

Chapter 2

1. Meaning and Measurement of Rate

- **Rate** is defined as the change in concentration of products or reactants in a course of time.

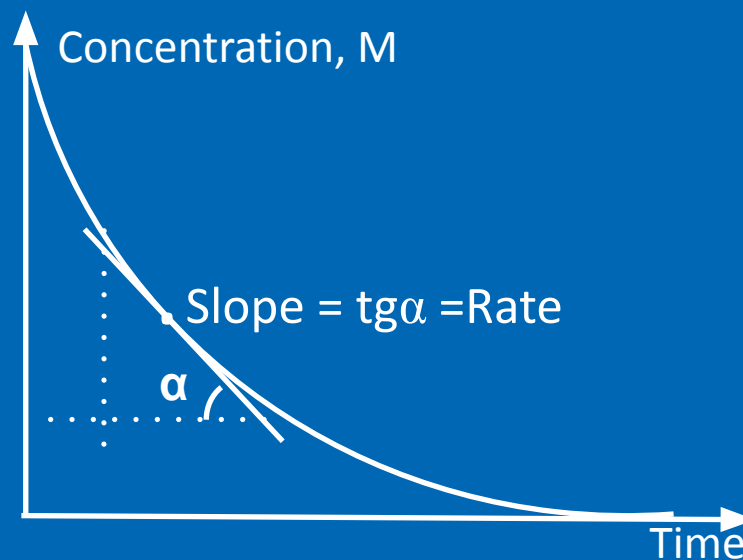
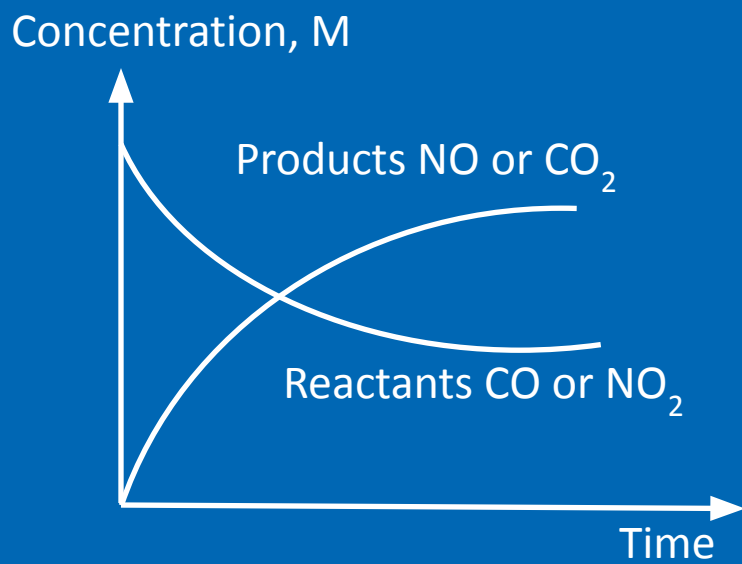
$$\text{Average Reaction Rate} = \frac{\text{change in concentration}}{\text{change in time}}$$

- Reaction rate is the maximum at the beginning of reaction.
- The reaction rate decreases as the concentration of reactants decrease.
- The study of reaction rates and reaction mechanisms is **chemical kinetics**.

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1. Meaning and Measurement of Rate

Lets have closer look to the reaction below.



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1. Meaning and Measurement of Rate



Rate expressions as follows;

$$\text{Rate} = -\frac{\Delta[\text{CO}]}{\Delta t} \quad \text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t}$$

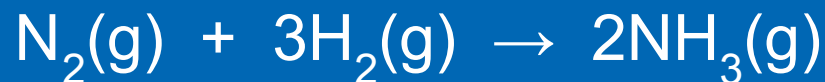
$$\text{Rate} = +\frac{\Delta[\text{CO}_2]}{\Delta t} \quad \text{Rate} = +\frac{\Delta[\text{NO}]}{\Delta t}$$

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1. Meaning and Measurement of Rate

Example 1

Find the rate relationship of reactants and products for the given reaction.



Solution

Rate expressions as follows;

$$\text{Rate} = -\frac{\Delta[\text{N}_2]}{\Delta t} \quad \text{Rate} = -\frac{\Delta[\text{H}_2]}{\Delta t} \quad \text{Rate} = +\frac{\Delta[\text{NH}_3]}{\Delta t}$$

Rate relationship

$$\text{Rate} = -\frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{\Delta[\text{H}_2]}{3\Delta t} = +\frac{\Delta[\text{NH}_3]}{2\Delta t}$$

- The decomposition of dinitrogen pentoxide can be represented by the equation;
- $$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$$
- The concentration of dinitrogen pentoxide decreases from 0,008 M to 0,004 M in 20 seconds. Find the average rate of consumption of dinitrogen pentoxide

- $\text{Rate}_{\text{N}_2\text{O}_5} = (0.008 - 0.004)/20 = 0.0002 = 2.10 \times 10^{-4} \text{ mol/L} \cdot \text{s}$

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Example 2

In the following decomposition reaction,



oxygen gas is produced at the average rate of $9.1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$. Over the same period, what is the average rate of the following:

- the production of nitrogen dioxide.
- the loss of nitrogen pentoxide.

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Solution

$$\begin{aligned}\text{rate NO}_2 \text{ production} &= 4 \times (9.1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}) \\ &= \mathbf{3.6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}}\end{aligned}$$

$$\begin{aligned}\text{rate loss of N}_2\text{O}_5 &= 2 \times (9.1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}) \\ &= \mathbf{1.8 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}}\end{aligned}$$

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3. Rate Expression and Rate Constant

Consider the one step following reaction;



- The rate expression is proportional to the product of [A] (to some power m) and [B] (to some power n). To create an equation instead of a proportion, use the rate constant k .

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

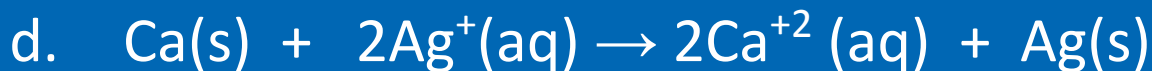
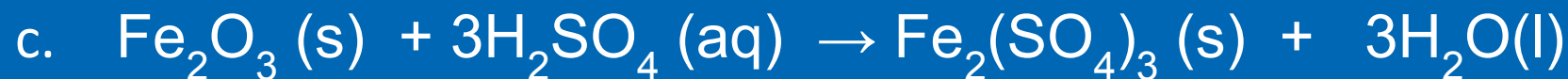
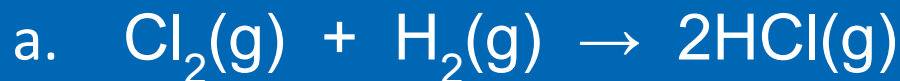
- m and n are order of reaction with respect to related substance, and k depends only on temperature and activation energy.
- Solids and liquids are not included in the expression, only gaseous and aqueous ions are indicated in the rate expression.

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3. Rate Expression and Rate Constant

Example 10

Write the possible rate expression of the following reactions.



Solution

a. $\text{Rate} = k[\text{Cl}_2][\text{H}_2]$

b. $\text{Rate} = k[\text{Cl}_2]$

c. $\text{Rate} = k[\text{H}_2\text{SO}_4]^3$

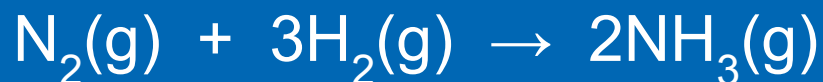
d. $\text{Rate} = k[\text{Ag}^+]^2$

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3. Rate Expression and Rate Constant

Example 11

Write the rate expression of the following one step reaction, determine the order of reaction in terms of N_2 and H_2 , and overall order.



Solution

$$\text{Rate} = k[\text{N}_2][\text{H}_2]^3$$

Order in terms of N_2 is 1 and 3 in terms of H_2

Overall order is $1+3 = 4$

Temperature

- The increase in temperature increases rate of reaction. And rate can be calculated by the formula below.

$$Vt_2 = Vt_1 \cdot \gamma^{(t_2 - t_1)/10}$$

γ is a constant and given in the question.

Vt_1 = velocity at initial temperature,

Vt_2 = velocity at final temperature

Ex: If temperature increases 10°C , rate increases 3 times. How many $^{\circ}\text{C}$ must the temperature be increased so that rate can increase 27 times?

$$\text{If } t_2 - t_1 = 10 \quad Vt_2 = 3Vt_1$$

$$\text{Then } \frac{Vt_2}{Vt_1} = 3 = Y^{10/10} \quad 3 = Y^1 \quad \text{so } Y = 3$$

$$\text{If } Vt_2 = 27 \cdot Vt_1 \quad \text{then} \quad \frac{Vt_2}{Vt_1} = 27 = 3^{(t_2 - t_1)/10}$$
$$(t_2 - t_1)/10 = 3$$

$$\text{So } t_2 - t_1 = 30^{\circ}\text{C}$$