Location and shape of phase boundary

One component (pure) system
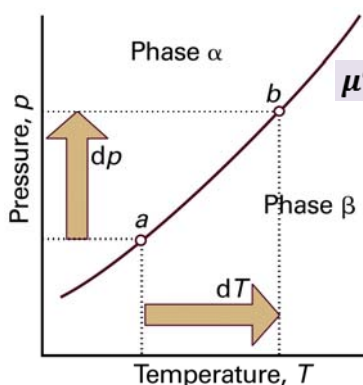
At point 'a' $\mu^\alpha(T,p) = \mu^\alpha(T,p)$

At point 'b'

$$\mu^\alpha(T + dT, p + dp) = \mu^\beta(T + dT, p + dp)$$

$$\mu^\alpha(T,p) + d\mu^\alpha = \mu^\beta(T,p) + d\mu^\beta$$

$$d\mu^\alpha = d\mu^\beta \qquad d\mu^i = -S_m^{\ i} dT + V_m^{\ i} dp$$

$$-S_m^\alpha dT + V_m^\alpha dp = -S_m^\beta dT + V_m^\beta dp$$

$$\frac{dp}{dT} = \frac{\left(S_m^\alpha - S_m^\beta\right)}{\left(V_m^\alpha - V_m^\beta\right)} \qquad \frac{dp}{dT} = \frac{\Delta S_{\beta\to\alpha}}{\Delta V_{\beta\to\alpha}}$$

Phase α

Phase β

b

a

dp

dT

Pressure, p

Temperature, T

Figure 4-12
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The Clapeyron Equation $\dfrac{dp}{dT} = \dfrac{\Delta S_{trans}}{\Delta V_{trans}}$

Applies to any phase equilibrium of any pure substance

Solid to Liquid Phase Boundary

If T_1 is melting point at p_1, and T_2 at p_2

$$\frac{dp}{dT} = \frac{\Delta S_{trs}}{\Delta V_{trs}} = \frac{\Delta H_{fus}}{T\Delta V_{fus}}$$

$$\int_{p_1}^{p_2} dp = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta p = \frac{\Delta H_{\text{fus}}}{\Delta V_{\text{fus}}} \ln \frac{T_2}{T_1}$$

$$\text{for, } T_2 \approx T_1, \ln\frac{T_2}{T_1} = \ln\left(1 + \frac{T_2 - T_1}{T_1}\right) \approx \frac{T_2 - T_1}{T_1} = \frac{\Delta T}{T_1}$$

$$\Delta p = \frac{\Delta H_{\text{fus}}}{T_1 \Delta V_{\text{fus}}} \Delta T$$

$$\Delta T = \frac{T_1 \Delta V_{\text{fus}}}{\Delta H_{\text{fus}}} \Delta p$$

Solid

Liquid

(T_2, p_2)

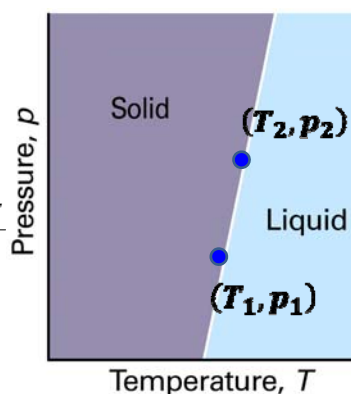(T_1, p_1)

Pressure, p

Temperature, T

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Melting point varies linearly with pressure

Liquid to Vapor Phase Boundary $\dfrac{dp}{dT} = \dfrac{\Delta S_{trs}}{\Delta V_{trs}} = \dfrac{\Delta H_{vap}}{T\Delta V_{vap}}$

$\Delta V_{vap} = V_m (g) - V_m (l) \cong V_m (g) = RT/p$ **(for ideal gas)**
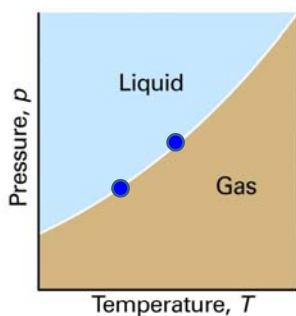

Liquid
Gas
Pressure, p
Temperature, T

Figure 4-14
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$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{TV_m} = \frac{\Delta H_{vap}}{T\,(RT)/p}$$

$$\frac{dp}{p}\frac{1}{dT} = \frac{\Delta H_{vap}}{RT^2} \qquad \text{(for ideal gas)}$$

$$\frac{d\ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

$$\int_{\ln p_1}^{\ln p_2} d\ln p = \frac{\Delta H_{vap}}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$\ln\frac{p_2}{p_1} = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\frac{d\ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

Clausius -Clapeyron Equation

Solid to Vapor Phase Boundary $\dfrac{dp}{dT} = \dfrac{\Delta S_{trs}}{\Delta V_{trs}} = \dfrac{\Delta H_{sub}}{T\Delta V_{sub}}$

$\Delta V_{sub} = V_m (g) - V_m (s) \cong V_m (g) = RT/p$ **(for ideal gas)**

$$\frac{d\ln p}{dT} = \frac{\Delta H_{sub}}{RT^2}$$

$$\ln\frac{p_2}{p_2} = -\frac{\Delta H_{sub}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$p_2 = p_1\exp(-\xi),$$

$$\xi = \frac{\Delta H_{sub}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$= \frac{\Delta H_{fus}+\Delta H_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Liquid
Solid
Gas
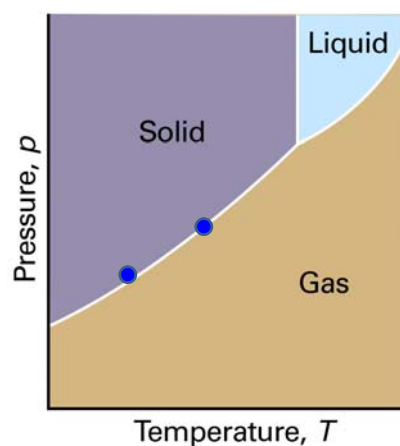Pressure, p
Temperature, T

Figure 4-15
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Location and shape of phase boundary
One component (pure) system

| Clapeyron Equation |

$$\frac{dp}{dT} = \frac{\Delta S_{\text{trs}}}{\Delta V_{\text{trs}}}$$

Solid to Liquid Phase Boundary

$$\frac{dp}{dT} = \frac{\Delta S_{\text{trs}}}{\Delta V_{\text{trs}}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}} \Delta V_{\text{fus}}}$$

Liquid to Vapor Phase Boundary

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{T V_m} = \frac{\Delta H_{\text{vap}}}{T(RT)/p}$$

| Clausius -Clapeyron Equation |

$$\frac{d\ln p}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}$$

For Solid to Vapor

$$\frac{d\ln p}{dT} = \frac{\Delta H_{\text{sub}}}{RT^2} = \frac{\Delta H_{\text{fus}} + \Delta H_{\text{vap}}}{RT^2}$$

Problem

Ice melts at 273 K at 1.0 bar.

$$\Delta H_{fus} = +6.008 \ kJ \ mol^{-1} \qquad \Delta V_{fus} = -1.613 \ m^3 \ mol^{-1}$$

The blade is 30 cm long and 0.03 cm wide. What is the pressure exerted by each blade on ice by a 50 kg skater?

Area of each blade in contact with ice = $9 \times 10^{-5} \ m^2$

Assume, weight on each leg = 25 kg

Pressure on each blade = $\dfrac{(25.0 \ kg) \times (9.8 \ m \ s^{-2})}{(9 \times 10^{-5} \ m^2)}$

$$= 27.2 \times 10^5 \ J \ m^{-3}$$

Ice skating shoe
©amazon.co.uk

$$\Delta T = \frac{T_1 \Delta V_{fus}}{\Delta H_{fus}} \Delta p \qquad \boxed{\Delta T = -1.92 \ K}$$

Temperature Dependence of Chemical Potential

$$dG = Vdp - SdT$$
$$d\mu = V_m dP - S_m dT$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S_m$$

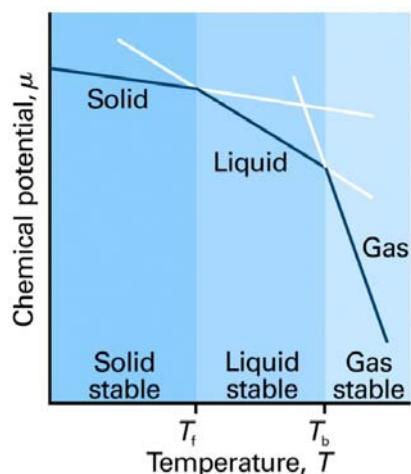$$S_m(\text{solid}) < S_m(\text{liquid}) \ll S_m(\text{gas})$$

Figure 4-9
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(isothermal) Pressure dependence of Chemical Potential

$$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \int_{G_1}^{G_2} dG = \int_{P_1}^{p_2} Vdp \qquad G_2 = G_1 + \int_{p_1}^{p_2} Vdp$$

for one component system, $\qquad \mu_2(T) = \mu_1(T) + \int_{P_1}^{p_2} V_m dp$

Case 1: liquid or solid; V weakly dependent on p

$$\mu_2(T) = \mu_1(T) + V_m(p_2 - p_1) \qquad \text{for one component system}$$

Case 2: ideal gas; V is dependent on p,

$$\mu_2(T) = \mu_1(T) + RT \ln \frac{p_2}{p_1}$$

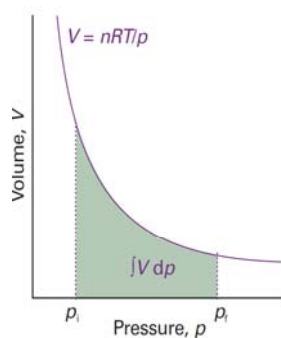$$\mu(T) = \mu^o(T) + RT \ln \frac{p}{p^o}$$

$$\mu(T) = \mu^o(T) + RT \ln p$$

μ^o = standard chemical potential, the chemical potential of the pure gas **at 1 bar** at temp T.
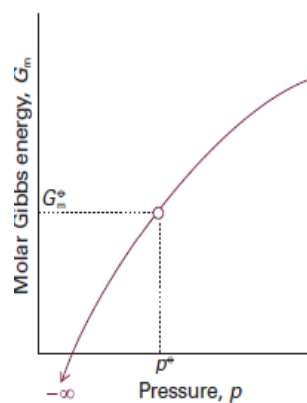
p expressed in bar.

Chemical Potential of an ideal gas
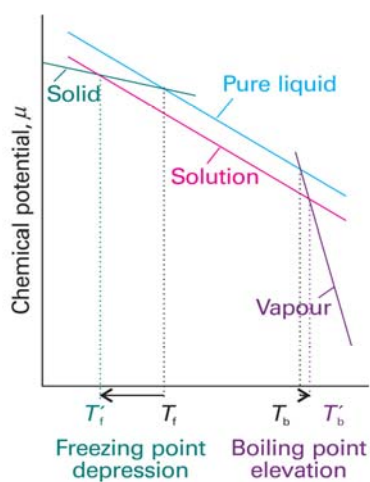
$$\mu_2 = \mu_1 + \int_{p_1}^{p_2} V_m dp$$
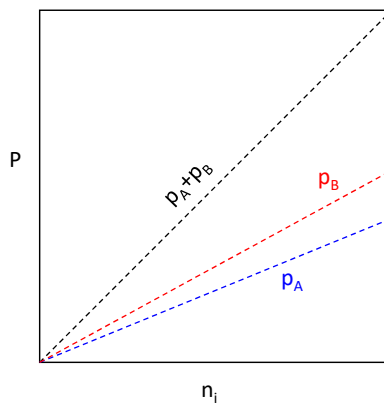
$$\mu(T) = \mu^o(T) + RT \ln \frac{p}{p^o}$$

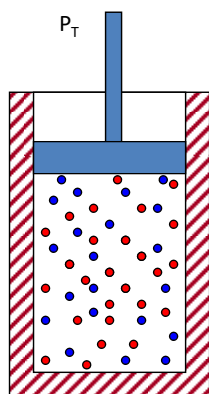## Effect of solute on boiling and melting points of solvent

$$\mu_A = \mu_A^* + RT \ln x_A$$

$$\mu_A = \mu_A^* + RT \ln a_A$$

Mixtures of ideal gases

P_T

$P = p_A + p_B$

Dalton's Law of partial pressures

If the gases are "ideal", then: $\quad p_A = x_A P \qquad p_B = x_B P$

where: $\qquad x_A = \dfrac{n_A}{n} \qquad\qquad x_B = \dfrac{n_B}{n}$

The Gibbs Energy of Mixing of Ideal Gases

$$\mu_i(T) = \mu_i^{\,o}(T) + RT \ln p_i$$

p_i = partial pressure of ith gas in bar.

Before mixing:

$$G_{\text{before mixing}} = \sum_i n_i \left(\mu_i^{\,o}(T) + RT \ln p \right)$$

After mixing:

$$G_{\text{mixture}} = \sum_i n_i \mu_i = \sum_i n_i \left(\mu_i^{\,o}(T) + RT \ln p_i \right)$$

$$= \sum_i n_i \left(\mu_i^{\,o}(T) + RT \ln x_i\, p \right)$$

Dalton's law of partial pressure, $p_i = x_i p$
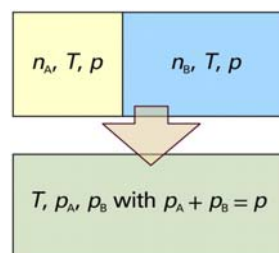
$n_A, T, p \qquad n_B, T, p$

T, p_A, p_B with $p_A + p_B = p$

$$\boxed{\Delta G_{mix} = nRT \sum_i x_i \ln x_i}$$

Gibbs free energy of mixing of ideal gases is always negative, and hence spontaneous

The Enthalpy of Mixing of Ideal Gases

$$\Delta G_{mix} = nRT \sum_i x_i \ln x_i$$

$$\Delta S_{mix} = -\left(\frac{\partial(\Delta G_{mix})}{\partial T}\right)_{p,n} = -nR \sum_i x_i \ln x_i$$

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} = 0$$

Ideal gases show no intermolecular interactions and
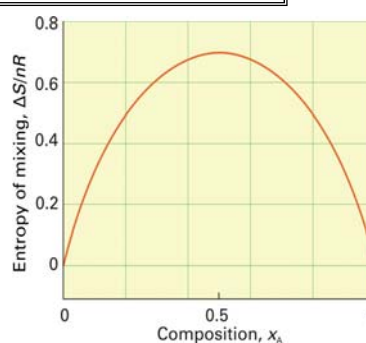hence change in enthalpy is zero

Gas mixtures

Perfect gases mix spontaneously in all proportions

$$\Delta S_{mix} = -\left(\frac{\partial(\Delta G_{mix})}{\partial T}\right)_{p,n}$$

$$\Delta V_{mix} = \left(\frac{\partial(\Delta G_{mix})}{\partial p}\right)_{T,n}$$

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix}$$

$$\Delta G_{mix} = nRT \{x_A \ln x_A + x_B \ln x_B\}$$

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

$$\Delta S_{mix} = -nR \{x_A \ln x_A + x_B \ln x_B\}$$

$$\Delta H_{mix} = 0$$

Equilibrium: Overview

Describing Chemical Equilibrium
- – Chemical Equilibrium – A Dynamic Equilibrium (the link to Chemical Kinetics)
- – The Equilibrium Constant
- – Heterogeneous Equilibria; solvents in homogeneous equilibria
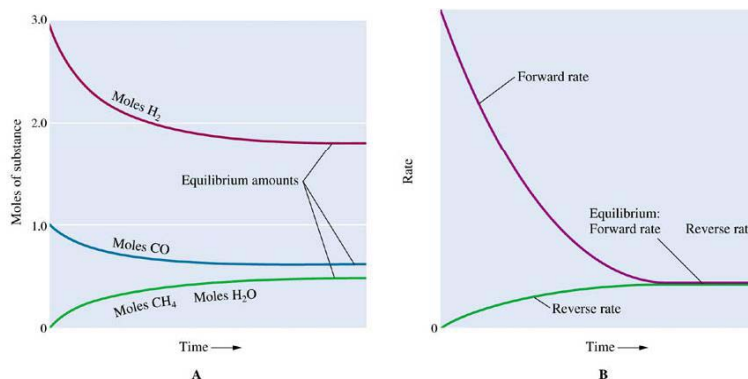
Using the Equilibrium Constant
- – Qualitatively Interpreting the Equilibrium Constant
- – Predicting the direction of a Reaction
- – Calculating Equilibrium Concentrations

Changing Reaction Conditions: Le Châtelier's Principle
- – Removing Products or Adding Reactants
- – Changing the Pressure or Temperature
- – Effect of a Catalyst

Chemical Equilibrium – A Dynamic Equilibrium

- Upon addition of reactants and/or products, reaction occurs until a constant amount of reactants and products are present = **equilibrium**
- Equilibrium is dynamic since product is constantly made (forward reaction), but at the same rate it is consumed (reverse reaction)
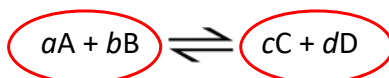
Chemical Equilibrium – A Dynamic Equilibrium

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

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$aA + bB \rightleftharpoons cC + dD$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$ **Law of Mass Action**

Equilibrium Will

K >> 1	Lie to the right	Favour products
K << 1	Lie to the left	Favour reactants

Homogenous equilibrium applies to reactions in which all reacting species **are in the same phase**

$$N_2O_4 \,(g) \rightleftharpoons 2NO_2 \,(g)$$
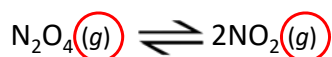
$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

In most cases

$$K_c \neq K_p$$

$$aA\,(g) + bB\,(g) \rightleftharpoons cC\,(g) + dD\,(g)$$

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

Δn = moles of gaseous products – moles of gaseous reactants
= $(c + d) - (a + b)$

Chemical Equilibrium

$$a\text{ A} + b\text{ B} \rightleftharpoons c\text{ C} + d\text{ D}$$

$$\Delta G_r^0 = \sum_{\text{pdts}} \upsilon \Delta G_f^0 - \sum_{\text{reactants}} \upsilon \Delta G_f^0$$

$$\Delta G_r^0 = c\Delta_f G_C^0 + d\Delta_f G_D^0 - a\Delta_f G_A^0 - b\Delta_f G_B^0$$

If $\Delta_r G\,^\circ > 0$ then the reaction will not go as written (the reverse reaction will go); if $\Delta_r G\,^\circ < 0$ then the reaction will go as written.

ΔG_r^0 can also be written in terms of chemical potentials of the components. All components are in their standard states

$$\Delta G_r^0 = c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0$$

$\Delta G_r^0 \neq 0$ **Chemical reactions are not equilibrium processes**

Chemical Equilibrium

Criterion for equilibrium at constant p and T

$$dG_{p,T} \leq 0$$

$$dG_{p,T} = \sum_i \mu_i dn_i \leq 0$$

Let the reaction proceed by an amount *dn* (*dn>0*)

$$dn_C = cdn$$
$$dn_D = ddn$$
$$dn_A = -adn$$
$$dn_B = -bdn$$
$$dG_{p,T} = c\mu_C dn + d\mu_D dn - a\mu_A dn - b\mu_B dn$$
$$= (c\mu_C + d\mu_D - a\mu_A - b\mu_B)dn$$
$$dG_{p,T} = \Delta G_r dn \leq 0 \qquad \boxed{\Delta G_r = c\mu_C + d\mu_D - a\mu_A - b\mu_B}$$

Chemical Equilibrium

$$\Delta G_r^0 = c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0$$

If the components are not in their standard states:

$$\Delta G_r = c\mu_C + d\mu_D - a\mu_A - b\mu_B$$

Write a general form of the chemical potential of component *i* in terms of the activity a_i – choose system e.g. ideal / real gas etc.

$$\mu_i = \mu_i^0 + RT \ln a_i$$

$$\Delta G_r = \Delta G_r^0 + RT(\ln a_C^c + \ln a_D^d - \ln a_A^a - \ln a_B^b)$$

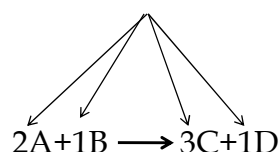$$\Delta G_r = \Delta G_r^0 + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

$$\Delta G_r = \Delta G_r^0 + RT \ln Q$$

Chemical Equilibrium

Stoichiometric numbers ν_i

$$\Delta G_r = \sum_i \upsilon_i \mu_i$$

$$\Delta G_r = 3\mu_C + \mu_D - 2\mu_A - \mu_B$$

$$2A + 1B \longrightarrow 3C + 1D$$

$$\Delta G_r = \sum_i \upsilon_i (\mu_i^0 + RT \ln a_i) = \sum_i \upsilon_i \mu_i^0 + RT \sum_i \upsilon_i \ln a_i$$

$$\Delta G_r^0 = \sum_i \upsilon_i \mu_i^0 = \sum_{pdts} \upsilon \Delta G_f^0 - \sum_{reactants} \upsilon \Delta G_f^0$$

$$= \Delta G_r^0 + RT \ln \prod_i a_i^{\upsilon_i}$$

$$= \Delta G_r^0 + RT \ln Q \qquad Q = \prod_i a_i^{\upsilon_i}$$

11

Chemical Equilibrium

$$\Delta G_r = \Delta G_r^0 + RT \ln \prod_i a_i^{\upsilon_i} = \Delta G_r^0 + RT \ln Q \qquad \boxed{Q = \prod_i a_i^{\upsilon_i}}$$

At equilibrium:

$$K = \left[\prod_i a_i^{\upsilon_i} \right]_{equilibrium}$$ **Thermodynamic equilibrium constant**

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

Practically a_i approximated by numerical values of molalities / by molar concentration / numerical values of partial pressures

$$\Delta G_r = 0 = \Delta G_r^0 + RT \ln K_a$$

$$\Delta G_r^0 = -RT \ln K_a$$

$$K_a = \exp^{-\frac{\Delta G^0}{RT}}$$

$$K_a = \exp^{-\frac{\Delta H^0 - T\Delta S^0}{RT}}$$

$$K_a = \exp^{-\frac{\Delta H^0}{RT}} \exp^{\frac{\Delta S^0}{R}}$$

Applications of Equilibrium Constants

Predicting the Direction of Reaction

- If $Q > K$ then the reverse reaction must occur to reach equilibrium
- If $Q < K$ then the forward reaction must occur to reach equilibrium
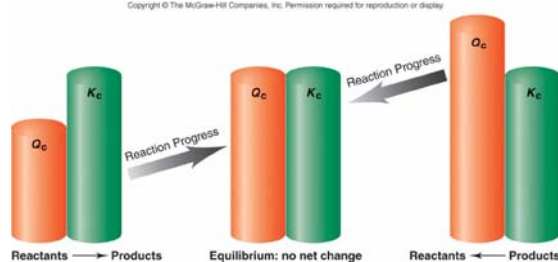
TABLE 18.4	Relation Between ΔG° and K as Predicted by the Equation ΔG° = −RT ln K		
K	**ln K**	**ΔG°**	**Comments**
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
= 1	0	0	Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive	Reactants are favored over products at equilibrium.