The Concept of Equilibrium

$\rightleftharpoons$

Reversible reactions

As the concentrations of the reactants decrease the rate of reaction in the forward direction decreases.

As the concentrations of the products increase the rate of reaction in the reverse direction increases.

Chemical Equilibrium

reached when rates of the forward and reverse reactions are equal and the concentrations of the reactants and products no longer change with time

Chemical equilibrium is dynamic: chemical reactions take place ,but concentrations of reactants and products remain unchanged

Consider a simple case:

$$\mathrm{A} \underset{k'}{\overset{k}{\rightleftarrows}} \mathrm{B}$$

(assume single unimolecular elementary step for forward and reverse processes)

Rate of forward reaction = $k\,[\mathrm{A}]$

Rate of backward reaction = $k'\,[\mathrm{B}]$

At equilibrium: $k\,[\mathrm{A}] = k'\,[\mathrm{B}]$

$$\frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{k}{k'} = K$$

K equilibrium constant

The Law of Mass Action

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

equilibrium constant

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

$$k = \frac{\text{products}}{\text{reactants}}$$

The NO_2 - N_2O_4 system at 25 ° C

Init: 0.670 *M* 0.000 *M*

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

equil: 0.643 *M* 0.0547 *M*

$$\frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0547)^2}{0.643} = 4.65 \times 10^{-3}$$

The NO_2 - N_2O_4 system at 25 ° C

Init: 0.500 *M* 0.0300 *M*

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

equil: 0. 491 *M* 0.0475 *M*

$$\frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0475\ \mathrm{M})^2}{0.491\ M} = 4.60 \times 10^{-3}$$

The NO_2 - N_2O_4 system at 25 ° C

Init: 0.000 *M* 0.200 *M*

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

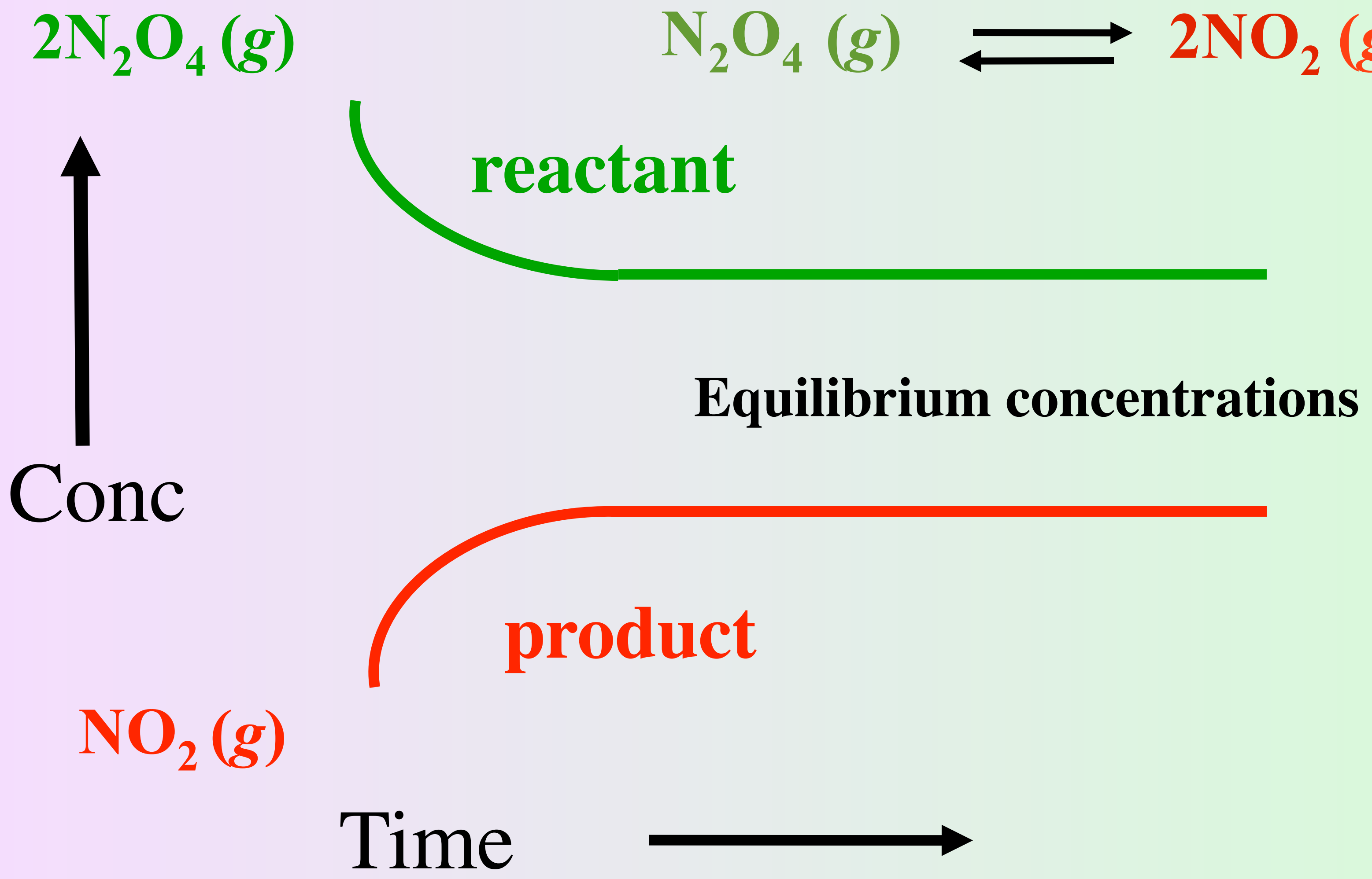
equil: 0.0898 *M* 0.0204 *M*

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

Change in concentrations

Initially only N_2O_4 is present

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



$2N_2O_4\ (g)$

reactant

Conc

Equilibrium concentrations

product

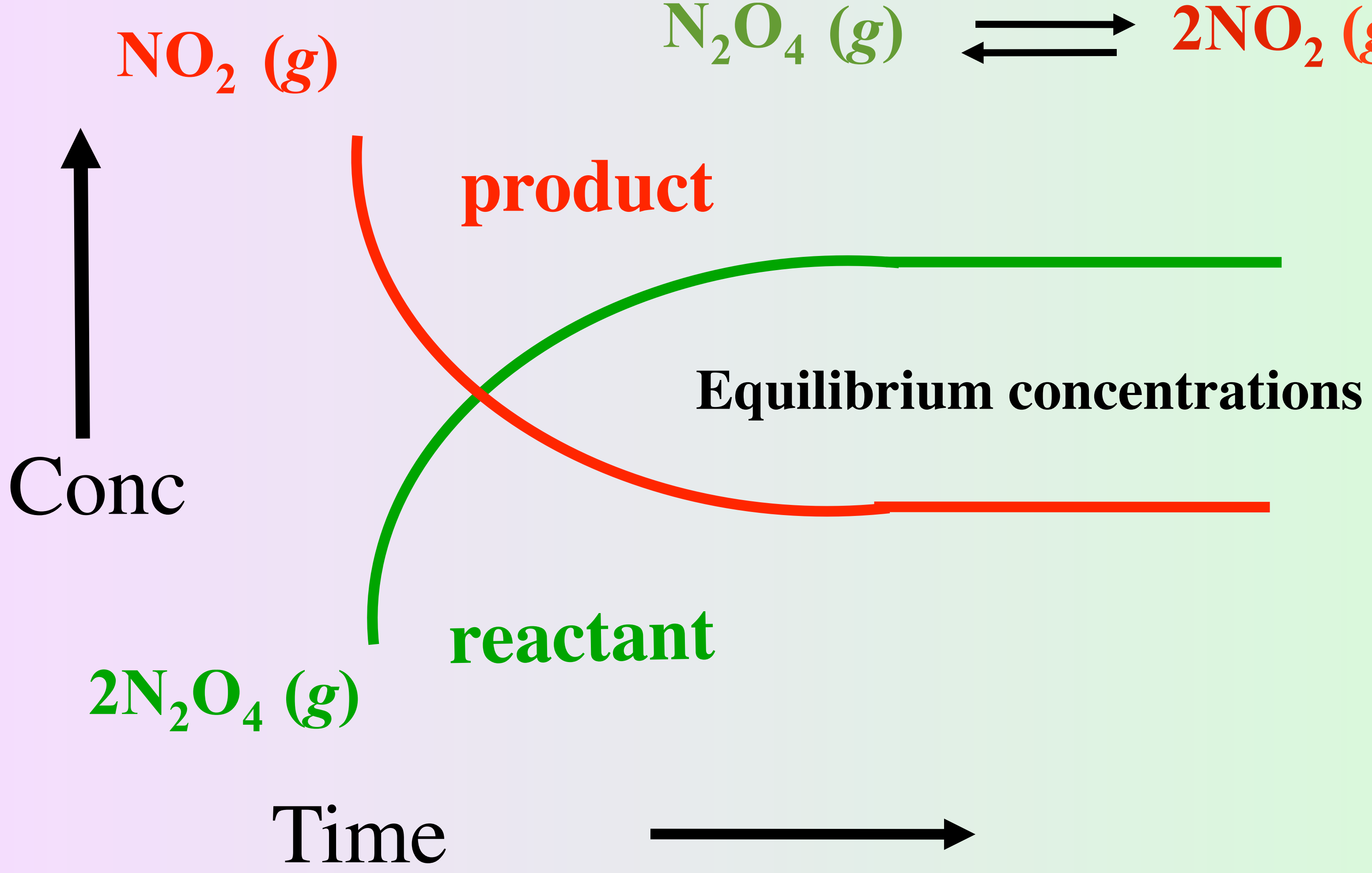
$NO_2\ (g)$

Time

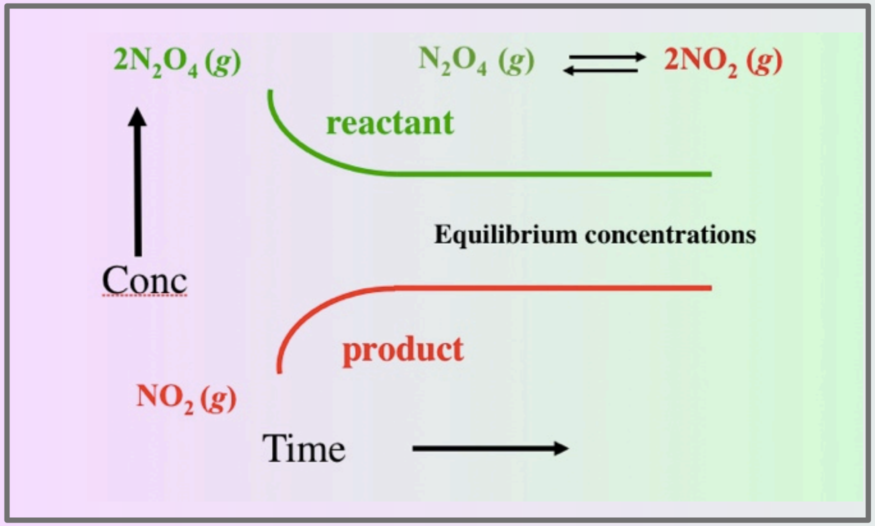
Change in concentrations

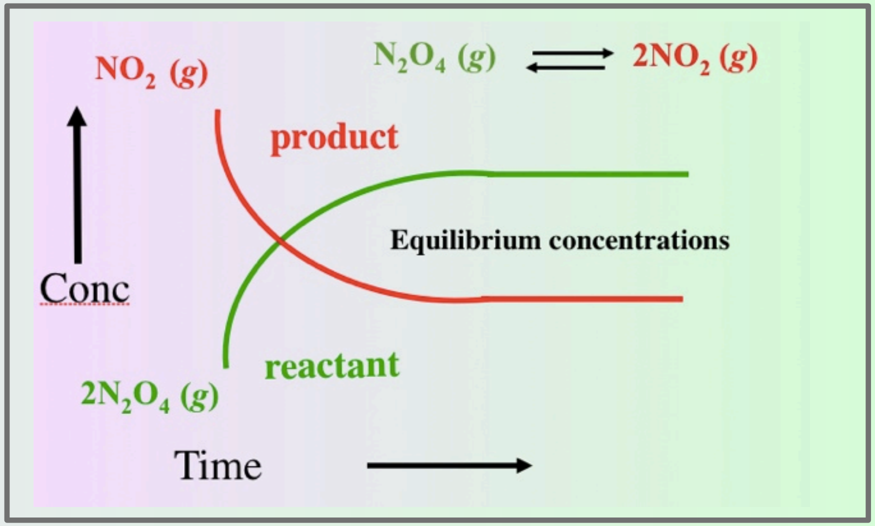
Initially only NO_2 is present

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



Equilibrium Can Be Reached from Either Direction





It doesn't matter whether we start with NO_2 or whether we start with N_2O_4, we will have the same proportions of the two substances at equilibrium.

The magnitude of the equilibrium constant

depends on temperature

depends on reaction

$$2O_3\,(g) \xrightleftharpoons{2300°C} 3O_2\,(g) \qquad K = 2.5 \times 10^{12}$$

$$Cl_2\,(g) \xrightleftharpoons{25°C} 2Cl\,(g) \qquad K = 1.4 \times 10^{-38}$$

$$CO(g) + H_2O\,(g) \xrightleftharpoons{830°C} H_2\,(g) + CO_2\,(g)$$

$$K = 5.1$$

Ways of Expressing Equilibrium Constants

Homogeneous equilibria

Heterogeneous equilibria

Homogeneous Equilibria

all reacting species are in the same phase

gas phase

equilibrium constant can be expressed in terms of pressure or concentration

solution phase

Example: homogeneous gas-phase

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

Where K_c is the equilibrium constant when concentrations are expressed in moles/liter

Alternatively:

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

$$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

Where K_p is the equilibrium constant when concentrations are expressed in pressure units

Practice Exercise

The equilibrium concentrations for the reaction

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

Are [CO] = 1.2×10^{-2} *M*, [Cl_2] = 0.054 *M* and [$COCl_2$] = 0.14 *M*. Calculate the equilibrium constant (K_c).

$$K_c = \frac{[COCl_2]}{[CO]\,[Cl_2]} = \frac{0.14}{(1.2 \times 10^{-2})\ (0.054)} = 2.2 \times 10^2$$

Practice Exercise

$$2NO_2\ (g) \rightleftharpoons 2NO\,(g) + O_2(g)$$

0.400 atm **0.270 atm** ?

The equilibrium constant K_p for the reaction shown as 158 at 1000 K. calculate the partial pressure of O_2

$$158 = \frac{(0.270)^2\, P_{(O2)}}{(0.400)^2} \qquad \frac{(0.400)^2\ (158)}{(0.270)^2} = P_{(O2)}$$

$$P_{(O2)} = 347 \text{ atm}$$

Relationship between K_p and K_c

Gas-phase concentrations can also be expressed in terms of partial pressures

$$PV = nRT$$

Therefore, $$P = \frac{n}{V} R T$$

i.e.:

$$P = (\text{molar concentration})\, R T$$

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

Δn =

the sum of the coefficients of the gaseous products **-** **the sum of the coefficients of the gaseous reactants**

Homogeneous Equilibria

all reacting species are in the same phase

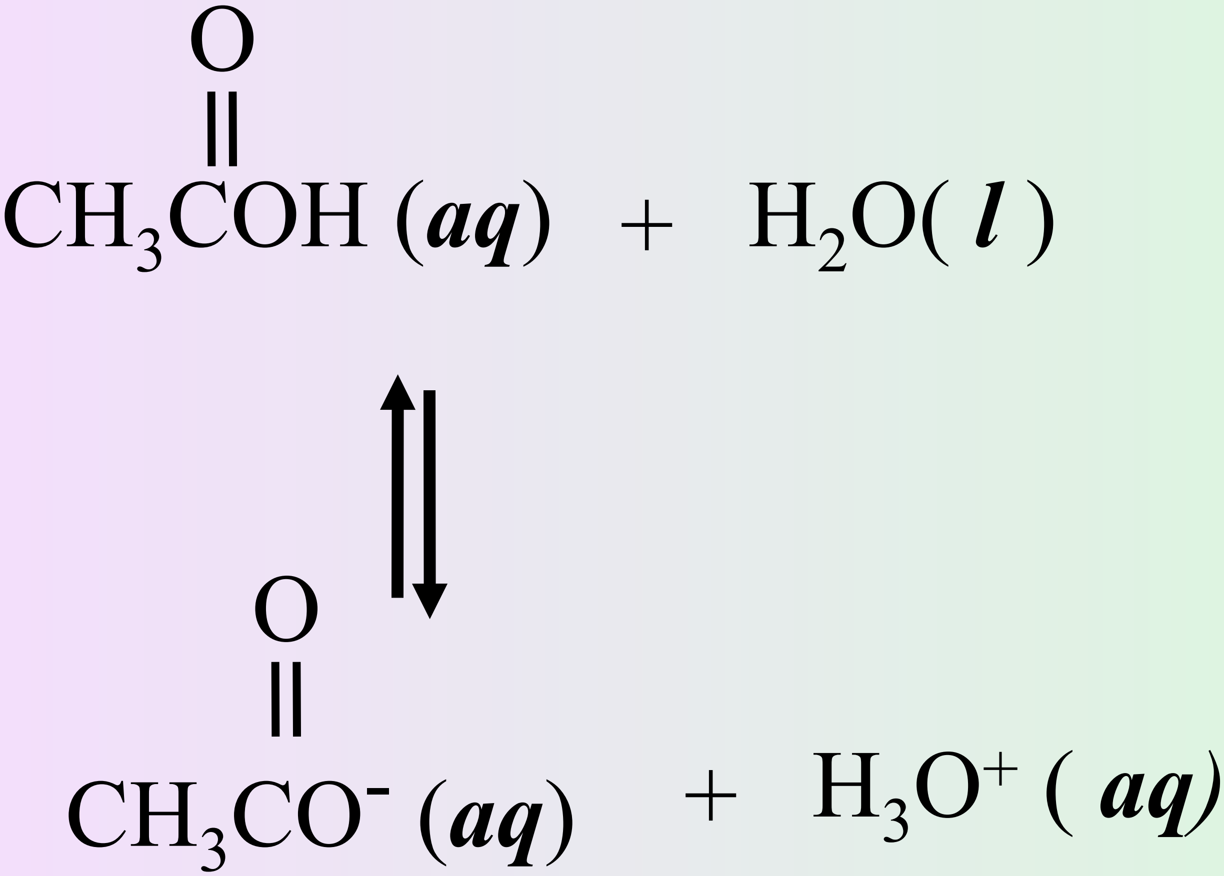
gas phase

equilibrium constant can be expressed in terms of pressure or concentration

solution phase

concentration term for the solvent does not appear in the expression for the equilibrium constant

Example: homogeneous aqueous-phase reaction



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}OH}\ (\boldsymbol{aq}) + \mathrm{H_2O}(\boldsymbol{l}) \rightleftharpoons \mathrm{CH_3\overset{O}{\overset{\|}{C}}O^-}\ (\boldsymbol{aq}) + \mathrm{H_3O^+}\ (\boldsymbol{aq})$$

Example: homogeneous aqueous-phase reaction

$$\mathrm{HOAc}\ (\boldsymbol{aq}) \quad + \quad \mathrm{H_2O}(\boldsymbol{l})$$

$$\uparrow\downarrow \qquad \mathbf{K}' = \frac{[^{-}\mathrm{OAc}\,]\,[\mathrm{H_3O^+}\,]}{[\mathrm{HOAc}]\,[\mathrm{H_2O}]}$$

$$^{-}\mathrm{OAc}\ (\boldsymbol{aq}) \quad + \quad \mathrm{H_3O^+}\ (\boldsymbol{aq})$$

Example: homogeneous aqueous-phase reaction

$$\mathrm{HOAc}\ (\boldsymbol{aq}) \quad + \quad \mathrm{H_2O}(\ \boldsymbol{l}\ )$$

$$\uparrow\downarrow \quad \mathbf{K}'\ [\mathrm{H_2O}] = \frac{[{}^{-}\mathrm{OAc}\ ]\ [\mathrm{H_3O^+}\ ]}{[\mathrm{HOAc}]}$$

$${}^{-}\mathrm{OAc}\ (\boldsymbol{aq}) \quad + \quad \mathrm{H_3O^+}\ (\ \boldsymbol{aq})$$

Example: homogeneous aqueous-phase reaction

$\mathrm{HOAc}\ (\boldsymbol{aq}) \quad + \quad \mathrm{H_2O}(\,\boldsymbol{l}\,)$

$\uparrow\downarrow$

$$\mathbf{K_c} = \frac{[\,^{-}\mathrm{OAc}\,]\,[\mathrm{H_3O^+}\,]}{[\mathrm{HOAc}]}$$

$^{-}\mathrm{OAc}\ (\boldsymbol{aq}) \quad + \quad \mathrm{H_3O^+}\ (\,\boldsymbol{aq})$

Heterogeneous Equilibria

all reacting species are not in the same phase

concentration term for solid or liquid does not appear in the expression for the equilibrium constant

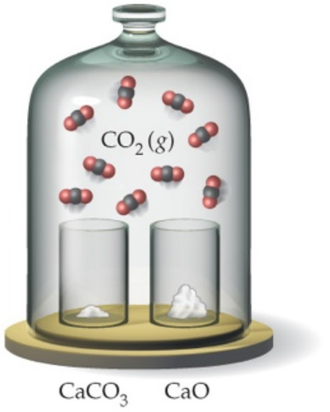
Example

$$CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2(g)$$

$$K_c = [CO_2]$$

$CaCO_3(s) \rightleftharpoons CO_2(g) + CaO(s)$

Large amount of $CaCO_3$, small amount of CaO, gas pressure P



Small amount of $CaCO_3$, large amount of CaO, gas pressure still P

© 2012 Pearson Education, Inc.

Increasing the surface area of the solid increases the rate forward and reverse reactions equally.

The amount of CO_2 above the solid remains the same.

Practice Exercise

$$Ni_{(s)} + 4CO_{(g)} \rightleftharpoons Ni(CO)_4\,_{(g)}$$

What is the expression for K_c and K_p for the reaction shown

$$K_c = \frac{[Ni(CO)_4]}{[CO]^4} \qquad K_p = \frac{P_{(Ni(CO)4)}}{P^4_{(CO)}}$$

Practice Exercise

What is the value for K_c and K_p for the equilibrium shown at 295 K?

$$NH_4HS\,(s) \rightleftharpoons NH_3\,(g) + H_2S\,(g)$$

0.265atm 0.265atm

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

$$K_p = P_{NH3}\ P_{H2S}$$

$$K_p = (0.265)^2$$

$$K_p = 0.0702$$

$$K_c = \frac{K_p}{(RT)^2}$$

Practice Exercise

What is the value for K_c and K_p for the equilibrium shown at 295 K?

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$$

0.265atm   0.265atm

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

$$K_p = P_{NH3}\ P_{H2S}$$

$$K_p = (0\,.265)^2$$

$$K_p = 0\,.0702$$

$$K_c = \frac{0.0702}{(\,.0821\ \text{Latm/mol K}(295\text{K})\,)^2}$$

Practice Exercise

What is the value for K_c and K_p for the equilibrium shown at 295 K?

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$$

0.265atm 0.265atm

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

$$K_p = P_{NH3}\ P_{H2S}$$

$$K_p = (0.265)^2$$

$$K_p = 0.0702$$

$$K_c = 0.00012$$

Multiple Equilibria

If a reaction can be expressed as the sum of two or more individual reactions, the equilibrium constant for the overall reaction is the product of the equilibrium constants of the individual reactions.

Multiple Equilibria

If a reaction can be expressed as the sum of two or more individual reactions, the equilibrium constant for the overall reaction is the product of the equilibrium constants of the individual reactions.

Practice Exercise

Given:

$$H_2S\,(aq) \rightleftharpoons H^+\,(aq) + HS^-\,(aq)$$

$$K'_c = 9.5 \times 10^{-8}$$

$$HS^-\,(aq) \rightleftharpoons H^+\,(aq) + S^{2-}\,(aq)$$

$$K''_c = 1.0 \times 10^{-19}$$

Calculate the equilibrium constant for:

$$H_2S\,(aq) \rightleftharpoons 2H^+(aq) + S^{2-}\,(aq)$$

Practice Exercise

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$

$$K = \frac{[H^+]^2\,[S^{2-}]}{[H_2S]}$$

$$K = \frac{[H^+]\;\cancel{[HS^-]}}{[H_2S]} \qquad \frac{[H^+]\;[S^{2-}]}{\cancel{[HS^-]}} \qquad = K'_c\;K''_c$$

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq)$$

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq)$$

Practice Exercise

$$H_2S\,(aq) \rightleftharpoons H^+\,(aq) + \cancel{HS^-}\,(aq)$$

$$K'_c = 9.5 \times 10^{-8}$$

$$\cancel{HS^-}\,(aq) \rightleftharpoons H^+\,(aq) + S^{2-}\,(aq)$$

$$K''_c = 1.0 \times 10^{-19}$$

$$H_2S\,(aq) \rightleftharpoons 2H^+(aq) + S^{2-}\,(aq)$$

$$K''_c K'_c = (9.5 \times 10^{-8})(1.0 \times 10^{-19}) = 9.5 \times 10^{-27}$$

The Form of K and the Equilibrium Equation

When the equation for a reversible reaction is written in the opposite direction,the equilibrium constant becomes the reciprocal of the original equilibrium constant.

The value of K also depends on how the equilibrium constant is balanced.

Practice Exercise

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

$K_c = 1.2$ at 375°C

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = 1.2$$

What is the expression for K_c for:

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

$$\frac{[N_2]\,[H_2]^3}{[NH_3]^2} = \left(\frac{[NH_3]^2}{[N_2]\,[H_2]^3}\right)^{-1} = 0.83$$

Practice Exercise

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

$K_c = 1.2$ at 375°C

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 1.2$$

What is the expression for K_c for:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

$$\frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = \left(\frac{[NH_3]^2}{[N_2][H_2]^3}\right)^{1/2} = 1.1$$

Practice Exercise

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

$K_c = 1.2$ at 375°C

What is K_p for the reaction

4 moles of gases on the left; 2moles of gases on the right

$$K_p = K_c(RT)^{-2}$$

$$K_p = 1.2[(0.0821\ \mathrm{Latm/molK})(648\ \mathrm{K})]^{-2}$$

$$K_p = 0.00043$$

Summary of Guidelines for Writing Equilibrium Constant Expressions

- The concentrations of the reacting species in solution are expressed in mol/L.

- In the gas phase, concentrations are expressed in mol/L or in atm.

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

Summary of Guidelines for Writing Equilibrium Constant Expressions

- The concentrations of pure solids, pure liquids, and solvents do not appear in the equilibrium constants expressions.

- Equilibrium constants do not have units.

- The balanced equation must be shown when the value for an equilibrium constant is given.

Summary of Guidelines for Writing Equilibrium Constant Expressions

- If a reaction can be expressed as the sum of two or more individual reactions, the equilibrium constant for the overall reaction is the product of the equilibrium constants of the individual reactions.

Summary of Guidelines for Writing Equilibrium Constant Expressions

- When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant become the reciprocal of the original equilibrium constant .

3.6 x 10^8 at 25 C

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

$$\frac{[NH_3]^2}{[N_2]\;[H_2]^3}$$