

### Introduction

**Equilibrium** = the point in a chemical reaction where the reactants and the products are formed and broken **at the same rate**

**Dynamic equilibrium** = a balance between the forward and backward rates that are **occurring simultaneously**

**Equilibrium law** = **mathematical description** of a chemical system **at equilibrium**

**Equilibrium constant** ( $K$  or  $K_{eq}$ ) = the numerical value **defining the equilibrium law** for a system **at a given temperature** (changes with temperature)

**Heterogeneous equilibrium** = products and reactants are in **at least 2 different states**; **pure solids/liquids** are **not** included in  $K_{eq}$  formula

### Equilibrium Constant ( $K_{eq}$ )

**$K_{eq}$  formula:**

If  $a[A] + b[B] \rightleftharpoons c[C] + d[D]$ ; then

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

**Magnitude of  $K_{eq}$ :** states whether the **equilibrium position favours products/reactants**

If  $K = 1$  [products] = [reactants]

If  $K \gg 1$  [products]  $\gg$  [reactants]

If  $K \ll 1$  [products]  $\ll$  [reactants]

**$K_{forward}$  vs  $K_{backward}$**

If  $a[A] \rightleftharpoons b[B]$ , then

$$K_{forward} = \frac{[B]^b}{[A]^a} \quad K_{backward} = \frac{[A]^a}{[B]^b}$$

So  $\therefore K_{forward} = \frac{1}{K_{backward}}$  @ equilibrium

**Purpose of  $K_{eq}$ :** to **determine equilibrium concentration** of chemical entities **given initial conditions** (I.C.E. table)

### Reaction Quotient ( $Q$ )

Helps to **determine the position of the equilibrium** of a system using the **rate law** for the system and comparing it with the  $K_{eq}$

If  $Q < K_{eq}$  [products] < [reactants]  
 $Q$  Reaction has not reached  $\rightleftharpoons$  yet; reaction needs to **shift right**

If  $Q > K_{eq}$  [products] > [reactants]  
 $Q$  Reaction has not reached  $\rightleftharpoons$  yet; reaction needs to **shift left**

If  $Q = K_{eq}$  [products] = [reactants]  
 $Q$  Reaction has not reached equilibrium yet; **no shift** will occur

### Variables Affecting Chemical Equilibria

**Le Châtelier's Principle:** When a chemical system **at equilibrium** is **disturbed** by a **change in property**, the system responds in a way that **opposes the change**

#### Concentration/Temperature

$\uparrow$  [conc]/T = shift to **consume**

$\downarrow$  [conc]/T = shift to **replace**

If you **add more** reactant/heat to a system, the system will **consume it** to make more product, and **vice versa**

If you **remove** reactant/heat from a system, the system will **replace it** from the existing product, and **vice versa**

#### Volume/Pressure (gases only)

$\uparrow V = \downarrow P$  = shift toward side with **more** gas entities (i.e. more mol of gas) (more space for particles)

$\downarrow V = \uparrow P$  = shift toward side with **fewer** gas entities (i.e. less mol of gas) (less space for particles)

**Catalysts/Inert (noble) gases**  $\rightarrow$  No effect

### Equilibria of Slightly Soluble Compounds

**Molar solubility:** The **amount of solute** (in mol) that can be **dissolved in 1 L** of solvent at a **certain temperature**

**T  $\propto$  solubility:** as temperature increases, so does molar solubility

All compounds have **some solubility**, even if they are considered "insoluble" (really **very low molar solubility**)

**Very soluble** compounds (**high molar solubility**) = **no**  $\rightleftharpoons$  (**complete disassociation** into ions)

**Slightly soluble** compounds (**low molar solubility**) = **has**  $\rightleftharpoons$  (**incomplete/partial disassociation** into ions)

As a compound is placed in a solvent, **some part of it will dissolve**, but at the same time, the **reverse reaction starts**

Eventually the two reactions reach equilibrium, creating a **saturated solution** (at this point, [conc] of ions remains **constant**)  $\rightarrow$  solubility equilibrium

**Equilibrium formula for solubility:**

If  $x[AaBb] (s) \rightleftharpoons a[A^{b+}] (aq) + b[B^{a-}] (aq)$ , then

$$K_{sp} = [A^{b+}]^a [B^{a-}]^b$$

**$K_{sp}$  (Solubility product constant):** the product of the [conc] of ions in a saturated solution

If **K** Amount (mol) of aqueous ions  $\ll$   
**sp** amount (mol) of solid substance  $\ll 1$

If **K** Amount (mol) of aqueous ions  $\gg$   
**sp** amount (mol) of solid substance  $\gg 1$

Molar solubility and the  $K_{sp}$  **describe the solubility of a substance** in different ways, meaning you can use one to solve for the other (using an ICE table)

**Using  $Q$  and  $K_{sp}$  to predict precipitate formation**



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## Equilibria of Slightly Soluble Compounds (cont)

If  $Q < K_s$  Not enough ions in solution (unsaturated); **no precipitate**; reaction will shift to the **right**

If  $Q > K_s$  Lots of ions in solution (saturated); **precipitate can form**; reaction will shift to the **left**

If  $Q = K_s$  System is at  $\rightleftharpoons$ ; **no precipitate** (saturated solution)

## pH and pOH

*pH/pOH*: The measure of **acidity/alkalinity** of a solution

*pH*: The measure of  $[H^+]$  in a solution

$$pH = -\log[H^+] \quad [H_3O^+] = [H^+] = 10^{-pH}$$

*pOH*: The measure of  $[OH^-]$  in a solution

$$pH = -\log[OH^-] \quad [OH^-] = 10^{-pOH}$$

The pH and pOH values are related to the exponent of  $K_w$  (14):

$$pH + pOH = 14$$

## Acids and Bases

*Arrhenius acid/base* = solution that **ionizes** into  $H^+$  (acid)/ $OH^-$  (base) **ions**

*Bronsted-Lowry acid/base* = solution that **donates** (acid)/**receives** (base)  $H^+$  **ions**

*Strong acid/base*: solution that **completely ionizes** (acid)/**disassociates** (base) into ions

*Weak acid/base*: solution that **partially ionizes** (acid)/**disassociates** (base) into ions

*Monoprotic acids*: acids that donate **one  $H^+$  ion**

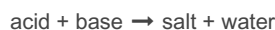
*Polyprotic acids*: acids that donate **more than one  $H^+$  ion**  
(*diprotic* = 2  $H^+$ , *triprotic* = 3  $H^+$ , etc.)

## Acids and Bases (cont)

*Amphiprotic substance*: substance that can behave like an acid or as a base (i.e. can **donate and receive  $H^+$  ions**)

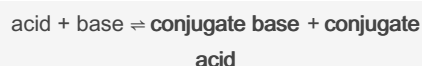
### Neutralization reactions

With **strong** acids/bases:



\***Complete** ionization, so **no equilibrium analysis\***

With **weak** acids/bases:



\***Partial** ionization, so **equilibrium has to be analyzed\***

### Acid/Base Constants ( $K_a$ and $K_b$ )

$K_a/K_b$  indicate the **strength** of an acid/base

If  $K_a/K_b \gg 1$  Strong acid/base (**complete** ionization/disassociation)

If  $K_a/K_b \ll 1$  Weak acid/base (**partial** ionization/disassociation)

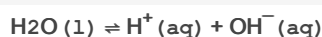
If one  $K$  is known, the other can be determined using  $K_w$  through the formula:

$$K_w = K_a \text{ (of acid)} \cdot K_b \text{ (of conjugate base)}$$

$$K_w = K_b \text{ (of base)} \cdot K_a \text{ (of conjugate acid)}$$

## Autoionization of Water and Water Constant ( $K_w$ )

Water can **dissociate** into ions **on its own**:



But the  $H^+$  ion can also **attack other  $H_2O$  molecules**:



Adding both reactions together:



All equilibria have a constant ( $K$ ) value, therefore:

$$K_w = [H_3O^+][OH^-]$$

( $H_2O (l)$  not included because it is **not (a q)**)

Since water is **neutral** ( $pH = 7$ ):

## Autoionization of Water and Water Constant ( $K_w$ ) (cont)

$$[H^+] = 1.0 \cdot 10^{-7} \rightarrow [H_3O^+] = 1.0 \cdot 10^{-7}$$

$$pH + pOH = 14 \rightarrow pOH = 7 \rightarrow [OH^-] = 1.0 \cdot 10^{-7}$$

If  $[H_3O^+] = 1.0 \cdot 10^{-7}$ , and  $[OH^-] = 1.0 \cdot 10^{-7}$ , then:

$$K_w = (1.0 \cdot 10^{-7})(1.0 \cdot 10^{-7}) = 1.0 \cdot 10^{-14}$$

$[^1]H_3O^+ (aq)$ : **Hydronium ion**

\* Value of  $K_w$  is **always**  $1.0 \cdot 10^{-14}$



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