

..... Chemical kinetics

1.Differentiate between molecularity and order.

Ans:

Molecularity :

- 1.Molecularity is the number of ions or molecules that take part in the rate-determining step.
- 2.It is always a whole number
- 3.The molecularity of the reaction is determined by looking at the reaction mechanism
- 4.It is theoretical concept
- 5.It is meaningful only for simple reactions or individual steps of a complex reaction

Order:

- 1.Number of molecules of the reactant whose concentration changes during the chemical change
- 2.It can either be a whole number or a fraction
- 3.The order of the reaction is determined by the experimental methods
- 4.It is experimental concept
- 5.It is meant for the reaction and not for its individual steps.

2.Define order of a reaction, molecularity of a reaction and half-life period. Show that for first order reactions the half-life period is independent of the initial concentration

Ans:

The order of a reaction is defined as the sum of the powers of concentration in the rate law.

Let us consider the example of a reaction which has the rate law

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

The order of such a reaction is $(m+n)$

Molecularity is the number of reacting molecules, such as atoms, which collide and result in a chemical reaction.

The half-life of a chemical reaction can be defined as the time taken for the concentration of a given reactant to reach 50% of its initial concentration

FIRST ORDER REACTIONS

Let us consider a first **order** reaction



Suppose that at the beginning of the reaction ($t = 0$), the concentration of A is a moles litre⁻¹. If after time t , x moles of A have changed, the concentration of A is $a - x$. We know that for a first **order** reaction, the rate of reaction, dx/dt , is directly proportional to the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k(a - x)$$

$$\text{or} \quad \frac{dx}{a - x} = k dt \quad \dots(1)$$

Integration of the expression (1) gives

$$\int \frac{dx}{a - x} = \int k dt$$

$$\text{or} \quad -\ln(a - x) = kt + I \quad \dots(2)$$

where I is the constant of integration. The constant k may be evaluated by putting $t = 0$ and $x = 0$.

Thus,

$$I = -\ln a$$

Substituting for I in equation (2)

$$\ln \frac{a}{a - x} = kt \quad \dots(3)$$

$$\text{or} \quad k = \frac{1}{t} \ln \frac{a}{a - x}$$

Changing into common logarithms

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \quad \dots(4)$$

The value of k can be found by substituting the values of a and $(a - x)$ determined experimentally at time interval t during the course of the reaction.

Sometimes the integrated rate law in the following form is also used :

$$k = \frac{2.303}{t_2 - t_1} \log \frac{(a - x_1)}{(a - x_2)}$$

where x_1 and x_2 are the amounts decomposed at time intervals t_1 and t_2 respectively from the start.

3. Deduce the rate expression for second order reaction where both the concentration terms are same. What is half-life period of the second order reaction?

Ans:

SECOND ORDER REACTIONS

Let us take a second **order** reaction of the type



Suppose the initial concentration of A is a moles litre⁻¹. If after time t , x moles of A have reacted, the concentration of A is $(a - x)$. We know that for such a second **order** reaction, rate of reaction is proportional to the square of the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k(a - x)^2 \quad \dots(1)$$

where k is the rate constant, Rearranging equation (1), we have

$$\frac{dx}{(a - x)^2} = k dt \quad \dots(2)$$

On integration, it gives

$$\frac{1}{a - x} = kt + I \quad \dots(3)$$

where I is integration constant. I can be evaluated by putting $x = 0$ and $t = 0$. Thus,

$$I = \frac{1}{a} \quad \dots(4)$$

Substituting for I in equation (3)

$$\frac{1}{a - x} = kt + \frac{1}{a}$$

$$kt = \frac{1}{a - x} - \frac{1}{a}$$

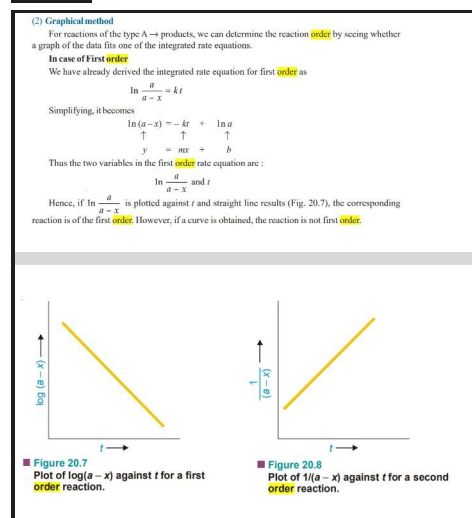
$$\text{Thus} \quad k = \frac{1}{t} \frac{x}{a(a - x)}$$

This is the integrated rate equation for a second **order** reaction.

half-life period of the second order reaction:

4. Describe the graphical method for the determination of order of reaction.

Ans:



5. Derive the integrated Arrhenius equation of activation energy. How is the energy of activation determined from the plot?

Ans:

Temperature Dependence of Reaction Rate and Arrhenius Equation

We know that the kinetic energy of a gas is directly proportional to its temperature. Thus as the temperature of a system is increased, more and more molecules will acquire necessary energy greater than E_a to cause productive collisions. This increases the rate of the reaction.

In 1889, Arrhenius suggested a simple relationship between the rate constant, k , for a reaction and the temperature of the system.

$$k = A e^{-E_a/RT} \quad \dots(1)$$

This is called the **Arrhenius equation** in which A is an experimentally determined quantity, E_a is

the activation energy, R is the gas constant, and T is Kelvin temperature.

Taking natural logs of each side of the Arrhenius equation, it can be put in a more useful form :

$$\ln k = -\frac{E_a}{RT} + \ln A \quad \dots(2)$$

$$\log k = -\frac{E_a}{2.303 RT} + \log A \quad \dots(3)$$

If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively, we can derive

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \dots(4)$$

Arrhenius equation is valuable because it can be used to calculate the activation energy, E_a , if the experimental value of the rate constant, k , is known.

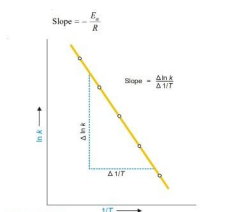


Figure 23.11
The plot of $\ln k$ versus $1/T$ gives a straight line. The slope of line $\Delta \ln k / \Delta 1/T$ gives E_a using the expression given above.

6.A solution of H₂O₂ when titrated against KMnO₄ solution at different time intervals gave the following results :

t (minutes)	0	10	20
Vol KMnO ₄ used for 10 ml H ₂ SO ₄	23.8 ml	14.7 ml	9.1 ml

Show that the decomposition of H₂O₂ is a first order reaction.

Ans:

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SOLUTION

The integrated rate equation for first order reaction is

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Since volume of KMnO₄ used in the titration is measure of concentration of H₂O₂ in solution,

$$a = 23.8 \text{ ml}$$

$$(a-x) = 14.7 \quad \text{when } t = 10 \text{ mins}$$

$$(a-x) = 9.1 \quad \text{when } t = 20 \text{ mins}$$

Substituting these values in the rate equation above, we have

$$k = \frac{2.303}{10} \log \frac{23.8}{14.7} = 0.2303 (\log 23.8 - \log 14.7)$$

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$$= 0.2303 (1.3766 - 1.1673)$$

$$= 0.04820$$

and

$$k = \frac{2.303}{20} \log \frac{23.8}{9.1}$$

$$= 0.10165 (\log 23.8 - \log 9.1)$$

$$= 0.10165 (1.3766 - 0.9595) = 0.04810$$

Since the value of k is almost constant, the decomposition of H₂O₂ is a **first order reaction**.

7.

SOLVED PROBLEM. Hydrolysis of ethyl acetate by NaOH using equal concentration of the reactants, was studied by titrating 25ml of the reaction mixture at different time intervals against standard acid. From the data given below, establish that this is a second order reaction.

t (mts)	0	5	15	25
ml acid used	16.00	10.24	6.13	4.32

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SOLUTION

The second order integrated rate equation is

$$k = \frac{1}{at} \cdot \frac{x}{a(a-x)} \quad \dots(1)$$

The volume of acid used at any time is a measure of concentration of the unreacted substances at that time.

Therefore,

a , initial concentration = 16.00
 after 5 mts ($a-x$) = 10.24 and $x = 5.76$

after 15 mts ($a-x$) = 6.13 and $x = 9.85$
 after 25 mts ($a-x$) = 4.32 and $x = 11.68$

Substituting values in the rate equation (1), we have

$$k = \frac{1}{16 \times 5} \cdot \frac{5.76}{10.24} = 0.0070$$

$$k = \frac{1}{16 \times 15} \cdot \frac{9.85}{6.13} = 0.0067$$

$$k = \frac{1}{16 \times 25} \cdot \frac{11.68}{4.32} = 0.00675$$

The values of k being fairly constant, this reaction is of the second order.

8. Compound A decomposes to form B and C the reaction is first order. At 25°C the rate constant for the reaction is 0.450s⁻¹. What is the half-life of A at 25°C?

Ans:

SOLVED PROBLEM 1. Compound A decomposes to form B and C the reaction is first order. At 25°C the rate constant for the reaction is 0.450 s⁻¹. What is the half-life of A at 25°C?

SOLUTION

We know that for a first order reaction, half-life $t_{1/2}$ is given by the expression

$$t_{1/2} = \frac{0.693}{k}$$

where k = rate constant

Substituting the value of $k = 0.450 \text{ s}^{-1}$, we have

$$t_{1/2} = \frac{0.693}{0.450 \text{ s}^{-1}} = 1.54 \text{ s}$$

Thus half-life of the reaction $A \rightarrow B + C$ is 1.54 seconds.

9. For a certain first order reaction $t_{0.5}$ is 100 sec. How long will it take for the reaction to be completed 75%?

SOLVED PROBLEM 6. For a certain first order reaction $t_{0.5}$ is 100 sec. How long will it take for the reaction to be completed 75%?

SOLUTION

Calculation of k

For a first order reaction

$$t_{1/2} = \frac{0.693}{k}$$

or

$$100 = \frac{0.693}{k}$$

$$\therefore k = \frac{0.693}{100} = 0.00693 \text{ sec}^{-1}$$

Calculation of time for 75% completion of reaction

The integrated rate equation for a first order reaction is

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

or

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

When $\frac{3}{4}$ initial concentration has reacted, it is reduced to $\frac{1}{4}$

Substituting values in the rate equation

$$t_{0.75} = \frac{2.303}{0.00693} \log \frac{[A]_0}{\frac{1}{4}[A]_0}$$

$$= \frac{2.303}{0.00693} \log 4 = 200 \text{ sec}$$

**10.50% of a first order reaction is complete in 23 minutes.
Calculate the time required to complete 90% of the reaction.**

SOLVED PROBLEM 7. 50% of a first order reaction is complete in 23 minutes. Calculate the time required to complete 90% of the reaction.

SOLUTION

Calculation of k

$$t_{0.5} = \frac{0.693}{k}$$

or

$$k = \frac{0.693}{t_{0.5}} = \frac{0.693}{23} = 0.0301304 \text{ min}^{-1}$$

Calculation of time for 90% completion of the reaction

For first order reaction, integrated rate equation is

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad \dots(1)$$

or

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]} \quad \dots(2)$$

When 90% of the initial concentration has reacted, 10% of it is left. That is,

$$[A] = \frac{1}{10} [A]_0$$

Substituting values in equation (2)

$$t = \frac{2.303}{0.0301304} \log \frac{[A]_0}{\frac{1}{10}[A]_0} = \frac{2.303}{0.0301304} \log 10$$

$$= \frac{2.303}{0.0301304} = 76.4 \text{ min}$$

11.Ans

SOLVED PROBLEM. The gas-phase reaction between methane (CH_4) and diatomic sulphur (S_2) is given by the equation



At 550°C the rate constant for this reaction is $1.1 \text{ l mol}^{-1} \text{ sec}$ and at 625°C the rate constant is $6.4 \text{ l mol}^{-1} \text{ sec}$. Calculate E_a for this reaction.

SOLUTION

Here

$$k_1 = 1.1 \text{ lre mol}^{-1} \text{ sec. } T_1 = 550 + 273 = 823 \text{ K}$$

$$k_2 = 6.4 \text{ lre mol}^{-1} \text{ sec. } T_2 = 625 + 273 = 898 \text{ K}$$

Substituting the values in the equation

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}}\right)$$

Solving for E_a gives

$$E_a = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}}\right)}$$

$$= 1.4 \times 10^5 \text{ J/mol}$$