

CHAPTER 1: CHEMICAL EQUILIBRIUM

Comprehensive Concept Notes, Rate Kinetics, Law of Mass Action, Kc Derivations & Applications.



Theory & Derivations



Dynamic Equilibrium Diagrams



Solved Numericals

Reversible vs. Irreversible Reactions

Irreversible Reactions

Unidirectional Flow: Proceeds strictly from reactants to products ($\rightarrow$).

Completion: Reactants convert completely into products over time.

Equilibrium: Never establishes chemical equilibrium.

Example: Combustion of methane or neutralization ($\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$).

Reversible Reactions

Bidirectional Flow: Proceeds in both forward and reverse directions ($\rightleftharpoons$).

Non-Completion: Reactions never complete; reactants & products coexist.

Equilibrium: Reaches dynamic equilibrium in closed systems.

Example: $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$ in a sealed flask.

Concept of Dynamic Equilibrium

Dynamic Nature

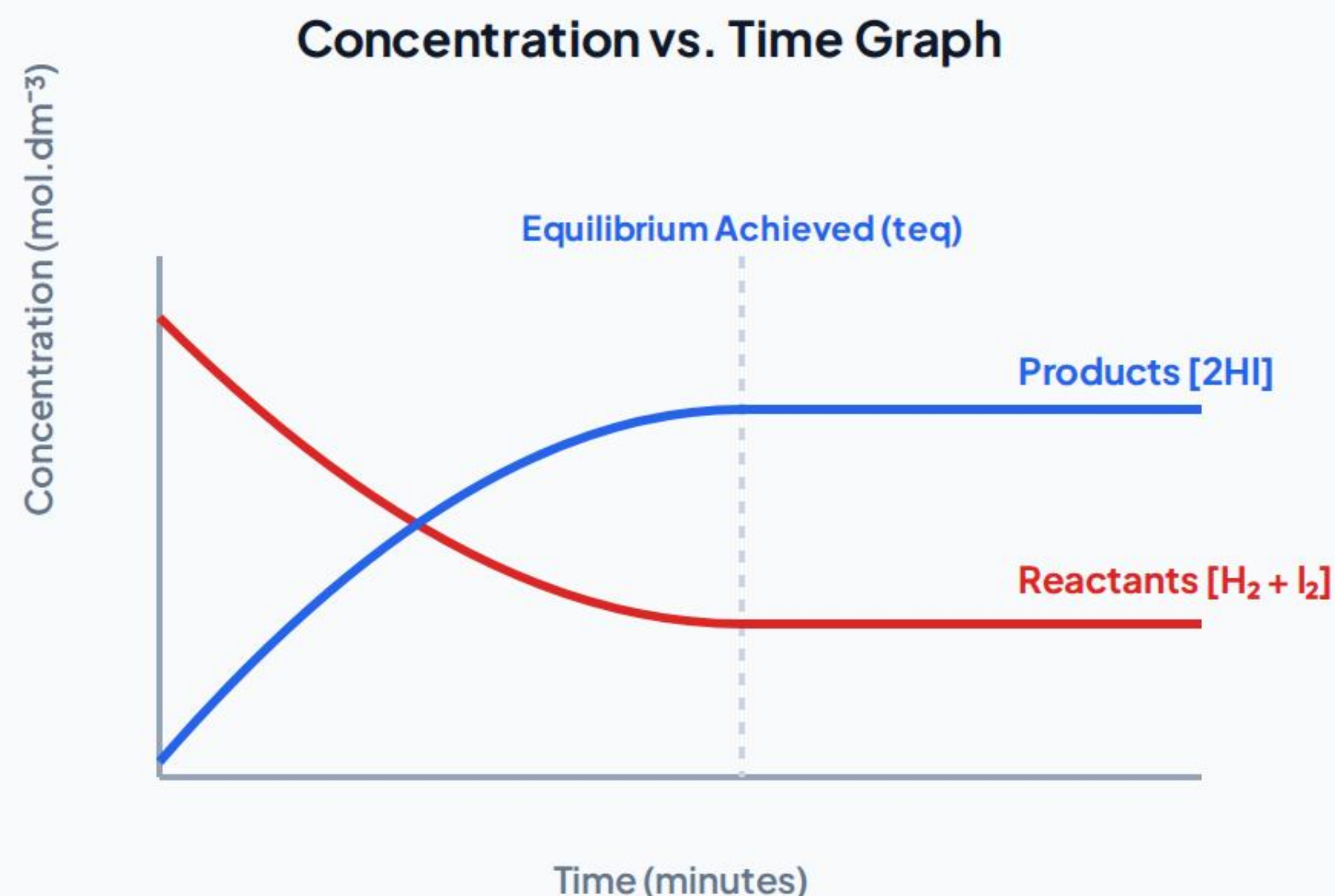
The reaction has **not stopped**. Forward and reverse processes occur simultaneously at identical rates ($R_f = R_r$).

Constant Concentrations

Amount of reactants and products remain constant at equilibrium, though not necessarily equal to each other.

Hydrogen-Iodine System

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ — Purple I_2 vapor fades until color intensity becomes constant.



1.1 CHARACTERISTICS

Macroscopic Properties of Equilibrium

→ Forward Reaction Profile

Moves left to right ($\text{Reactants} \rightarrow \text{Products}$).
Initial rate is maximum, gradually slowing over time.

← Reverse Reaction Profile

Moves right to left ($\text{Products} \rightarrow \text{Reactants}$).
Initial rate is zero, gradually speeding up as products accumulate.

🔒 Closed System Requirement

Equilibrium requires a sealed container. Neither reactants nor products can enter or escape the system.

↔ Reversibility & Recovery

Equilibrium can be approached from either side and re-established if disturbed by changing concentration, pressure, or temperature.

Law of Mass Action (Guldberg & Waage)

"The rate at which a substance reacts is directly proportional to its active mass, and the rate of a chemical reaction is directly proportional to the product of the active masses of reacting substances."

Active Mass Definition

Refers to molar concentration in $\text{mol} \cdot \text{dm}^{-3}$.
Represented by square brackets $[]$.

General Proportionality

For reactant A : $\text{Rate} \propto [A]$.
For reactants $A + B$: $\text{Rate} \propto [A] \times [B]$.

Equilibrium Constant Ratio

Ratio of product concentrations to reactant concentrations remains constant at a given temperature.

Derivation of Equilibrium Constant Expression (K_c)

Hypothetical Reversible Reaction: $aA + bB \rightleftharpoons cC + dD$

STEP 1**Forward Reaction Rate**

$$R_f \propto [A]^a [B]^b$$

$$R_f = k_f [A]^a [B]^b$$

STEP 2**Reverse Reaction Rate**

$$R_r \propto [C]^c [D]^d$$

$$R_r = k_r [C]^c [D]^d$$

STEP 3**Equilibrium ($R_f = R_r$)**

$$k_f [A]^a [B]^b = k_r [C]^c [D]^d$$

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

Units of Equilibrium Constant (K_c)

Case 1: Equal Moles ($\Delta n = 0$)

When total reactant moles equal product moles, concentration units cancel out completely.

Reaction:



Result: NO UNITS

Case 2: Unequal Moles ($\Delta n \neq 0$)

When moles of reactants and products are unequal, K_c carries specific molar units.

Reaction:



Unit: $\text{mol}^{-2} \cdot \text{dm}^6$

1.3 WORKED EXAMPLE

Solved Numerical Problem

Problem: $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{2(g)}$ at 230°C . Measured concentrations at equilibrium: $[\text{NO}] = 0.0542\text{ mol}\cdot\text{dm}^{-3}$, $[\text{O}_2] = 0.127\text{ mol}\cdot\text{dm}^{-3}$, $[\text{NO}_2] = 15.5\text{ mol}\cdot\text{dm}^{-3}$. Calculate K_c .

STEP 1: Write Expression

$$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]}$$

STEP 2: Substitute Values

$$K_c = \frac{(15.5)^2}{(0.0542)^2 \times 0.127}$$

STEP 3: Final Answer

$$6.44 \times 10^5 \text{ mol}^{-1}\cdot\text{dm}^3$$

Predicting Direction of Reaction (Q_c vs. K_c)

$$Q_c < K_c$$

Forward Shift

Reactants exceed equilibrium proportion. Reaction moves left-to-right to produce more products.

$$Q_c = K_c$$

At Equilibrium

System is in dynamic balance. Forward and reverse rates are exactly equal ($R_f = R_r$).

$$Q_c > K_c$$

Reverse Shift

Products exceed equilibrium proportion. Reaction moves right-to-left to restore reactants.

Predicting Extent of Reaction

Large K_c Value ($K_c \gg 1$)

Reaction proceeds almost to completion. Equilibrium mixture consists predominantly of products.

Nearly 100% Products

Moderate K_c Value ($K_c \approx 1$)

Equilibrium mixture contains appreciable amounts of both reactants and products.

Balanced Mixture

Small K_c Value ($K_c \ll 1$)

Reaction barely proceeds in the forward direction. Mixture consists mostly of unchanged reactants.

Mostly Reactants

Chapter 1 Key Takeaways Pipeline

01

Reversible Core

Dynamic state established when $R_f = R_r$ in a closed system.

02

Mass Action

$\text{Rate} \propto \text{Active Mass}$. $K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$.

03

Units Check

No units if $\Delta n = 0$; specific molar units if $\Delta n \neq 0$.

04

Kc Applications

Predicts direction (Q_c vs K_c) & extent (K_c magnitude).

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