

## 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**.

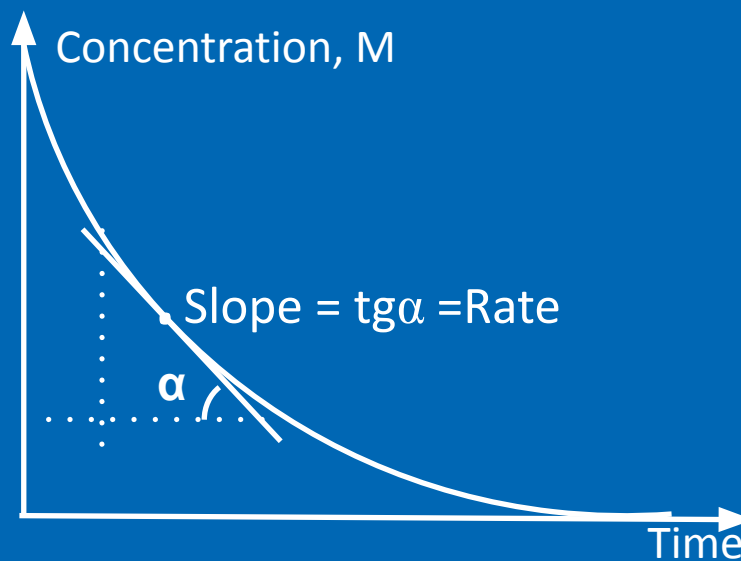
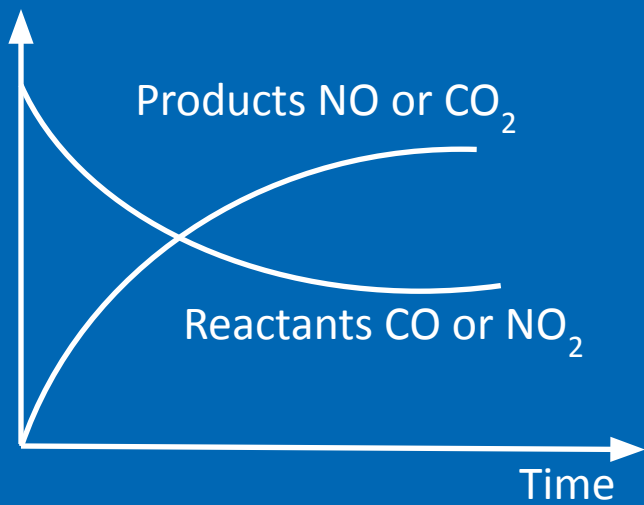
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# 1. Meaning and Measurement of Rate

Lets have closer look to the reaction below.



Concentration, M



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### 1. Meaning and Measurement of Rate



Rate expressions as follows;

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

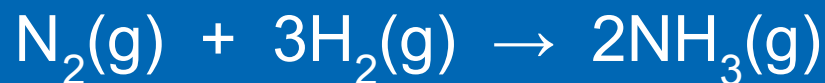
$$\text{Rate} = +\frac{\Delta[\text{CO}_2]}{\Delta t} \quad \text{Rate} = +\frac{\Delta[\text{NO}]}{\Delta t}$$

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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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# 1. Meaning and Measurement of Rate

### *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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### 1. Meaning and Measurement of Rate

*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  $k$ .

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

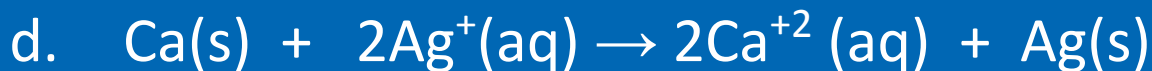
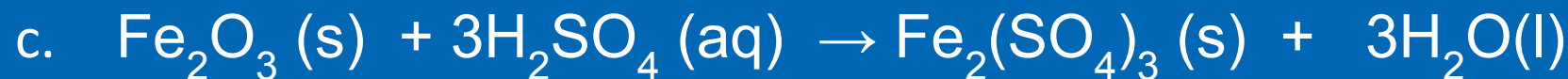
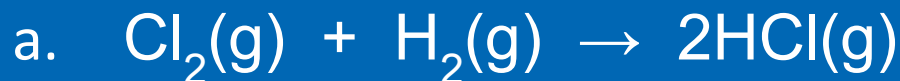
- $m$  and  $n$  are order of reaction with respect to related substance, and  $k$  depends only on temperature and activation energy.
- Solids and liquids are not included in the expression, only gaseous and aqueous ions are indicated in the rate expression.

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

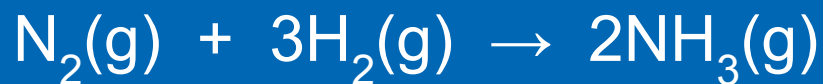
d.  $\text{Rate} = k[\text{Ag}^+]^2$

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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

$$\text{Rate} = k[N_2][H_2]^3$$

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.

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

$\gamma$  is a constant and given in the question.

$Vt_1$  = velocity at initial temperature,

$Vt_2$  = velocity at final temperature

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

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

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

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

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