

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 $\therefore K_{forward} = 1/K_{backward}$ @ 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 α 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 $x[A_aB_b] (s) \rightleftharpoons a[A^{b+}] (aq) + b[B^{a-}] (aq)$, 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_{sp} Amount (mol) of aqueous ions \ll
 sp amount (mol) of solid substance $\ll 1$

If K_{sp} 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

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

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**)

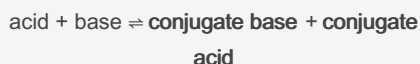
Neutralization reactions

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)

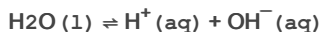
If one K is known, the other can be determined using K_w through the formula:

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

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

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 (aq)**)

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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