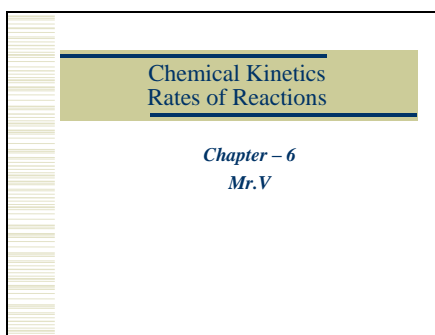


Slide 1



Chemical Kinetics  
Rates of Reactions

Chapter - 6  
Mr.V

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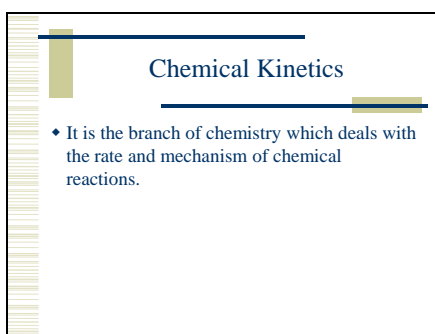
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Slide 2



Chemical Kinetics

- ♦ It is the branch of chemistry which deals with the rate and mechanism of chemical reactions.

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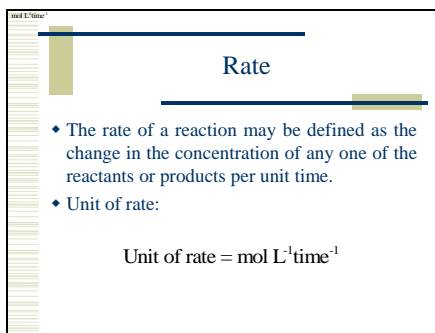
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Slide 3



Rate

- ♦ The rate of a reaction may be defined as the change in the concentration of any one of the reactants or products per unit time.
- ♦ Unit of rate:

Unit of rate =  $\text{mol L}^{-1}\text{time}^{-1}$

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Slide 4

Average Rate

- ♦ Total change in concentration by total time taken is known as average rate.

$$\text{Average rate} = \frac{[\text{Total change in concentration}]}{[\text{Total time taken}]}$$

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Slide 5

Instantaneous rate  $\frac{dx}{dt}$

- ♦ The rate of change of concentration of any one of the reactants or products at that particular instant of time.  
For the reaction  $A \rightarrow B$

$$\text{Rate of reaction} = -\frac{d[A]}{dt}$$
$$\text{Rate of reaction} = \frac{d[B]}{dt}$$

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Slide 6

Rate from Graph

- ♦ The rate can be determined by finding the slope of the tangent to the curve at the point corresponding to that instant of time.

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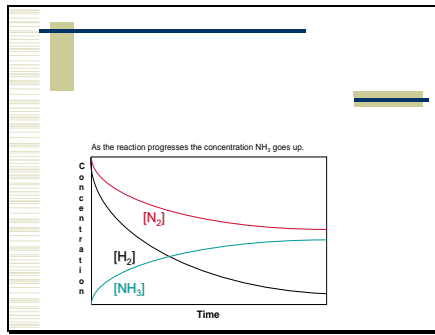
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Slide 7



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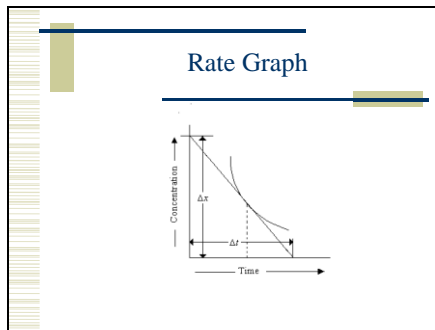
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Slide 8



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Slide 9

### Examples of differential rates

$A + B \rightleftharpoons C + D$

Differential rate for A =  $-\frac{d[A]}{dt}$

Differential rate for B =  $-\frac{d[B]}{dt}$

Differential rate for C =  $+\frac{d[C]}{dt}$

Differential rate for D =  $+\frac{d[D]}{dt}$

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Slide 10

### Law of Mass Action

- ♦ This law gives the theoretical dependence of rate of reaction on concentration.

Law of mass action  
 $aA + bB \rightleftharpoons cC + dD$   
Rate<sub>i</sub> = k<sup>i</sup> [A]<sup>a</sup> [B]<sup>b</sup>  
Rate<sub>o</sub> = k<sup>o</sup> [C]<sup>c</sup> [D]<sup>d</sup>  
At equilibrium Rate<sub>i</sub> = Rate<sub>o</sub>

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Slide 11

### Rate law

- ♦ The rate law is an experimentally determined factor. It does not depend on the law of mass action. The dependence of rate of the different concentration terms is expressed using order of a reaction.

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Slide 12

### Methods for measuring rates

**Methods for measurement of rates:**

- Change in colour
- Change in pressure for gaseous systems
- Formation of a precipitate
- Fast scan IR
- Change in electrical conductivity
- Change in pH

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Slide 13

**Order of reaction**

- ♦ It may be defined as the sum of the powers to which the concentration terms are raised in a rate law expression.

$$aA + bB \rightarrow cC + dD$$
$$\text{Rate} = k [A]^x [B]^y$$

*order 'n' of the reaction = x + y*

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Slide 14

**Different orders**

- ♦ Zero order
- ♦ First order
- ♦ Second order
- ♦ Third order
- ♦ Fractional order

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Slide 15

**Zero order reaction**

- ♦ A **zero order reaction** is independent of the concentration of reactants.
- ♦ The rate of the reaction does not depend on the concentration terms or in other words an increase in the quantity of the reactants does not increase the rate of the reaction.
- ♦ Photochemical formation of HCl from hydrogen and chlorine is a zero order reaction.

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Slide 16

Example of Zero order

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$
$$Rate = k[H_2]^0 [Cl_2]^0$$
$$Order 'n' = 0 + 0 = 0$$

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Slide 17

Unit for 'k' - Zero order reaction

- Same as rate

$$Rate = k[H_2]^0 [Cl_2]^0$$
$$Order 'n' = 0 + 0 = 0$$
$$k = \frac{Rate}{[H_2]^0 [Cl_2]^0}$$
$$k = \frac{molL^{-1}T^{-1}}{[H_2]^0 [Cl_2]^0}$$
$$k = molL^{-1}T^{-1}$$

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Slide 18

First order reaction

- The rate of a first order reaction depends on one concentration term only.
- It is possible that there could be more than one reactants involved in the reaction.
- All nuclear fission reactions are first order decay or disintegration.
- Hydrolysis of esters: are first order reactions

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Slide 19

**Example of first order reaction**

- Hydrolysis of esters

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$
$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]^1$$
$$\text{Order} = 1$$

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Slide 20

**Unit for 'k' - First order reaction**

- Time<sup>-1</sup>

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$
$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]^1$$
$$\text{Order} = 1$$
$$k = \frac{\text{Rate}}{[\text{CH}_3\text{COOC}_2\text{H}_5]}$$
$$k = \frac{\text{molL}^{-1}\text{T}^{-1}}{[\text{molL}^{-1}]}$$
$$k = \text{Time}^{-1}$$

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Slide 21

**Second order reaction**

- The rate of a second order reaction is dependent on two concentration terms.
- This depends on the mechanism of the reaction

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Slide 22

**Mechanism of reaction**

- ♦ Slowest step is the rate determining step in this multi step reaction.

Step 1:  $\text{NO}_2 + \text{F}_2 \xrightarrow{\text{Slow}} \text{NO}_2\text{F} + \text{F}$

Step 2:  $\text{NO}_2 + \text{F} \xrightarrow{\text{Fast}} \text{NO}_2\text{F}$

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Total:  $2 \text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$

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Slide 23

**Example of Second order**

- ♦  $2\text{NO}_{2(g)} + \text{F}_{2(g)} \rightarrow 2\text{NO}_2\text{F}_{(g)}$   
*Experimentally it has been found*  
Rate of reaction  $\propto [\text{NO}_2]^1 [\text{F}_2]^1$   
Order 'n' = 1 + 1 = 2

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Slide 24

**Unit for 'k' Second order rxn**

- ♦  $2\text{NO}_{2(g)} + \text{F}_{2(g)} \rightarrow 2\text{NO}_2\text{F}_{(g)}$   
*Experimentally it has been found*  
Rate of reaction  $\propto [\text{NO}_2]^1 [\text{F}_2]^1$   
Order 'n' = 1 + 1 = 2

$$k = \frac{\text{Rate}}{[\text{NO}_2]^1 [\text{F}_2]^1}$$
$$k = \frac{\text{molL}^{-1}\text{T}^{-1}}{[\text{molL}^{-1}][\text{molL}^{-1}]}$$
$$k = \text{Lmol}^{-1}\text{T}^{-1}$$

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Slide 25

### Molecularity

- ♦ The number of reacting species (atoms, ions or molecules) that must collide with each other simultaneously so as to result in a chemical reaction is called molecularity

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Slide 26

### Pseudo Uni-molecular reactions

- ♦ Reactions in which the ORDER is one but molecularity is two is called pseudounimolecular reactions.
- ♦ E.g. Hydrolysis of Esters.  
$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$
$$Rate = k[CH_3COOC_2H_5]$$
$$Order = 1$$
$$Molecularity\ is\ two$$

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Slide 27

### Factors affecting rate

- ♦ Nature of reactants
- ♦ Concentrations of reactants
- ♦ Temperature
- ♦ Catalyst
- ♦ Radiation

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Slide 28

**Collision Theory**

- ♦ Molecules must collide to react.
- ♦ Concentration affects rates because collisions are more likely.
- ♦ Must collide hard enough. (Right amount of energy)
- ♦ Temperature and rate are related.
- ♦ Only a small number of collisions produce reactions.

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Slide 29

**Nature of reactants**

- ♦ Physical state of reactants
  - Gases
  - Liquid
  - Solid
- ♦ Particle size of reactants
  - Larger the surface area the greater is the rate of reaction. Powdered substances react faster.
- ♦ Chemical nature of reactants
  - Types of bonds

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Slide 30

**Concentration of reactants**

- ♦ The rate of the reaction decreases with decrease in concentration.
- ♦ This is obvious from the law of mass action.
- ♦ When the concentration is large the chance of reactants coming in contact with each other is greater.
- ♦ Hence the rate of the reaction will increase

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Slide 31

### Temperature

- ♦ Rise in temperature increases rate of reaction why?
- ♦ Rise in temperature increases number of collisions but the rate of reaction is not proportional to the number of collisions why?

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Slide 32

### Rise of temperature increases rate of reaction why?

- ♦ All collisions are not effective.
- ♦ Effective collisions are those collisions that lead to the formation of products.
- ♦ These molecules possess **Activation Energy**
- ♦ The minimum energy that reactant molecules should possess in order that they change into products is called **ACTIVATION ENERGY**
- ♦ **The value of this energy depends on the energy of the reactants**

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Slide 33

### Effect of temperature

Threshold Energy → ← Energy Barrier

$E_a$   $E_a$ , Energy of Activation

Reactants → Products  $\Delta H$

Progress of reaction →

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Slide 34

What is proper orientation

- ♦ Molecules that have the energy of activation should be properly aligned (oriented) for the collisions to be effective.

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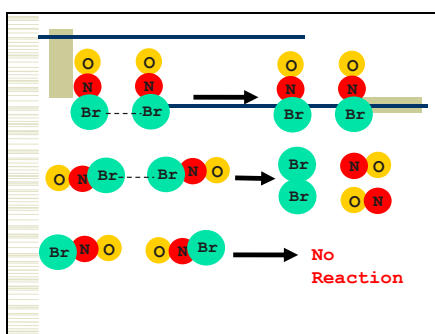
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Slide 35



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Slide 36

Rise in temperature increases number of collisions but the rate of reaction is not proportional to the number of collisions why?

- ♦ This is based on probability and distributions of energies of reacting molecules within a system
- ♦ This can be explained using the "Maxwell Boltzman Distribution Curves"

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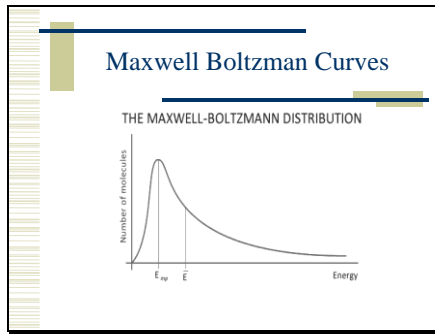
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Slide 37



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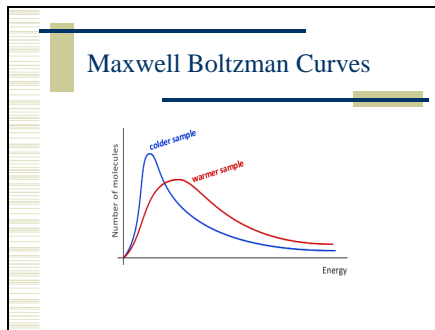
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Slide 38



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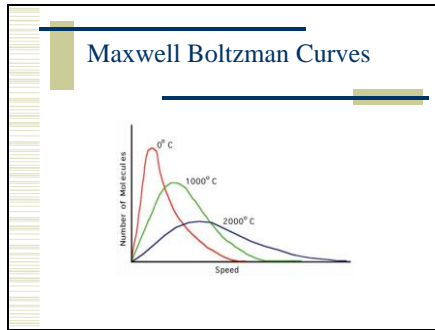
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Slide 39



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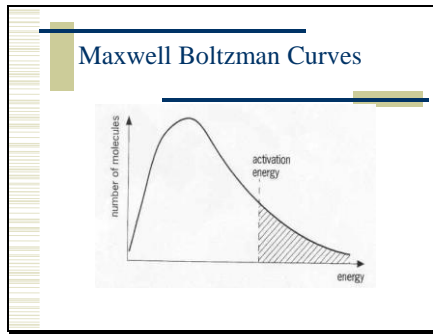
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Slide 40



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Slide 41

### Temperature

- ♦ As a rule generally speaking a rise in temperature increases the rate of reaction (whether endothermic or exothermic)
- ♦ This is because all reactions occur only if the reactants molecules possess *Threshold Energy*

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Slide 42

### Threshold energy

- ♦ It may be defined as the minimum amount of energy which the colliding molecules must possess in order that the collisions may become effective.

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Slide 43

### Energy of Activation

- ♦ The extra amount of energy which the molecules of the reactants have to absorb so that their energy becomes equal to the threshold energy is called **Activation Energy**. (Refer graph)
- ♦ Activation Energy = Threshold Energy - Energy possessed by the reactant molecules.
- ♦ *Fast reactions have low activation energy*
- ♦ *Slow reactions have high activation energy*

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Slide 44

### Catalyst

The diagram illustrates the energy profile of a reaction. The vertical axis represents Energy, and the horizontal axis represents the Progress of reaction. Two curves are shown: a higher curve representing the uncatalyzed reaction and a lower curve representing the catalyzed reaction. The energy barrier (the peak of the curve) is lower for the catalyzed reaction. The energy of activation ( $E_a$ ) is the energy difference between the reactants and the peak. The threshold energy is the energy level of the reactants. The products are at a lower energy level than the reactants, and the enthalpy change ( $\Delta H$ ) is the energy difference between the reactants and products.

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Slide 45

### Catalyst

- ♦ A catalyst is a substance that increases the speed of a reaction without itself undergoing any chemical change.
- ♦ A catalyst provides an alternate path with lower energy barrier. It decreases the *energy of activation* of the reaction.

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Slide 46

**Radiation**

- ◆ Photochemical reactions: Reactions which take place in the presence of light.
- ◆ Reaction between  $H_2$  and  $Cl_2$
- ◆ Steps involved in photochemical reactions

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Slide 47

**Examples**

- ◆ Photography
- ◆ Photosynthesis
- ◆ Blue Printing
- ◆ Reaction between  $H_2$  and  $Cl_2$  in the formation of HCl

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Slide 48

**Photochemical reactions**

- ◆ Chain initiation
- ◆ Chain propagation
- ◆ Chain termination

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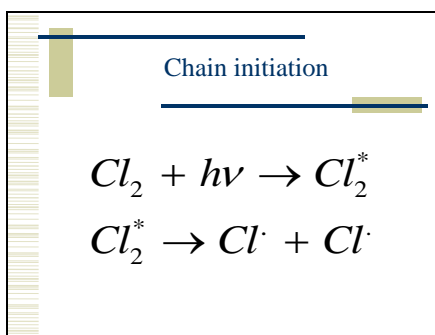
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Slide 49



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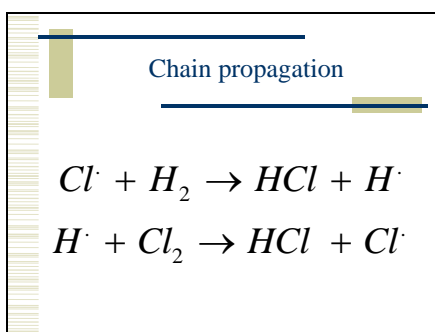
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Slide 50



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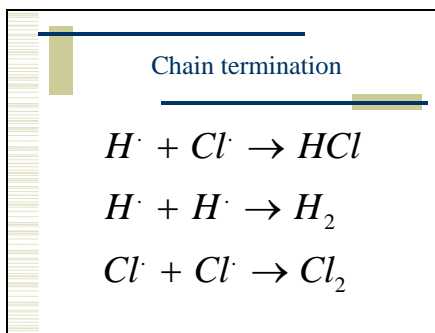
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Slide 51



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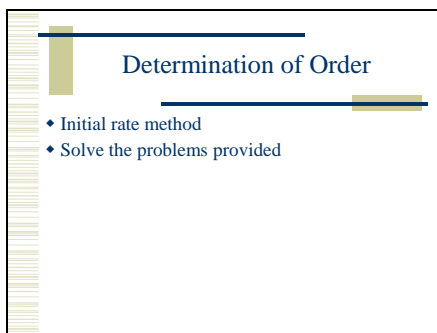
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Determination of Order

- ◆ Initial rate method
- ◆ Solve the problems provided

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