**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 Keq) = 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 Keq formula.

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**Equilibrium Constant (Keq)**

Keq formula:

If a[A] + b[B] ⇌ c[C] + d[D], then

\[
\text{Keq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}
\]

Magnitude of Keq states whether the equilibrium position favours products/reactants.

- If K = 1: [products] = [reactants]
- If K > 1: [products] > [reactants]
- If K < 1: [products] < [reactants]

**Kforward vs Kbackward**

\[
\begin{align*}
\text{If } a[A] &\neq b[B], \text{ then} \\
\text{Kforward} = &\ (B)^b \quad \text{Kbackward} = &\ (A)^a \\
\quad + (A)^b \\
&\ (B)^b
\end{align*}
\]

So: Kforward = 1/Kbackward @ equilibrium.

**Purpose of Keq**: to determine equilibrium concentration of chemical entities given initial conditions (I.C.E. table).

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**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 Keq.

- If Q < Keq: reaction has not reached equilibrium yet; reaction needs to shift right.
- If Q > Keq: reaction has not reached equilibrium yet; reaction needs to shift left.
- If Q = Keq: reaction has reached equilibrium yet; no shift will occur.

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**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
  - T ≥ 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 shift (complete dissociation into ions).
  - Slightly soluble compounds (low molar solubility) = has shift (incomplete/partial dissociation into ions).

- Volume/Pressure (gases only)
  - If you add more reactant/reactant to a system, the system will consume it to make more product, and vice versa.
  - If you remove reactant/reactant from a system, the system will replace it from the existing product, and vice versa.

- Catalysts
  - Catalysts/inert (noble) gases → No effect.

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**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 ≥ 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 shift (complete dissociation into ions).
- Slightly soluble compounds (low molar solubility) = has shift (incomplete/partial dissociation 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) → solubility equilibrium.

**Equilibrium formula for solubility**:

If x[AaBb] (s) ⇌ a[Ab+] (aq) + b[Bb-] (aq), then

\[
Ksp = \text{[Ab+] } \times \text{[Bb-]}
\]

**Ksp** (Solubility product constant): the product of the concentration of ions in a saturated solution.

- If Amount (mol) of aqueous ions < 1, Ksp amount (mol) of solid substance.
- If Amount (mol) of aqueous ions > 1, Ksp amount (mol) of solid substance.

Molar solubility and the Ksp 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 Ksp to predict precipitate formation**.
**Polyprotic acids:** acids that donate more than one H⁺ ion

(tribasic = 2 H⁺, tribasic = 3 H⁺, etc.)

**Acids and Bases (cont)**

**Amphoteric 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:

- acid + base → salt + water

*Complete ionization, so no equilibrium analysis*

With weak acids/bases:

- acid + base ≠ conjugate base + conjugate acid

*Partial ionization, so equilibrium has to be analyzed*

**Acid/Base Constants (Kₐ and Kₖₐ)***

Kₐ/Kₖₐ indicate the strength of an acid/base

If $K_a/K_b > 1$ → Strong acid/base (complete ionization/disassociation)

If $K_a/K_b < 1$ → Weak acid/base (partial ionization/disassociation)

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

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

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

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

Water can dissociate into ions on its own:

$$H_2O(l) \leftrightarrow H^+(aq) + OH^-(aq)$$

But the H⁺ ion can also attack other H₂O molecules:

$$H_2O(l) + H^+(aq) \rightarrow H_3O^+(aq)$$

Adding both reactions together:

$$2H_2O(l) \leftrightarrow 2H_3O^+(aq) + OH^-(aq)$$

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

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

(H₂O(l) not included because it is not (aq))

Since water is neutral (pH = 7):

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}$$

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

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

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

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

\[Image \text{Gr. 12 Chemical Systems and Equilibrium Cheat Sheet} \]