# EQUILIBRIUM LAW - $K_{eq}$

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A simple mathematical relationship defines each reaction at chemical equilibrium.

$$H_{2(g)} + I_{2(g)} <===> 2\ HI_{(g)}$$

$$K_{eq} = \frac{[HI_{(g)}]^2}{[H_{2(g)}][I_{2(g)}]}$$

# EQUILIBRIUM LAW - $K_{eq}$

- can always be developed from the balanced chemical equation
- $K_{eq}$ will always have a specific value at specific environmental conditions
  - if the conditions change, the $K_{eq}$ will also change
- units for $K_{eq}$ will never be used

# EQUILIBRIUM LAW - $K_{eq}$

## Example #1

a) $N_{2(g)} + 3\ H_{2(g)} <====> 2\ NH_{3(g)}$

$$k_{eq} = \frac{[NH_{3(g)}]^2}{[N_{2(g)}][H_{2(g)}]^3}$$

b) $2\ H_{2(g)} + O_{2(g)} <====> 2\ H_2O_{(g)}$

$$k_{eq} = \frac{[H_2O_{(g)}]^2}{[H_{2(g)}]^2\ [O_{2(g)}]}$$

c) $2\ NO_{2(g)} <====> N_2O_{4(g)}$

$$k_{eq} = \frac{[N_2O_{4(g)}]}{[NO_{2(g)}]^2}$$

# EQUILIBRIUM LAW - $K_{eq}$

How are the equilibrium laws of the following equations related?

i) $N_{2(g)} + 3\ H_{2(g)} \text{ <====> } 2\ NH_{3(g)}$

ii) $2NH_{3(g)} \text{ <====> } N_{2(g)} + 3\ H_{2(g)}$

i) $k_{eq} = \dfrac{[NH_{3(g)}]^2}{[N_{2(g)}][H_{2(g)}]^3}$

ii) $k_{eq} = \dfrac{[N_{2(g)}][H_{2(g)}]^3}{[NH_{3(g)}]^2}$

# EQUILIBRIUM LAW - $K_{eq}$

If the direction of an equation is reversed, the equilibrium constant is the reciprocal of the original equilibrium constant.

$$K_{eq\ forward} = 1 / K_{eq\ reverse}$$

# EQUILIBRIUM LAW - $K_{eq}$

How are the equilibrium laws of the following equations related?

i) $PCl_{3(g)} + Cl_{2(g)} <===> PCl_{5(g)}$

ii) $2\ PCl_{3(g)} + 2\ Cl_{2(g)} <===> 2\ PCl_{5(g)}$

i) $k_{eq} = \dfrac{[PCl_{5(g)}]}{[PCl_{3(g)}][Cl_{2(g)}]}$

ii) $k_{eq} = \dfrac{[PCl_{5(g)}]^2}{[PCl_{3(g)}]^2[Cl_{2(g)}]^2}$

# EQUILIBRIUM LAW - $K_{eq}$

When the coefficients of a balanced equation are multiplied by a factor, the equilibrium constant is raised to the exponent of the same factor.

$$K_{eq\ rxn\ ii)} = [K_{eq\ rxn\ i)}]^x$$

# EQUILIBRIUM LAW - $K_{eq}$

What is the equilibrium law of the sum of the following reactions?

i) $2\ N_{2(g)} + O_{2(g)} <=> \cancel{2\ N_2O_{(g)}}$

$$k_{eq} = \frac{[N_2O_{(g)}]^2}{[N_{2(g)}]^2[O_{2(g)}]}$$

ii) $\cancel{2\ N_2O_{(g)}} + 3\ O_{2(g)} <=> 4\ NO_{2(g)}$

$$k_{eq} = \frac{[NO_{2(g)}]^4}{[N_2O_{(g)}]^2[O_{2(g)}]^3}$$

$$k_{eq} = \frac{[NO_{2(g)}]^4}{[N_{2(g)}]^2[O_{2(g)}]^4}$$

$$K_{eq\ final} = \frac{\cancel{[N_2O_{(g)}]^2}}{[N_{2(g)}]^2[O_{2(g)}]} \times \frac{[NO_{2(g)}]^4}{\cancel{[N_2O_{(g)}]^2}[O_{2(g)}]^3}$$

# EQUILIBRIUM LAW - $K_{eq}$

When chemical equilibria are added together, the equilibrium constants are multiplied together.

$$K_{eq\ final\ rxn} = K_{eq\ rxn\ 1} \times K_{eq\ rxn\ 2}$$

# EQUILIBRIUM LAW - $K_{eq}$

## Example #2

At 25°C, $K_{eq} = 7.0 \times 10^{25}$ for:

$$2\ SO_{2(g)} + O_{2(g)} <===> 2\ SO_{3(g)}$$

What is the value of $K_{eq}$ for:

$$SO_{3(g)} <===> SO_{2(g)} + ½\ O_{2(g)}$$

$K_{eq} = 7.0 \times 10^{25}$ inversed, to the power of 0.5

$= 1.195 \times 10^{-13}$

$= 1.2 \times 10^{-13}$

# EQUILIBRIUM LAW - $K_{eq}$

## MAGNITUDE OF $K_{eq}$

The value of $K_{eq}$ (large or small) can provide a hint to the ratio of reactants to products at equilibrium.

# EQUILIBRIUM LAW - $K_{eq}$

## MAGNITUDE OF $K_{eq}$

1. $K_{eq}$ is very large ($K_{eq} > 1$)
   - [products] > [reactants]

2. $K_{eq} \approx 1$
   - [products] ≈ [reactants]

3. $K_{eq}$ is very small ($K_{eq} < 1$)
   - [products] < [reactants]

# EQUILIBRIUM LAW - $K_{eq}$

## MAGNITUDE OF $K_{eq}$

Example #3

Which of the following reactions will tend to proceed farthest toward completion?

a) $H_{2(g)} + Br_{2(g)} \Longleftrightarrow 2\ HBr_{(g)}$

$K_{eq} = 1.4 \times 10^{-21}$

b) $2\ NO_{(g)} \Longleftrightarrow N_{2(g)} + O_{2(g)}$

$K_{eq} = 2.1 \times 10^{30}$

c) $2\ BrCl_{(g)} \Longleftrightarrow Br_{2(g)} + Cl_{2(g)}$

$K_{eq} = 0.195$

# EQUILIBRIUM LAW - $K_{eq}$

## EQUILIBRIUM INVOLVING PURE SOLIDS AND LIQUIDS

# EQUILIBRIUM LAW - $K_{eq}$

## EQUILIBRIUM – SOLIDS AND LIQUIDS

What is the concentration of a solid or liquid? (i.e. $H_2O$)

Does the concentration of these pure compounds change?

ex. 1 mol $NaHCO_3$ occupies 38.9 $cm^3$

2 mol $NaHCO_3$ occupies 77.8 $cm^3$

Molar concentration remains the same. Solids and liquids are unaffected by concentration

# EQUILIBRIUM LAW - $K_{eq}$

## EQUILIBRIUM – SOLIDS AND LIQUIDS

In the equilibrium law, solids and liquids do not need to be included as it becomes part of the equilibrium constant.

$$NH_{3(aq)} + H_2O_{(l)} \Longleftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$k_{eq} = \frac{[NH_4^+{}_{(aq)}][OH^-{}_{(aq)}]}{[NH_{3(aq)}]}$$

# EQUILIBRIUM LAW - $K_{eq}$

## EQUILIBRIUM – SOLIDS AND LIQUIDS

### Example #4

Write the equilibrium law for the following reactions:

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

$$k_{eq} = [CO_{2(g)}]$$

b) $2\ NaHCO_{3(s)} \Longleftrightarrow Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)}$

$$k_{eq} = [H_2O_{(g)}][CO_{2(g)}]$$

c) $CaO_{(s)} + SO_{2(g)} \Longleftrightarrow CaSO_{3(s)}$

$$k_{eq} = \frac{1}{[SO_{2(g)}]}$$

# EQUILIBRIUM LAW - $K_{eq}$

## EQUILIBRIUM – SOLIDS AND LIQUIDS

### Example #4

d) $2\ Hg_{(l)} + Cl_{2(g)} \Longleftrightarrow Hg_2Cl_{2(s)}$

$$k_{eq} = \frac{1}{[Cl_{2(g)}]}$$

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

$$k_{eq} = \frac{1}{[NH_{3(g)}][HCl_{(g)}]}$$

# EQUILIBRIUM LAW - $K_{eq}$

## EFFECT OF TEMPERATURE ON $K_{eq}$

# EQUILIBRIUM LAW - $K_{eq}$

## EQUILIBRIUM – TEMPERATURE

Will temperature change the value of $K_{eq}$?  Why or why not?

Reactions are endothermic or exothermic and therefore will be affected by the addition or removal of heat.

# EQUILIBRIUM LAW - $K_{eq}$

## EQUILIBRIUM – TEMPERATURE

$$3\ H_{2(g)} + N_{2(g)} \Longleftrightarrow 2\ NH_{3(g)} + \text{heat}$$

a) What is the equilibrium law?

$$k_{eq} = \frac{[NH_{3(g)}]^2}{[H_{2(g)}]^3[N_{2(g)}]}$$

b) Which way does equilibrium shift when temperature increases? How will $K_{eq}$ change?

Shifts to the left. Since the denominator increases, $K_{eq}$ decreases (is smaller in value)

c) When temperature decreases?

Shifts to the right. Since the numerator increases, $K_{eq}$ increases (is larger in value)

# EQUILIBRIUM LAW - $K_{eq}$

## EQUILIBRIUM – TEMPERATURE

$$\text{heat} + PCl_{5(g)} \Longleftrightarrow PCl_{3(g)} + Cl_{2(g)}$$

a) What is the equilibrium law?

$$k_{eq} = \frac{[PCl_{3(g)}][Cl_{2(g)}]}{[PCl_{5(g)}]}$$

b) Which way does equilibrium shift when temperature increases? How will $K_{eq}$ change?

Shifts to the right. Since the numerator increases, $K_{eq}$ increases (is larger in value)

c) When temperature decreases?

Shifts to the left. Since the denominator increases, $K_{eq}$ decreases (is smaller in value)

# EQUILIBRIUM LAW - $K_{eq}$

## Textbook homework:

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