - \frac{1}{2}\log[\mathrm{HA}]$$

Exercise:

The pK_a of hydrocyanic acid, HCN(*aq*), is given as 9.31. Calculate the pH of 0.2M HCN(*aq*).

Solution:

$$\begin{aligned} \mathrm{pH} &\approx \frac{1}{2}\mathrm{p}K_a - \frac{1}{2}\log[\mathrm{HCN}] \\ &\approx \frac{1}{2}\times 9.31 - \frac{1}{2}\log 0.20 = 5.0 \end{aligned}$$

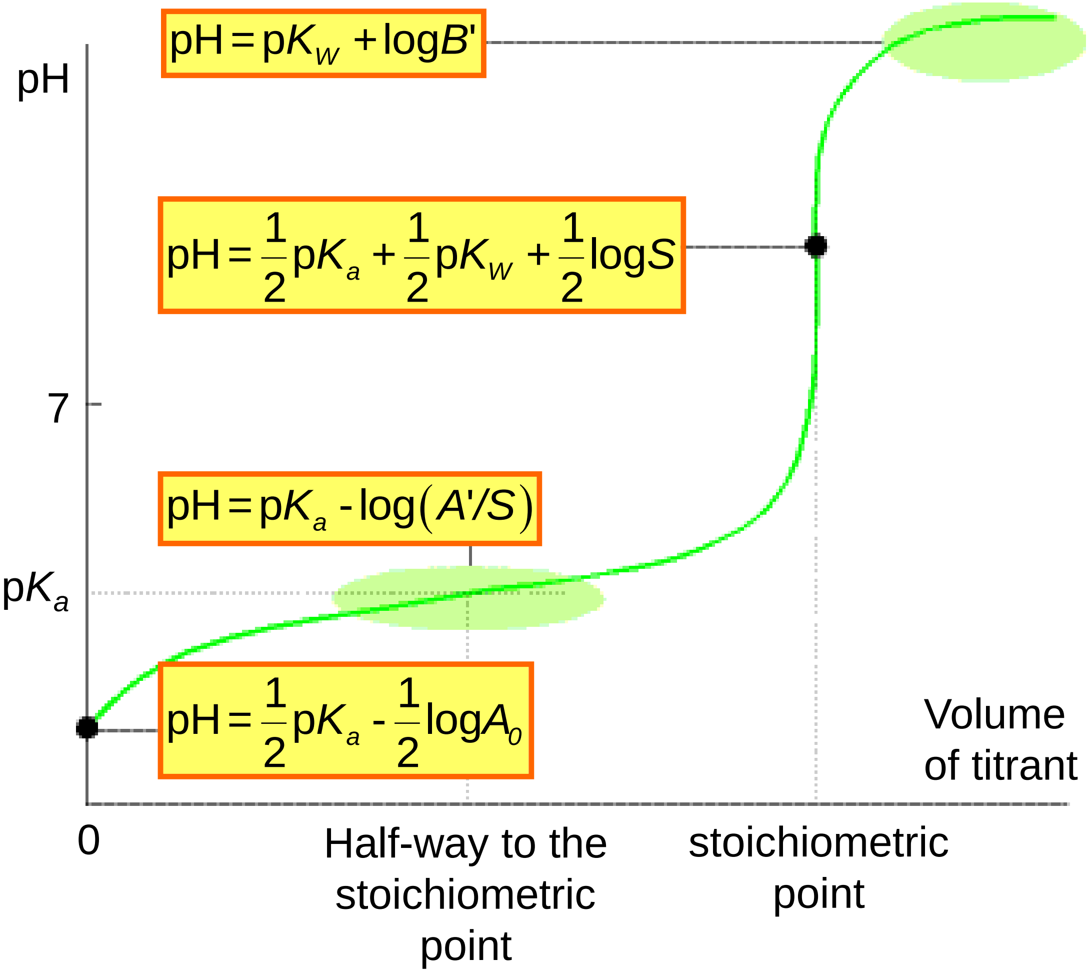


Figure 6.11
A summary of the regions of the pH curve of the titration of a weak acid with a strong base, and the equations used in different regions.