Kinetics: The Rates of Reactions

– Chemical kinetics – studies the reaction rates and mechanisms

16.1 Factors Affecting the Reaction Rate

• **Chemical nature of the reactants** – each reaction has its own characteristic rate

• **Concentration** – the reaction rate increases with increasing the reactant concentrations (the collision frequency increases)

– The reactants must collide in order to react

Rate ∝ Collision freq. ∝ Concentration

• **Physical state** – the reaction rate increases with the degree of mixing (contact) between the reactants (depends on the reactant's phase)

• **Temperature** – the reaction rate increases with increasing the temperature (increases the collision frequency and the average kinetic energy of the molecules)

– The reactants must collide with sufficient energy in order to react

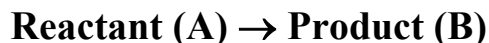*Rate ∝ Collision energy ∝ Temperature*

• **Catalyst** – increases (or decreases) the reaction rate by changing the reaction path (mechanism)

16.2 Expressing the Reaction Rate

• **Reaction rate** – change in the concentration (*C*) of reactants or products per unit time (*t*)

$$\text{Rate} = \Delta C / \Delta t$$

– **Units → M/s or mol/L·s**

Reactant (A) → Product (B)
$$\Delta C < 0 \qquad \Delta C > 0$$

➤ The rate is positive by convention, but ΔC is (-) for the reactants and (+) for the products

⇒ **Rate = -Δ[A]/Δt   or   Rate = Δ[B]/Δt**

➤ Square brackets represent the concentrations of the reactant [A] and product [B] in mol/L

Reaction Rate and Stoichiometry

• ΔC is dependent on the stoichiometric coefficients of the reactants and products

For a reaction,   **A → 2B**

➤ The concentration of **B** changes twice faster than the concentration of **A**

$$\Delta[B]/\Delta t = 2(-\Delta[A]/\Delta t)$$

➤ To make the rate independent of the choice of a reactant or product, we use the convention:

For a reaction, $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

$$Rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Example:

For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of formation of NH_3 is **1.4 M/min**. Calculate the rate of disappearance of H_2 and the reaction rate.

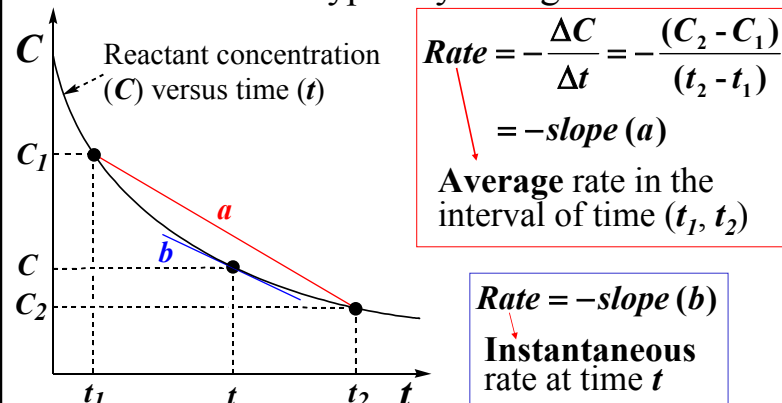$$\frac{\Delta[NH_3]}{\Delta t} = 1.4\frac{M}{min} \quad \rightarrow \quad 1.4\frac{mol\ NH_3}{L \cdot min}$$

$$1.4\frac{mol\ NH_3}{L \cdot min} \times \frac{3\ mol\ H_2}{2\ mol\ NH_3} = \boxed{2.1\frac{mol\ H_2}{L \cdot min}}$$

$$Rate = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = \frac{1}{2}1.4\frac{mol\ NH_3}{L \cdot min} = \boxed{0.70\frac{mol\ NH_3}{L \cdot min}}$$

Average and Instantaneous Rates

• The reaction rate typically changes with time

$$Rate = -\frac{\Delta C}{\Delta t} = -\frac{(C_2 - C_1)}{(t_2 - t_1)}$$

$$= -slope\ (a)$$

Average rate in the interval of time (t_1, t_2)

$$Rate = -slope\ (b)$$

Instantaneous rate at time t

➢ The instantaneous rate at time t is given by the slope of the **tangent** (b) to the curve at this time

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➢ As the interval of time (t_1, t_2) gets smaller, the slope of a approaches the slope of b and the average rate approaches the instantaneous rate

⇒ The instantaneous rate can be estimated by measuring the average rate in a narrow time interval

➢ Normally the term reaction rate refers to the instantaneous rate

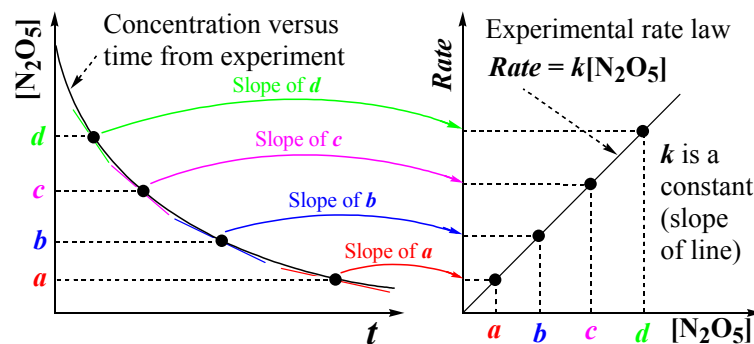• **Initial rate** – the instantaneous rate at time, $t=0$ (the starting point of the reaction)

– For most reactions the rate decreases gradually after the starting point so the slope of the tangents gets smaller with time

– Initial rates are easier to measure and depend on the initial concentrations which are normally known

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16.3 Rate Laws

• **Rate law** – the dependence of the instantaneous rate on the concentrations of the different species in the reaction → **determined experimentally**

Example: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

Concentration versus time from experiment

Experimental rate law
$Rate = k[N_2O_5]$

k is a constant (slope of line)

– For most reactions of the type

$$a\text{A} + b\text{B} + \ldots \rightarrow \textbf{Products}$$

the rate law can be expressed in the form:

$$\textit{Rate} = k[\text{A}]^m[\text{B}]^n \ldots$$

$\rightarrow$ **k** – **rate constant** (depends on the nature of A, B, … and the temperature)

$\rightarrow$ **m, n, …** – **reaction orders** with respect to A, B, …

$\rightarrow$ **$m + n + \ldots$** – **overall order** of the rate law

Example: $2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)$
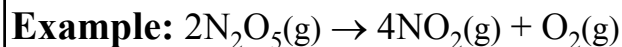
Rate law $\rightarrow$ *Rate* $= k[\text{N}_2\text{O}_5]$

$m = 1 \rightarrow$ first order in N_2O_5

$m + n + \ldots = 1 \rightarrow$ first order overall