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

Equilibrium Constant (Keq)

Keq formula:

If **a[A] + b[B] ⇌ c[C] + d[D]**; then

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

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

If **a[A] ⇌ b[B]**, then

$K_{forward} = ([B]^b) \div ([A]^a)$	$K_{backward} = ([A]^a) \div ([B]^b)$

So ∴ $K_{forward} = {}^1/K_{backward}$ @ equilibrium

Purpose of Keq: 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 Keq

If Q < Keq	[products] < [reactants] Reaction has not reached ⇌ yet; reaction needs to **shift right**
If Q > Keq	[products] > [reactants] Reaction has not reached ⇌ yet; reaction needs to **shift left**
If Q = Keq	[products] = [reactants] 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

↑ [conc]/T = shift to **consume**

↓ [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)

↑ V = ↓ P = shift toward side with **more** gas entities (i.e. more mol of gas) (more space for particles)

↓ V = ↑ P = shift toward side with **fewer** gas entities (i.e. less mol of gas) (less space for particles)

Catalysts/Inert (noble) gases → 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** ⇌ (**complete disassociation** into ions)

Slightly soluble compounds (**low** molar solubility) = **has** ⇌ (**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**) → solubility equilibrium

Equilibrium formula for solubility:

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

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

Ksp (Solubility product constant): the product of the [conc] of ions in a saturated solution

If **Ksp ≪ 1**	Amount (mol) of aqueous ions ≪ amount (mol) of solid substance
If **Ksp ≫ 1**	Amount (mol) of aqueous ions ≫ 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

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Equilibria of Slightly Soluble Compounds (cont)

If Q < K_{sp}	Not enough ions in solution (unsaturated); **no precipitate**; reaction will shift to the **right**
If Q > K_{sp}	Lots of ions in solution (saturated); **precipitate can form**; reaction will shift to the **left**
If Q = K_{sp}	System is at ⇌; **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$[H^+]$ = -log$[H_3O^+]$	**$[H_3O^+] = [H^+] = 10^{-pH}$**

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

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

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:

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 (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 (of acid) **· K_b** (of conjugate base)

K_w = K_b (of base) **· K_a** (of conjugate acid)

Autoionization of Water and Water Constant (Kw)

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

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

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

$$H_2O(l) + H^+(aq) \rightleftharpoons H_3O^+(aq)$$ [1]

Adding both reactions together:

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

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 (Kw) (cont)

$$[H^+] = 1.0\cdot10^{-7} \rightarrow [H_3O^+] = 1.0\cdot10^{-7}$$

$$pH + pOH = 14 \rightarrow pOH = 7 \rightarrow [OH^-] = 1.0\cdot10^{-7}$$

If $[H_3O^+] = 1.0\cdot10^{-7}$, and $[OH^-] = 1.0\cdot10^{-7}$, then:

$$K_w = (1.0\cdot10^{-7})(1.0\cdot10^{-7}) = 1.0\cdot10^{-14}*$$

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

* Value of K_w is **always** $1.0\cdot10^{-14}$

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