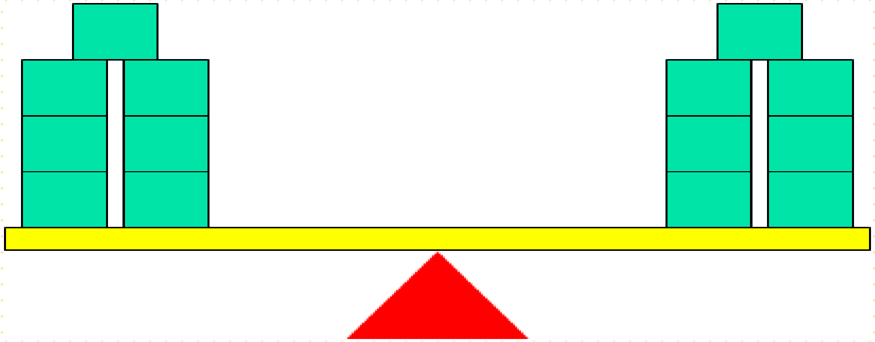
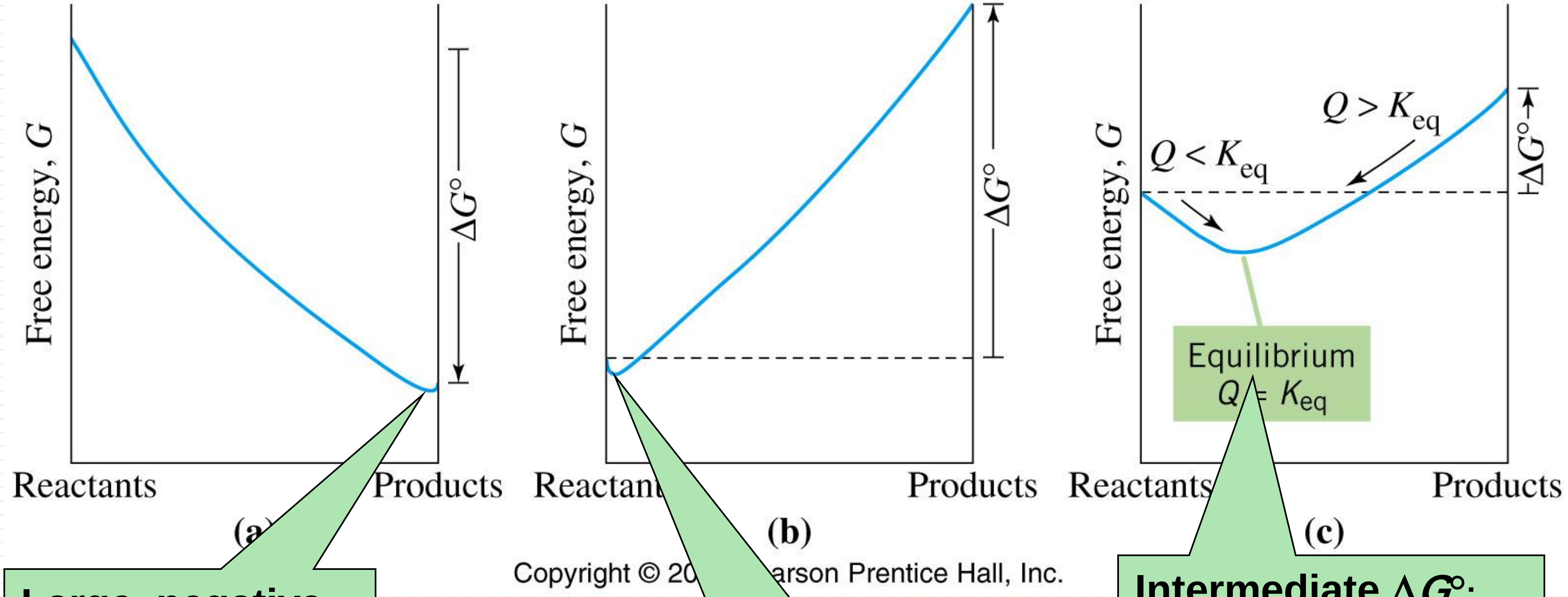
Chapter (4)

Chemical Reaction Equilibrium



Jan., 31st , 2018

The Sign and Magnitude of ΔG°



Large, negative $\Delta G°$; equilibrium lies far to *right*.

Large, positive $\Delta G°$; equilibrium lies far to *left*.

Intermediate $\Delta G°$; equilibrium lies in intermediate position.

Equilibrium & Gibbs Energy

$$dU = TdS - PdV + \sum_i \mu_i dn_i,$$

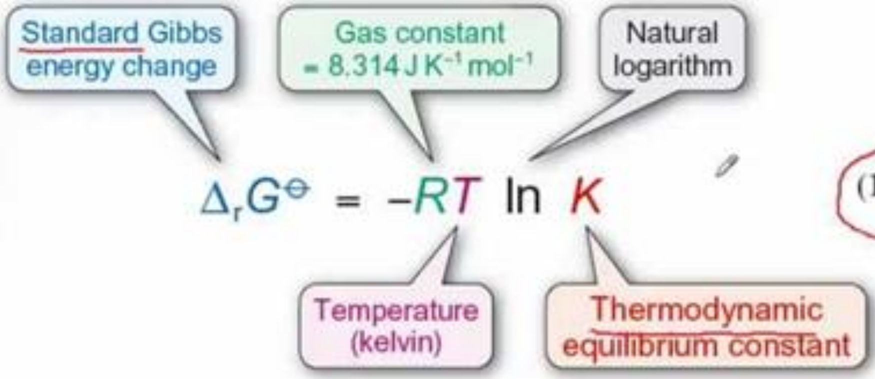
$$dH = TdS + VdP + \sum_i \mu_i dn_i,$$

$$dA = -SdT - PdV + \sum_i \mu_i dn_i,$$

$$dG = -SdT + VdP + \sum_i \mu_i dn_i,$$

where μ_i is the chemical potential defined as (for constant n_j with j≠i):

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}.$$



Standard Gibbs energy change

Gas constant = 8.314 J K⁻¹ mol⁻¹

Natural logarithm

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

Temperature (kelvin)

Thermodynamic equilibrium constant

(15.4)

$$R \rightleftharpoons P$$

$$\Delta_r G = G(\text{product}) - G(\text{reactant})$$

$$G(\text{product}) = G^\ominus(\text{product}) + RT \ln(a(\text{product}))$$

$$G(\text{reactant}) = G^\ominus(\text{reactant}) + RT \ln(a(\text{reactant}))$$

$$\Delta_r G = [G^\ominus(\text{product}) - G^\ominus(\text{reactant})] + [RT \ln(a(\text{product})) - RT \ln(a(\text{reactant}))]$$

$$\Delta_r G = \Delta_r G^\ominus + RT \ln\left(\frac{a(\text{product})}{a(\text{reactant})}\right)$$

Equilibrium & Gibbs Energy

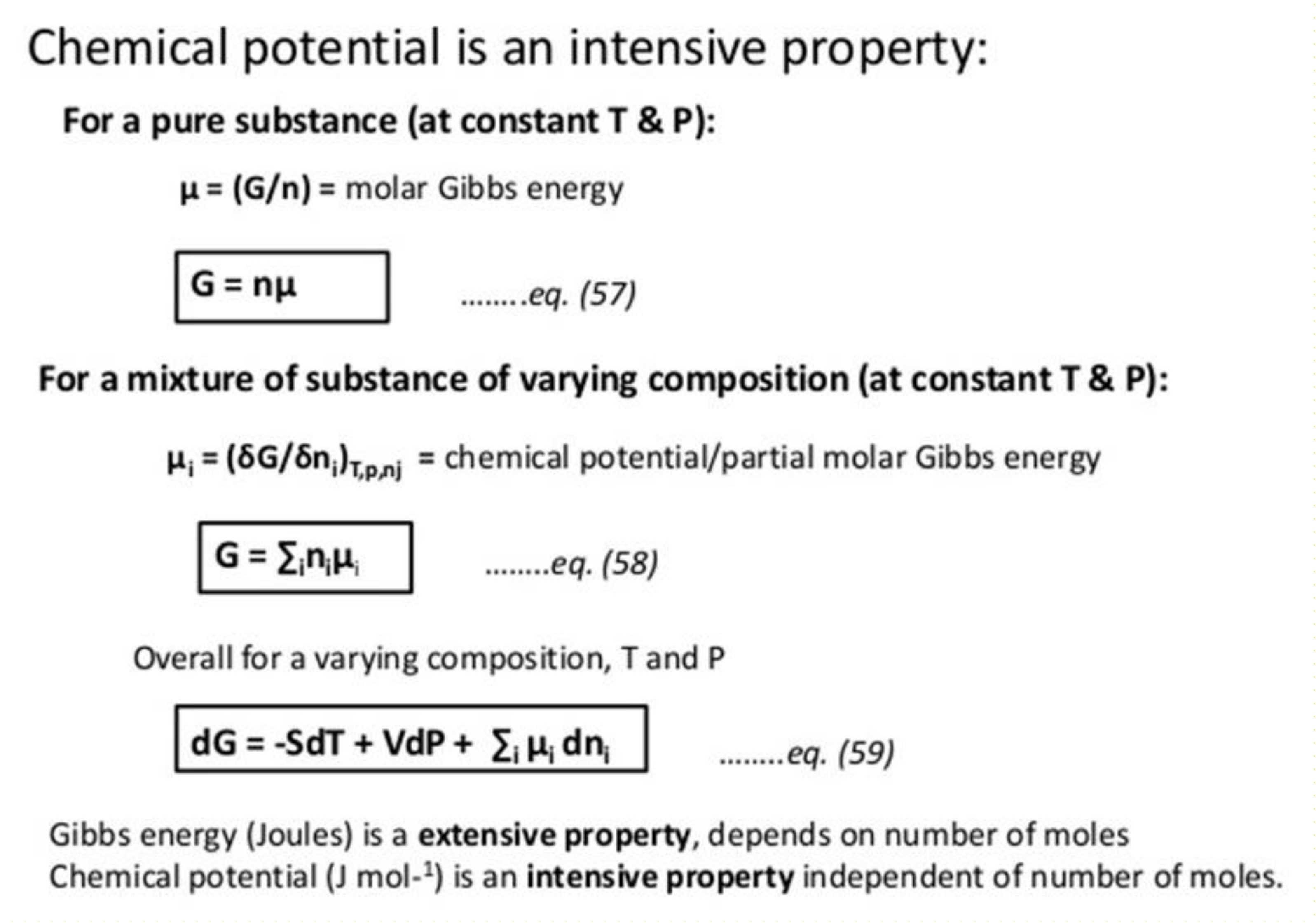
- Consider a reversible reaction taking place at constant temperature:

$$aA + bB \leftrightarrow cC + dD$$

- The reactants A and B combine to form products C and D. The concentrations of A and B decrease until they reach values that do not change with time.
- The time-invariant concentrations of reactants and products are called equilibrium concentrations
- The ratio of these concentrations (or activities –active concentrations) is characteristic for each reaction, and is called the equilibrium constant, K:

$$K \equiv \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}$$

Equilibrium & Gibbs Energy



Chemical potential is an intensive property:

For a pure substance (at constant T & P):

$\mu = (G/n)$ = molar Gibbs energy

$\boxed{G = n\mu}$ ....*eq. (57)*

For a mixture of substance of varying composition (at constant T & P):

$\mu_i = (\delta G/\delta n_i)_{T,p,nj}$ = chemical potential/partial molar Gibbs energy

$\boxed{G = \sum_i n_i \mu_i}$ ....*eq. (58)*

Overall for a varying composition, T and P

$\boxed{dG = -SdT + VdP + \sum_i \mu_i \, dn_i}$ ....*eq. (59)*

Gibbs energy (Joules) is a **extensive property**, depends on number of moles
Chemical potential (J mol-^{1}) is an **intensive property** independent of number of moles.

Free Energy and Equilibrium

The ***standard free-energy of reaction (ΔG^0_{rxn})*** is the free-energy change for a reaction when it occurs under standard-state conditions.

$$aA + bB \longrightarrow cC + dD$$

$$\Delta G^0_{rxn} = \Sigma n \Delta G^0_f \text{ (products)} - \Sigma m \Delta G^0_f \text{ (reactants)}$$

$\Delta G° < 0$ favors products spontaneously

$\Delta G° > 0$ favors reactants spontaneously

Does not tell you it will go to completion!

$$aA + bB \underset{\Delta G°_{rev}}{\overset{\Delta G°_{fwd}}{\rightleftharpoons}} cC + dD \qquad \Delta G°_{fwd} = -\Delta G°_{rev}$$

The value of $\Delta G°$ calculated under the standard conditions characterizes the "driving force" of the reaction towards equilibrium.

Gibbs Free Energy and Chemical Equilibrium

ΔG^0 describes a reaction in standard state conditions

ΔG must be used when the reaction is **not** in standard state conditions

So we derive this equation: $\Delta G = \Delta G^0 + RT\ln Q$

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature (K)

Q is the reaction quotient

At ________________________

$\Delta G = 0 \qquad Q = K$

$$0 = \Delta G^0 + RT\ln K$$

$$\Delta G^0 = -RT\ln K \longleftarrow$$

Kp for gases

Kc for reactions in solution

pp.592ff

Deriving The van’t Hoff Equation

- We know that rate constants vary with temperature.
- Considering that equilibrium constants are ratios of rate constants of the forward and back reaction, *we would also expect equilibrium constants to vary with temperature*.
- Using our relationship of the standard free energy with standard enthalpy and entropy:

$$\Delta G^{o}_{rxn} = \Delta H^{o}_{rxn} - T\Delta S^{o}_{rxn}$$

- And relating this expression to the equilibrium constant, K, we obtain:

$$-RT\ln K = \Delta H^{o} - T\Delta S^{o}$$

$$\boxed{\ln K = -\frac{\Delta H^{o}_{rxn}}{RT} + \frac{\Delta S^{o}_{rxn}}{R}}$$

Chemical equilibrium in a reaction mixture of ideal gases:

For a pure ideal gas at 298 K:

$$\mu = \mu^o + RT\ln p$$

For a mixture of ideal gases at 298 K, the chemical potential (μ_i) of the i^{th} gas:

$$\mu_i = \mu^o_i + RT\ln p_i$$

(where p_i is the partial pressure of the i^{th} gas
and μ^o_i is the chemical potential of the i^{th} gas in pure form)

Lets consider the following reaction mixture:

$$\alpha A\,(g) + \beta B\,(g) \rightarrow \gamma C\,(g) + \delta D\,(g)$$

We know that the ΔG for the reaction:

$$\Delta G = \Sigma_i \, \mu_i \, \nu_i$$

$$= \gamma\mu^o_C + \gamma RT\ln p_C + \delta\mu^o_D + \delta RT\ln p_D - \alpha\mu^o_A - \alpha RT\ln p_A - \beta\mu^o_B - \beta RT\ln p_B$$

$$\Delta G = (\gamma\mu^o_C + \delta\mu^o_D - \alpha\mu^o_A - \beta\mu^o_B) + RT\ln (p_c^{\gamma}\, p_D^{\delta}/p_A^{\alpha}\, p_B^{\beta})$$

$$\Delta G = \Delta G^o + RT\ln (p_c^{\gamma}\, p_D^{\delta}/p_A^{\alpha}\, p_B^{\beta})$$

Free Energy & the Equilibrium Constant

At equilibrium, $Q = K$ and $\Delta G = 0$, so

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$0 = \Delta G^\circ + RT \ln K.$$

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

From the above we can conclude:

If $\Delta G^\circ < 0$, then $K > 1$.
If $\Delta G^\circ = 0$, then $K = 1$.
If $\Delta G^\circ > 0$, then $K < 1$.

The real scoop: units of equilibrium constants

Equilibrium constants are *really* defined in terms of **activity**, not concentration.

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

becomes:

$$K_c = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

Activity is unitless, so K is unitless.

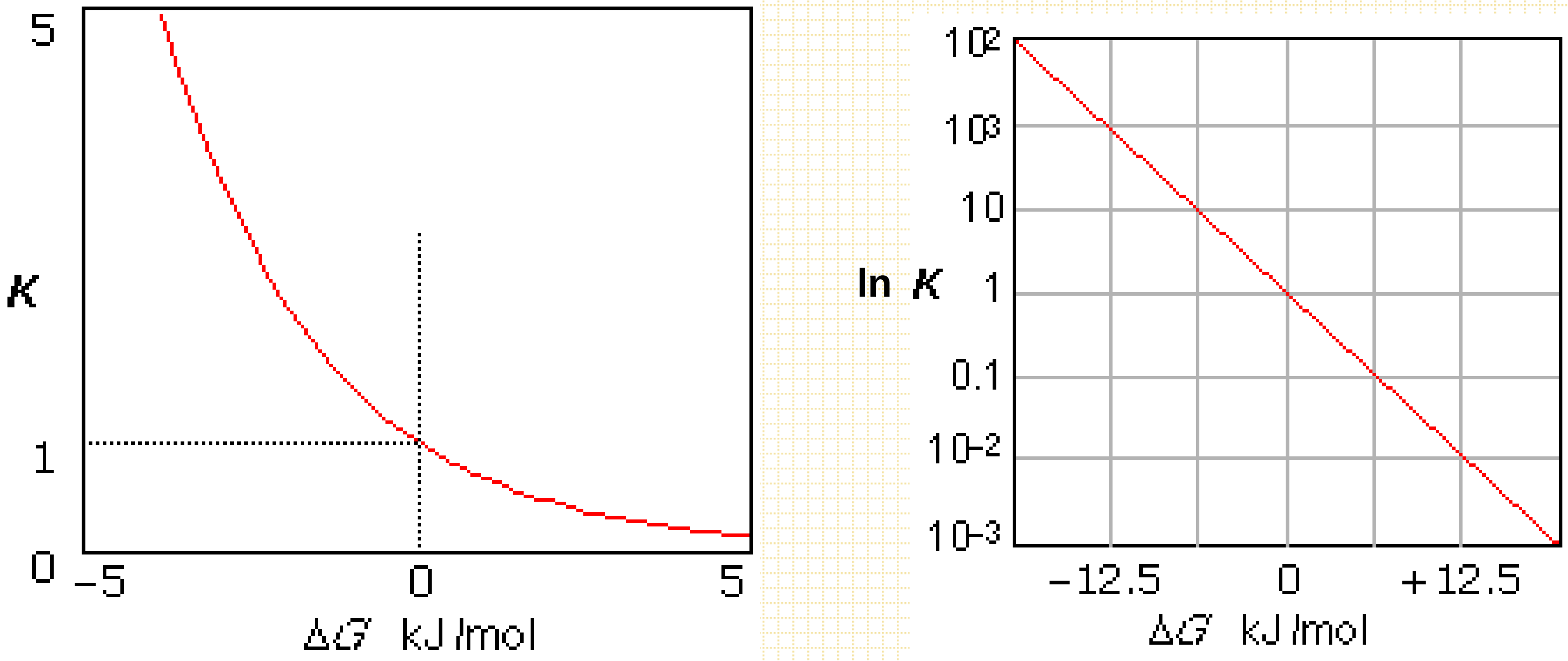
$$for\ pure\ liquids:\ a = 1.0$$

$$for\ pure\ solids:\ a = 1.0$$

$$for\ solutions:\ a_A = [A]\,\gamma$$

$$for\ dilute\ solutions:\ \gamma = 1.0\ M^{-1}$$

Relationship between ΔGº and K



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

These two plots show this relation linearly (left) and logarithmically (right). Notice that an equilibrium constant of unity implies a standard free energy change of zero, and that positive values of ΔG° lead to values of K less than unity.

Equilibrium Law for Gaseous Reactions

$$PV = nRT$$

$$\therefore P = \frac{n}{V} RT$$

$$\therefore P = [Gas]RT$$

For gaseous reactions use partial pressures, *P*, to give an equilibrium constant (K_p)

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

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \text{ OR } K_p = \frac{P_{NH_3}^2}{P_{N_2} \bullet P_{H_2}^3}$$

$$Kp = \frac{P_{NH_3}^2}{P_{N_2} \bullet P_{H_2}^3} = \frac{[NH_3]^2 (RT)^2}{[N_2](\mathrm{RT}) \bullet [H_2]^3 (RT)^3} = \frac{[NH_3]^2}{[N_2][H_2]^3} \bullet (RT)^{-2}$$

$$Kp = K_c (RT)^{\Delta n}$$

Equilibrium Constants for Gaseous Reactions

Consider the reaction: $2SO_{2(g)} + O_{2(g)} \rightleftarrows 2SO_{3(g)}$

$$K_c = \frac{[SO]^2}{[SO_2]^2[O_2]} \qquad \text{and} \quad K_p = \frac{(P_{SO3})^2}{(P_{SO2})^2(P_{O2})}$$

Assuming ideal behavior,

where **PV = nRT and P = (n/V)RT = [M]RT**

and $P_{SO3} = [SO_3]RT$; $P_{SO2} = [SO_2]RT$; $P_{O2} = [O_2]RT$

$$K_p = \frac{[SO_3]^2(RT)^2}{[SO_2]^2(RT)^2[O_2](RT)} = \frac{[SO_3]^2}{[SO_2]^2[O_2]}(RT)^{-1} = K_c(RT)^{-1}$$

Equilibrium Constants for Gaseous Reactions

- In general, for reactions involving gases such that,

$$aA + bB \rightleftarrows cC + dD$$

where A, B, C, and D are all gases, and a, b, c, and d are their respective coefficients,

$$\boldsymbol{K_p = K_c(RT)^{\Delta n}}$$

$$\boldsymbol{\{\Delta n = (c + d) - (a + b)\}}$$

(In heterogeneous systems, only the coefficients of the gaseous species are counted.)

Relationship between K_c and K_p

For other reactions:

1. $2NO_2(g) \rightleftarrows N_2O_4(g)$; $K_p = K_c(RT)^{-1}$
2. $H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$; $K_p = K_c$
3. $N_2(g) + 3H_2(g) \rightleftarrows 2\,NH_3(g)$; $K_p = K_c(RT)^{-2}$

Relationships between chemical equations and the expressions of equilibrium constants

- The expression of equilibrium constant depends on how the equilibrium equation is written. For example, for the following equilibrium:
- $H_2(g) + I_2(g) \rightleftarrows 2\ HI(g)$;

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

- For the reverse reaction:
- $2HI(g) \rightleftarrows H_2(g) + I_2(g)$;

$$K_c' = \frac{[H_2][I_2]}{[HI]^2} = 1/K_c$$

- And for the reaction: $HI(g) \rightleftarrows \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$;

$$K_c'' = \sqrt{\frac{[H_2][I_2]}{[HI]^2}} = \sqrt{K_c'} = 1/\sqrt{K_c}$$

Equilibrium Constant for Heterogeneous Reactions

$$2NaHCO_3(s) \Leftrightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

(in a sealed container)

$$K = \frac{[CO_2][H_2O][Na_2CO_3]}{[NaHCO_3]^2}$$

therefore

$$[CO_2][H_2O] = \frac{K[NaHCO_3]^2}{[Na_2CO_3]} = K_C$$

- The molar concentration of a solid or pure liquid is its density divided by molar mass.
- Neither density nor molar mass is a variable, the concentrations of solids and pure liquids are constant.

Relationship between ΔGº and K_P

$\Delta G^o = -RT \ln K_P$

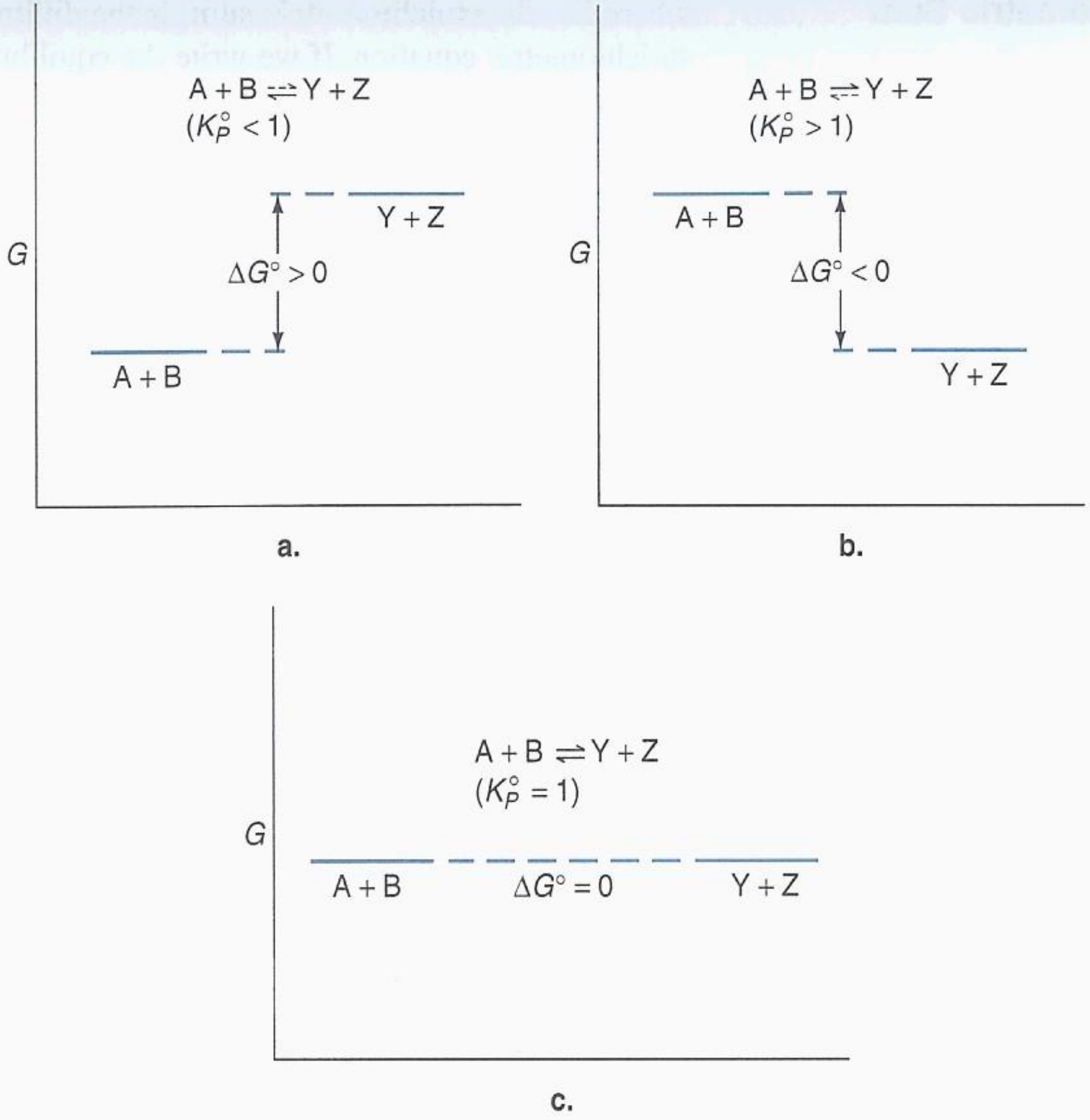
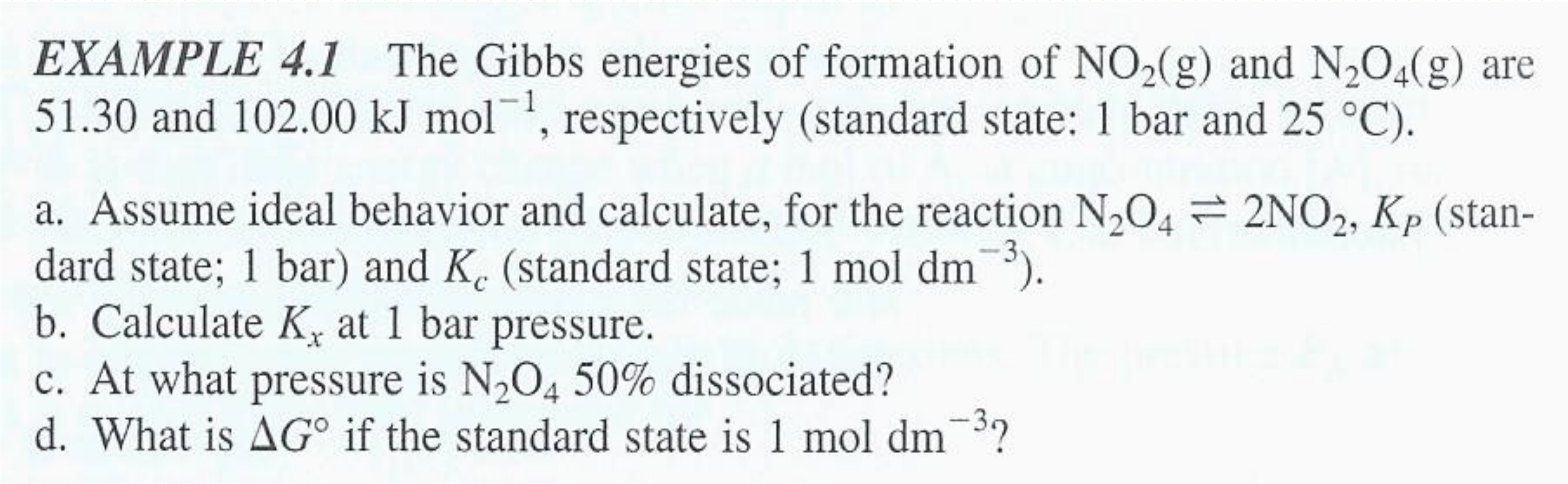


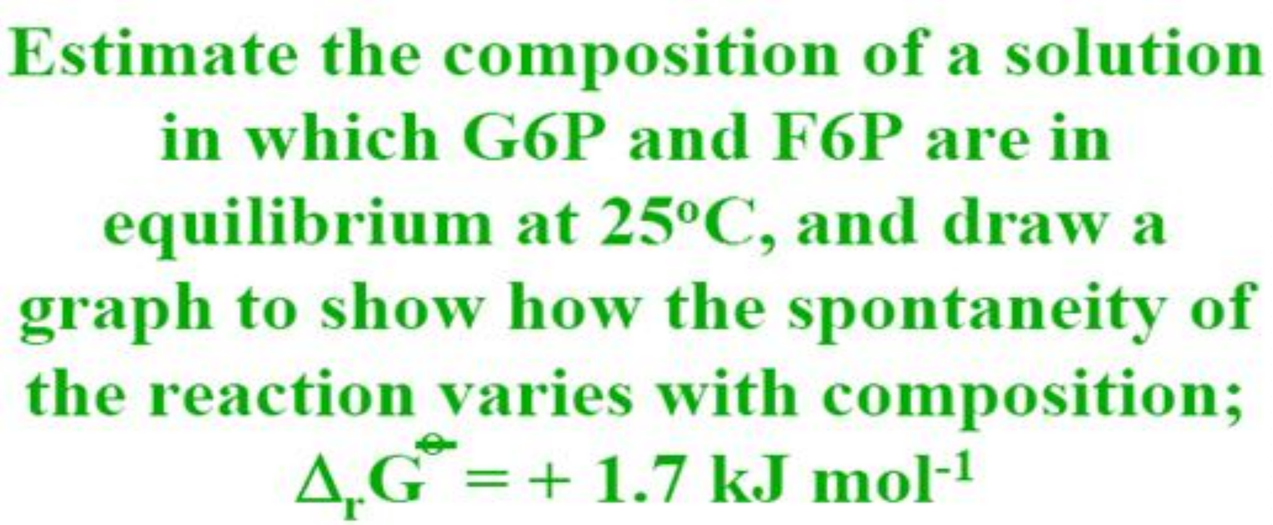
FIGURE 4.1
A standard Gibbs energy diagram, illustrating the relationship between ΔG° for a reaction and the equilibrium constant K_P.
(a) ΔG° is positive and $K_P^\circ < 1$;
(b) ΔG° is negative and $K_P^\circ > 1$;
(c) ΔG° is zero and $K_P^\circ = 1$.

Relationship between ΔGº and K_P



EXAMPLE 4.1 The Gibbs energies of formation of $NO_2(g)$ and $N_2O_4(g)$ are 51.30 and 102.00 kJ mol^{-1}, respectively (standard state: 1 bar and 25 °C).

a. Assume ideal behavior and calculate, for the reaction $N_2O_4 \rightleftharpoons 2NO_2$, K_P (standard state; 1 bar) and K_c (standard state; 1 mol dm^{-3}).
b. Calculate K_x at 1 bar pressure.
c. At what pressure is N_2O_4 50% dissociated?
d. What is $\Delta G°$ if the standard state is 1 mol dm^{-3}?



Estimate the composition of a solution in which G6P and F6P are in equilibrium at 25°C, and draw a graph to show how the spontaneity of the reaction varies with composition; $\Delta_r G^{\ominus} = +1.7$ kJ mol^{-1}

Examples on Reaction Equilibria Types

Homogeneous equilibria:

$CH_4(g) + H_2O(g) \rightleftarrows CO(g) + 3H_2(g)$;

$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$;

$HF(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + F^-(aq)$;

Heterogeneous equilibria:

$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$;

$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2\ Cl^-(aq)$;

Test for Chemical Equilibrium

For a chemical reaction of the form:

$$aA + bB \rightleftharpoons yY + zZ$$

The equilibrium constant is given by:

$$K_C = \frac{[Y]^y [Z]^z}{[A]^a [B]^b}$$

One of the most difficult task, especially for extremely slow reaction, is to tell whether a reaction is at equilibrium or not.

Example : $2H_2 + O_2 \rightarrow 2H_2O$

Two practical ways to test for the equilibrium condition:

1. Adding catalysts: Catalysts don't change the position of the equilibrium, but they increase the reaction rate and accelerate its approach to equilibrium.

2. Adding a small amount of a reactant or a product and observe the change in the reaction course.

Shifts of Chemical Equilibrium

Consider the production of ammonia

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

- As the pressure increases, the amount of ammonia present at equilibrium increases.
- As the temperature decreases, the amount of ammonia at equilibrium increases.

Le Châtelier’s Principle: if a system at equilibrium is disturbed, the system will move in such a way as to counteract the disturbance.

Shifts of Chemical Equilibrium

Effects of Volume and Pressure Changes

1. As volume is decreased pressure increases.
2. If pressure is increased the system will shift to counteract the increase. That is, the system shifts to remove gases and decrease pressure.
3. An increase in pressure favors the direction that has fewer moles of gas.
4. In a reaction with the same number of product and reactant moles of gas, ***pressure has no effect.***

Shifts of Chemical Equilibrium

Effects of Volume and Pressure Changes

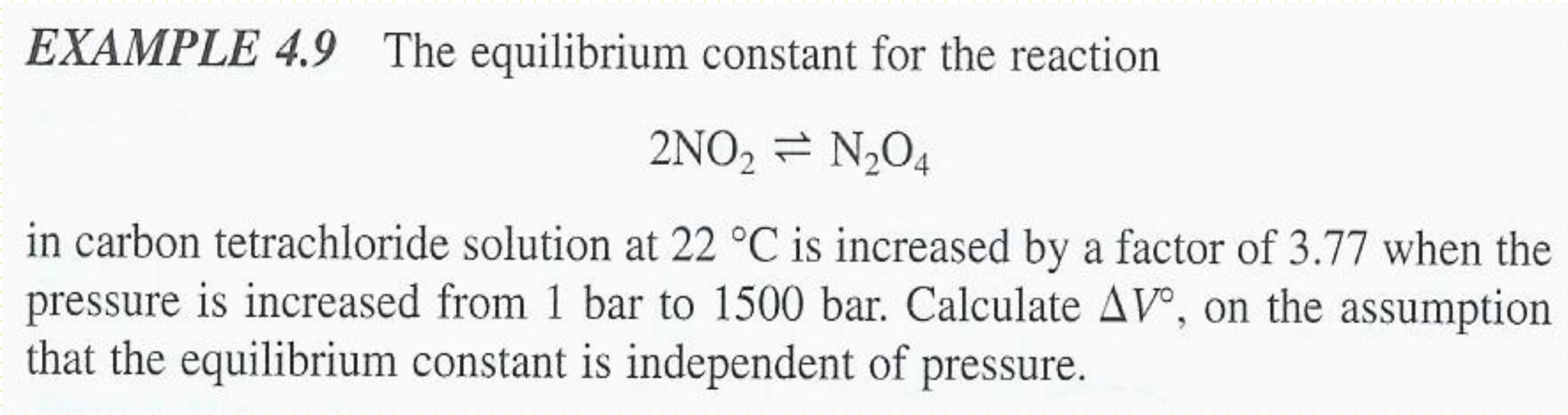
Example:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

- An increase in pressure (decreasing the volume) favors the formation of colorless N_2O_4.
- The system moves to reduce the number moles of gas (i.e. backward reaction is favored).

$P \propto 1/V$ and $V \propto n$ thus $P \propto 1/n$

Dependence of Equilibrium Constant on Pressure



EXAMPLE 4.9 The equilibrium constant for the reaction

$$2NO_2 \rightleftharpoons N_2O_4$$

in carbon tetrachloride solution at 22 °C is increased by a factor of 3.77 when the pressure is increased from 1 bar to 1500 bar. Calculate $\Delta V°$, on the assumption that the equilibrium constant is independent of pressure.

Sample problem 2:

In an industrial process N_2 at 1 bar is mixed with H_2 at 3 bar and the two gases are allowed to reach equilibrium with the product ammonia in a reactor of constant volume. At the temperature of the reaction, K = 977. What are the equilibrium partial pressures of the three gases?

Shifts of Chemical Equilibrium

Change in Reactant or Product Concentrations

Consider the rxn: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

1. If H_2 is added while the system is at equilibrium, the system must respond to counteract the added H_2 .
2. The system must consume the H_2 and produce products until a new equilibrium is established.
3. So, $[H_2]$ and $[N_2]$ will decrease and $[NH_3]$ increases.

In General:

- Adding a reactant or product shifts the equilibrium *away from the increase.*
- Removing a reactant or product shifts the equilibrium *towards the decrease.*

Shifts of Chemical Equilibrium

Effect of Temperature Changes

- The equilibrium constant is temperature dependent.
- For an endothermic reaction, $\Delta H > 0$ and heat can be considered as a reactant.
- For an exothermic reaction, $\Delta H < 0$ and heat can be considered as a product.

Shifts of Chemical Equilibrium

Effect of Temperature Changes

- Adding heat (i.e. heating the vessel) favors away from the increase:
  - if **ΔH > 0**, adding heat favors the forward reaction,
  - if **ΔH < 0**, adding heat favors the reverse reaction.

- Removing heat (i.e. cooling the vessel), favors towards the decrease:
  - if **ΔH > 0**, cooling favors the reverse reaction,
  - if **ΔH < 0**, cooling favors the forward reaction.

Temperature Dependence of K_P

$$\frac{\partial \ln K_P}{\partial T}\bigg|_P = \frac{\partial}{\partial T}\left(\frac{-\Delta G^o}{RT}\right) = \frac{\Delta H^o}{RT^2}$$ van't Hoff's equation (differential form)

If we can assume that ΔHº is independent of temperature then we can integrate this equation to give

$$\ln\left(\frac{K_P(T_2)}{K_P(T_1)}\right) = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ van't Hoff's equation (integrated form)

This result indicates that for exothermic reactions increasing the temperature, decreases K_P and vice versa for endothermic reactions.

Van't Hoff Equation

$$\frac{d\ln K_P^\circ}{d(1/T)} = -\frac{\Delta H^\circ}{R}$$

Dependence of Equilibrium Constant on Temperature

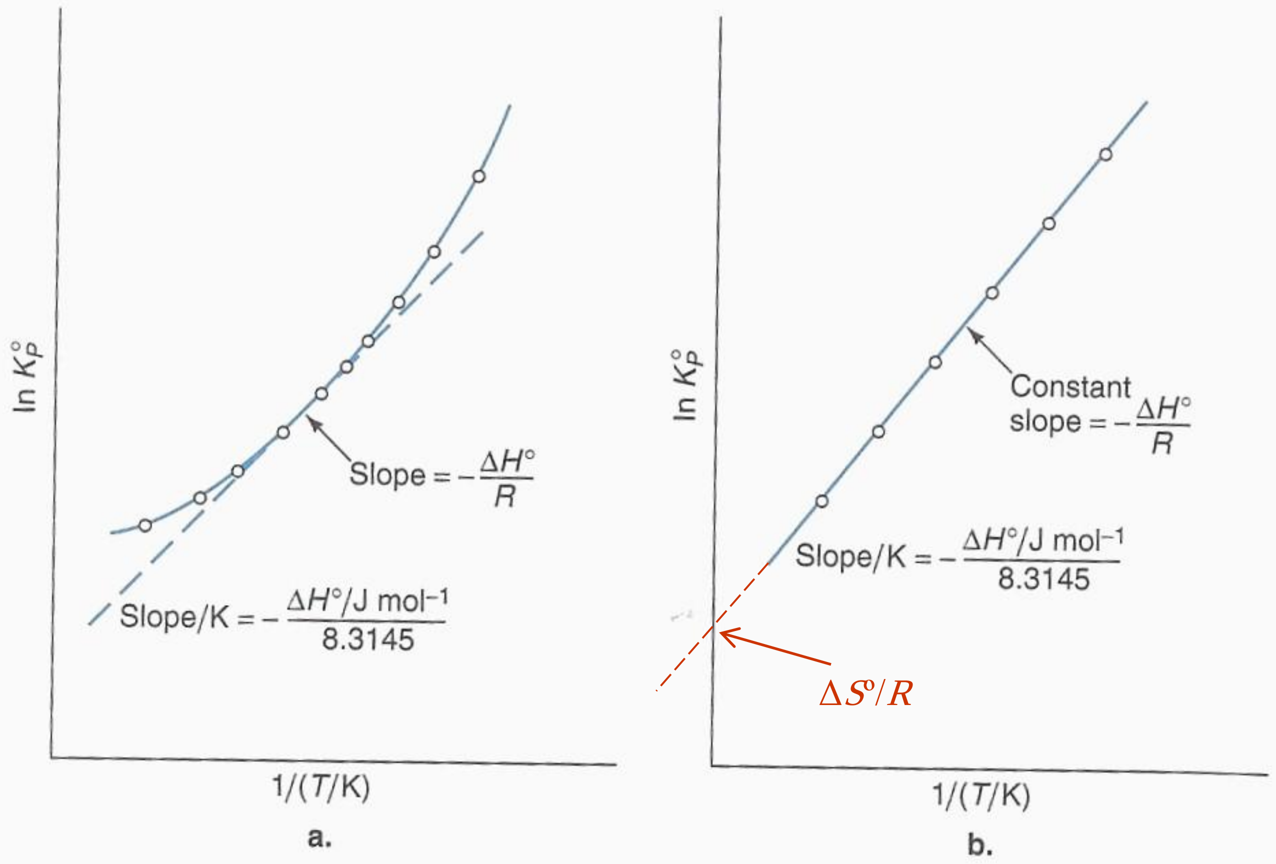


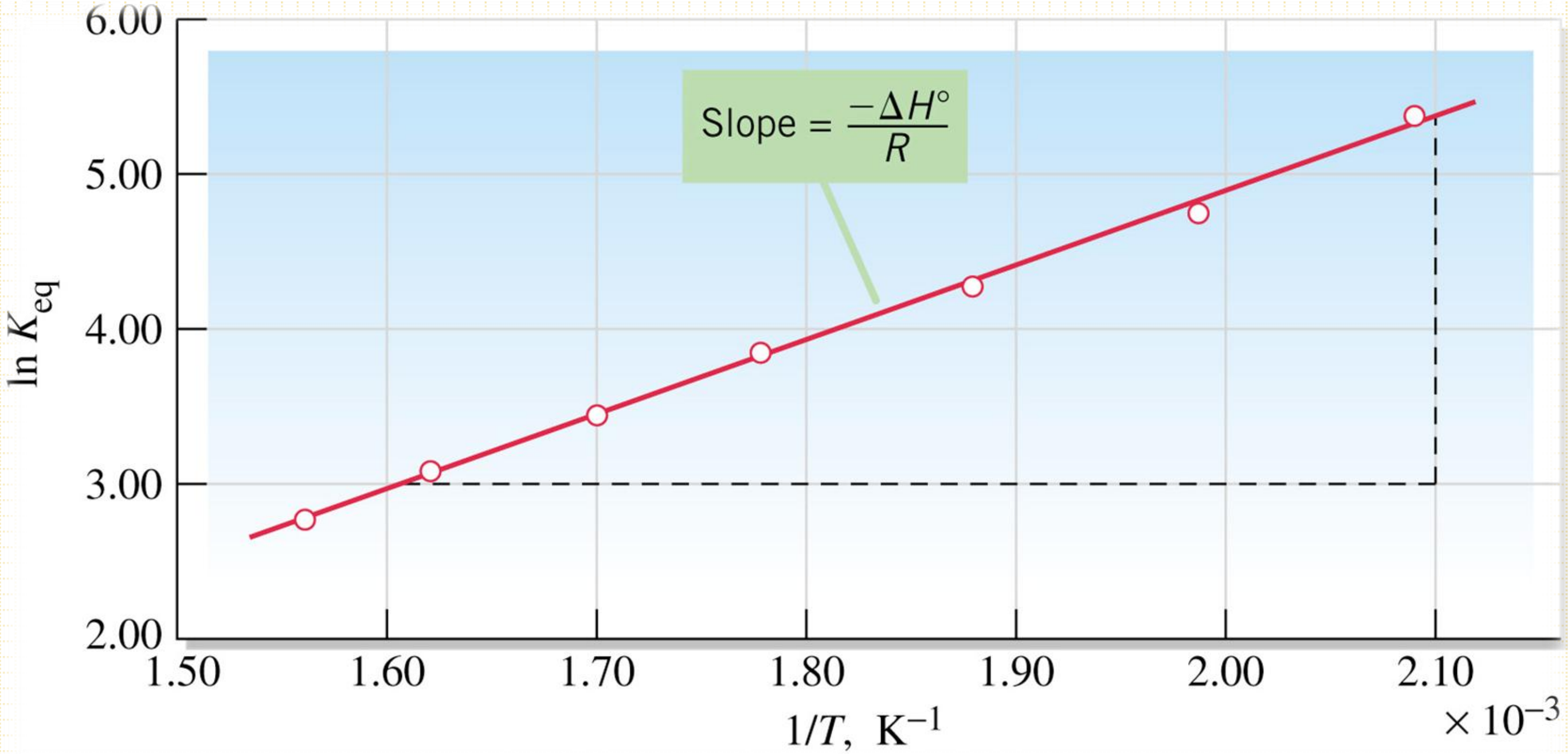
FIGURE 4.2
Schematic plots of ln K_P° against 1/*T*. (a) ΔH° is temperature dependent; (b) ΔH° is independent of temperature, in which case Eq. 4.76 applies.

Example

Consider this reaction at 298 K:

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $\Delta H^\circ_{298} = -41.2\text{ kJ}$

Determine K_{eq} for the reaction at 725 K.



Equilibrium Constant K_c

$$aA_{(aq)} + bB_{(aq)} \rightleftharpoons cC_{(aq)} + dD_{(aq)}$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Conc of product and reactant at equilibrium

Equilibrium expression HOMOGENEOUS gaseous rxn

$$4NH_{3(g)} + 5O_{2(g)} \leftrightarrow 4NO_{(g)} + 6H_2O_{(g)}$$

$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

$$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$$

$$K_c = \frac{[NH_3]^2}{[N_2]^1[H_2]^3}$$

$$2SO_{2(g)} + O_{2(g)} \leftrightarrow 2SO_{3(g)}$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]^1}$$

Equilibrium expression HOMOGENEOUS liquid rxn

→ Reactant/product same phase

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \leftrightarrow CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

$$K_c = \frac{[CH_3COOC_2H_5]^1[H_2O]^1}{[CH_3COOH]^1[C_2H_5OH]^1}$$

Equilibrium expression HETEROGENOUS rxn

→ Reactant/product diff phase

$$NH_4Cl_{(s)} \leftrightarrow NH_{3(g)} + HCl_{(g)}$$

$$K_c = \frac{[NH_3]^1[HCl]^1}{[\cancel{NH_4Cl}]^0}$$

$$K_c = [NH_3]^1[HCl]^1$$

$$CaCO_{3(s)} \leftrightarrow CaO_{(g)} + CO_{2(g)}$$

$$K_c = \frac{[CaO]^1[CO_2]^1}{[\cancel{CaCO_3}]^0}$$

$$K_c = [CaO]^1[CO_2]^1$$

$$Cu^{2+}{}_{(aq)} + 4NH_{3(aq)} \leftrightarrow [Cu(NH_3)_4]^{2+}$$

$$K_c = \frac{[\,[Cu(NH_3)_4]^{2+}\,]}{[Cu^{2+}]^1[NH_3]^4}$$

Van't Hoff Equation

Relationship bet Temp and K_c

Gibbs free energy change — Equilibrium constant

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

Gibbs free energy change

Enthalpy change — Entropy change

$$\Delta G^{\theta} = \Delta H - T\Delta S$$

$$-RT\ln K = \Delta H - T\Delta S$$

$$\downarrow$$

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\downarrow$$

$$\ln K = -\frac{\Delta H}{RT} + c$$

$H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$ $\Delta H = -9.6\,kJmol^{-1}$

Temp/K	345	385	500	700
K_c	1000	31.6	0.035	0.00007

$H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$ $\Delta H = -9.6\,kJmol^{-1}$

$\ln K_c$	6.9	3.45	-3.3	-9.5
$1/T(\times 10^{-3})$	2.9	2.6	2	1.4

! ΔH=-ve

$$K_c = e^{-\frac{\Delta H}{RT}}$$

Plot K_c against Temp

Temp increase ↑ – K_c decrease ↓

$$\ln K = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + c$$

Plot ln K_c against 1/T

Using K_c and Temp to find ΔH

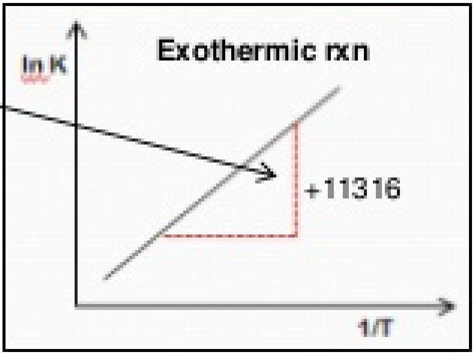
$$Gradient = -\frac{\Delta H}{R}$$

$$\downarrow$$

$$+11316 = -\frac{\Delta H}{8.31}$$

$$\downarrow$$

$$\Delta H = -94000J$$ ✓



Conclusion → **Exo rxn =-ΔH** → **Temp increase ↑** → **K_c decrease ↓** → **Relationship bet Temp, K_c and ΔH** ✓

Integrated van't Hoff Equation with constant $\Delta_r H^o$

$$\frac{d(\ln K)}{dT} = \frac{\Delta_r H^o}{RT^2} \longrightarrow \int d\ln K = \int \frac{\Delta_r H^o}{RT^2}\,dT = \frac{\Delta_r H}{R}\int \frac{1}{T^2}\,dT$$

This integrates to: $\ln K = -\dfrac{\Delta_r H^o}{RT} + C$

Identification of the Integration Constant, C

$$\Delta_r G^o = -RT\ln K = \Delta_r H^o - T\Delta_r S^o$$

$$\ln K = \frac{\Delta_r H^o - T\Delta_r S^o}{-RT} = -\frac{\Delta_r H^o}{RT} + \frac{\Delta_r S}{R}$$

In a plot of lnK vs. 1/T, (a) the slope is $-\Delta_r H/R$

(b) the intercept is $+\Delta_r S/R$

Shifts of Chemical Equilibrium

The Effect of Catalysts

- A catalyst lowers the activation energy barrier for the reaction.
- Therefore, a catalyst will *decrease the time taken to reach equilibrium.*
- A catalyst does not affect the composition of the equilibrium mixture or the value of equilibrium constant.

Effect of Temperature on Equilibrium

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

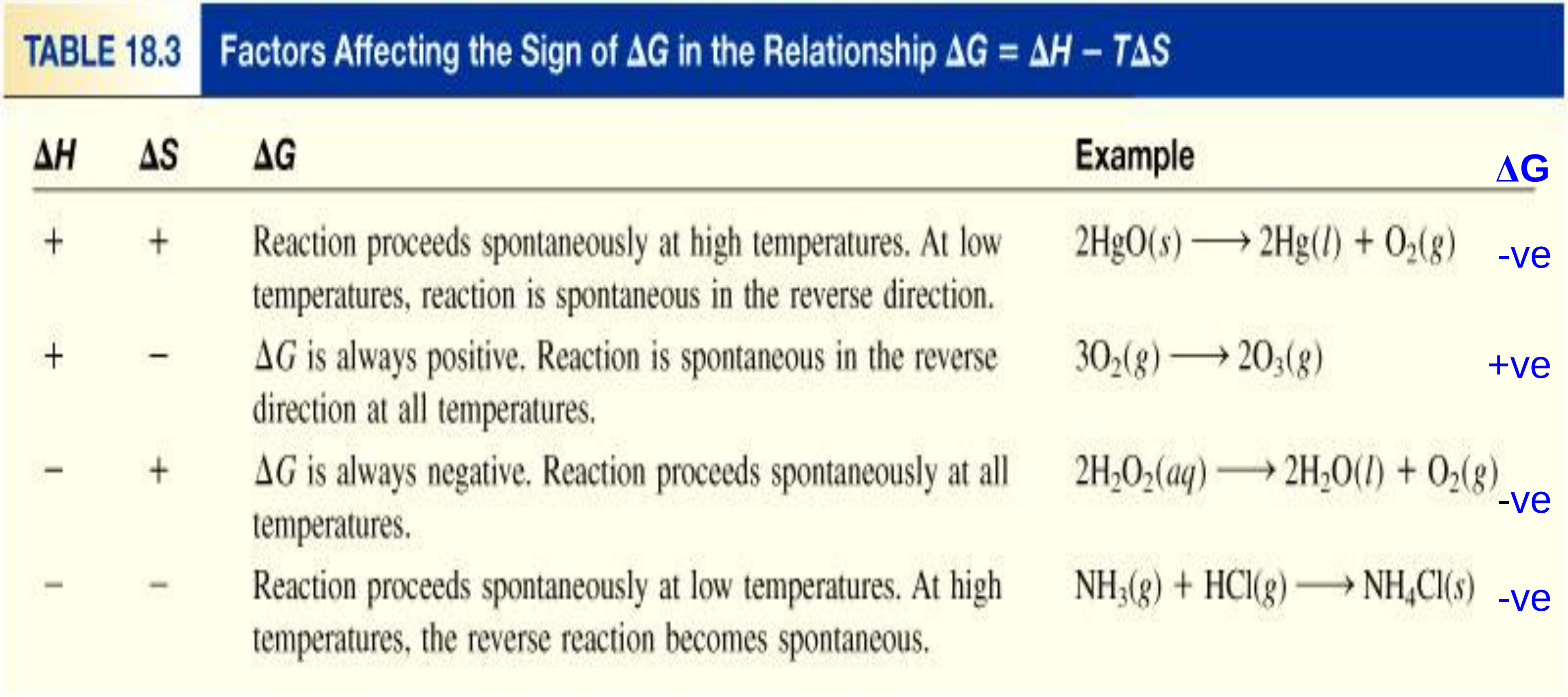


TABLE 18.3 Factors Affecting the Sign of ΔG in the Relationship $\Delta G = \Delta H - T\Delta S$

ΔH	ΔS	ΔG	Example	ΔG
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$	-ve
+	−	ΔG is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3O_2(g) \longrightarrow 2O_3(g)$	+ve
−	+	ΔG is always negative. Reaction proceeds spontaneously at all temperatures.	$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$	-ve
−	−	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$	-ve

Reaction Spontaneity
& Temperature Changes

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

All of the four possible choices of signs for ΔH^o and ΔS^o give different temperature behaviors for ΔG^o.

ΔH^o	ΔS^o	ΔG^o	Description
–	+	–	Spontaneous at all T
+	–	+	Non-spontaneous at all T
–	–	+ or –	Spontaneous at low T; Non-spontaneous at high T
+	+	+ or –	Non-spontaneous at low T; Spontaneous at high T

Examples:

Several channels of the reaction between CO and H_2 at 300K

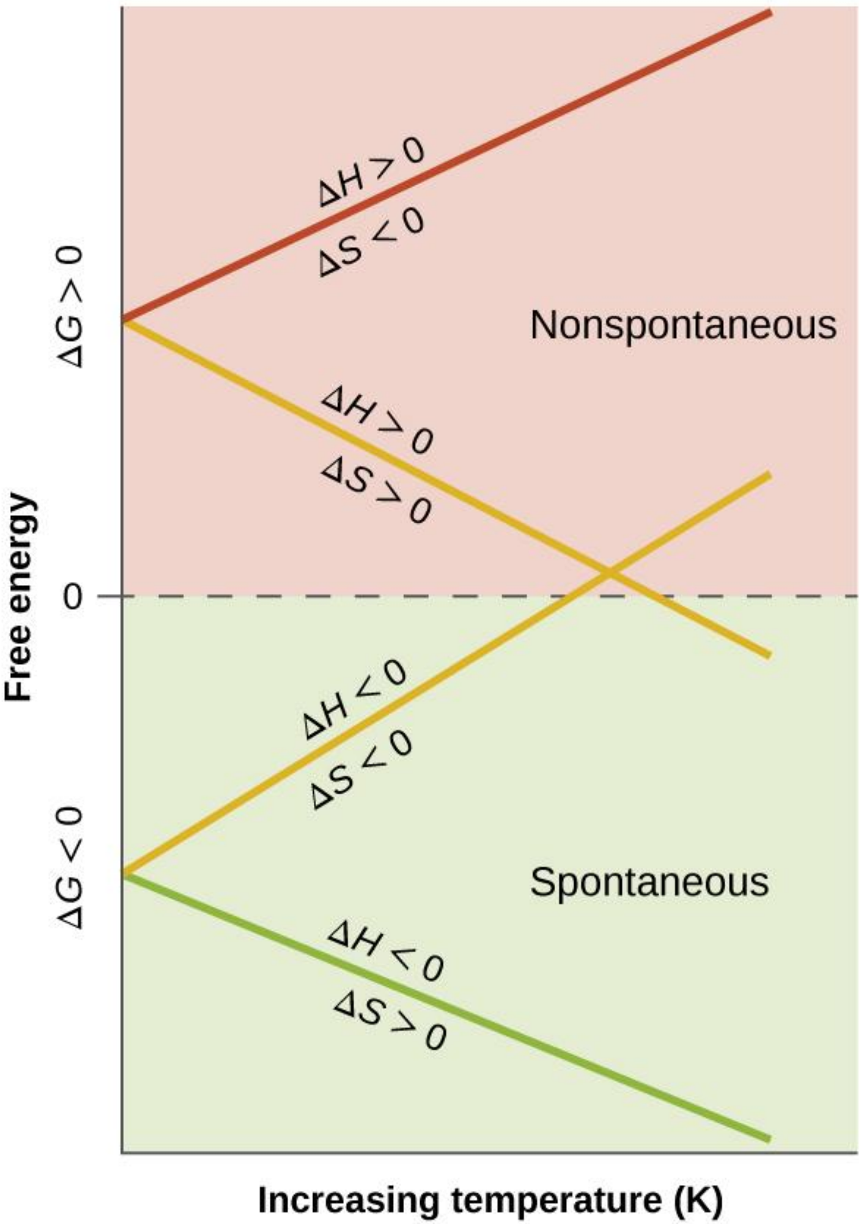
reaction	ΔH kJ/mol	$-T\,\Delta S$ kJ/mol	ΔG kJ/mol
$CO+H_2 \rightarrow C+H_2O$	-130	+39	-91
$CO+2H_2 \rightarrow CH_3OH$	-85	+65	-20
$2CO+2H_2 \rightarrow CH_3COOH$	-257	+147	-110

Several channels of the reaction between CO and H_2 at 600K

reaction	ΔH kJ/mol	$-T\,\Delta S$ kJ/mol	ΔG kJ/mol
$CO+H_2 \rightarrow C+H_2O$	-130	+78	-52
$CO+2H_2 \rightarrow CH_3OH$	-85	+130	45
$2CO+2H_2 \rightarrow CH_3COOH$	-257	+394	137

at this **T**, **CH_3OH** and **CH_3COOH** will spontaneously dissociate

These estimates tell us nothing about the ***reaction rate*** ! (the process of transformation of diamond into graphite also corresponds to negative ΔG = -2.9 kJ/mol, but our experience tells us that this process is extremely slow).


ΔH > 0
ΔS < 0
Nonspontaneous
ΔH > 0
ΔS > 0
ΔG > 0
Free energy
0
ΔH < 0
ΔS < 0
ΔG < 0
Spontaneous
ΔH < 0
ΔS > 0
Increasing temperature (K)

Factors affecting “K”: Summary

1. Temperature is the ONLY factor that actually changes *the value of K*.
2. Change in total pressure can shift the equilibrium in the forward or backward direction depending on the stoichiometry of reaction (# of moles of gas in both sides).
3. Adding or removing materials only shift equilibrium forward or backward. K remains constant.
4. Catalyst speeds the reaction to reach equilibrium quickly. *It does not affect the value of K.*

A Problem To Consider

Find the value for the equilibrium constant, K, at 25°C (298 K) for the following reaction. The standard free-energy change, ΔG°, at 25°C equals –13.6 kJ.

$$2NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$$

Substituting numerical values into the equation,

$$\ln K = \frac{-13.6 \times 10^3\ \mathrm{J}}{-8.31\ \mathrm{J/(mol \cdot K)} \times 298\ \mathrm{K}} = 5.49$$

$$K = e^{5.49} = 2.42 \times 10^2$$