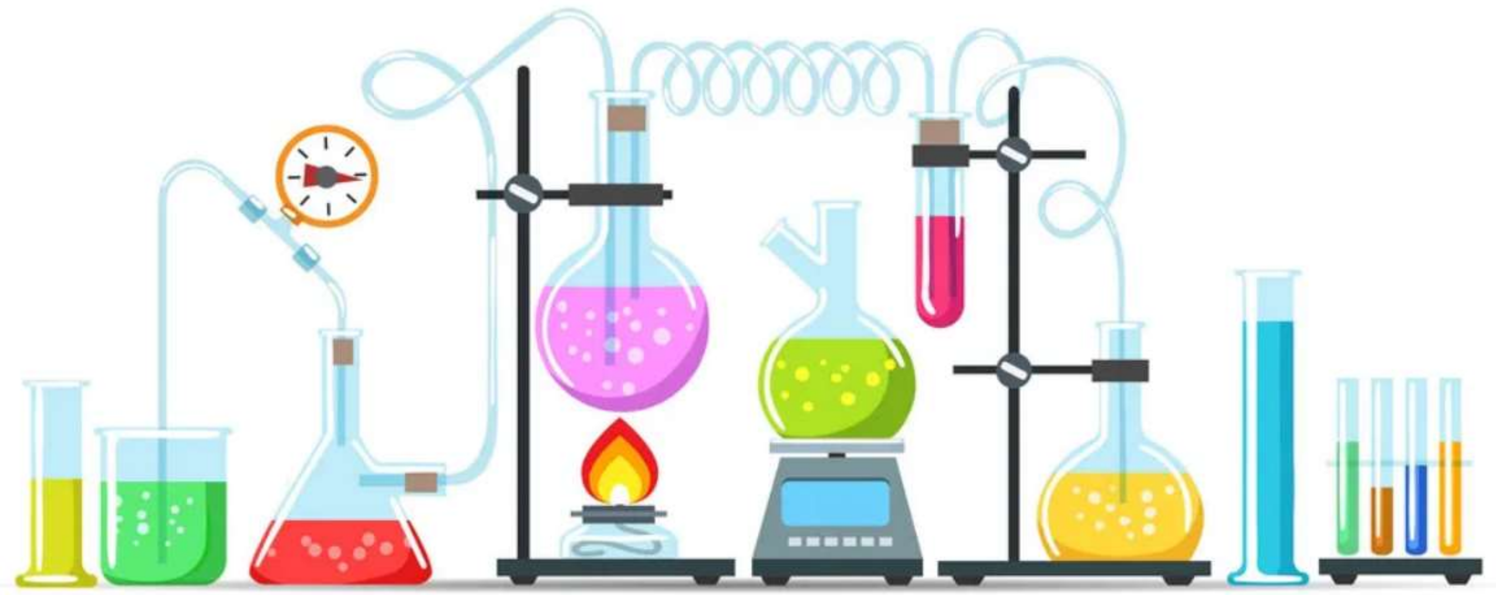
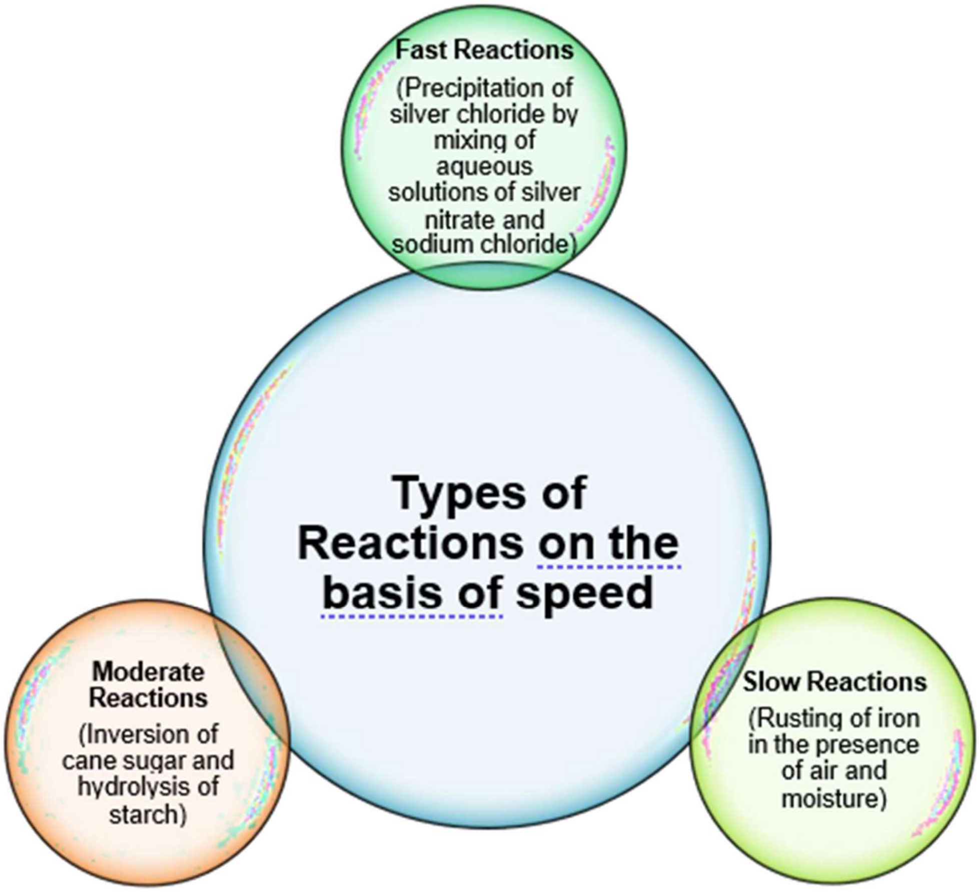
CHEMISTRY



CHEMICAL KINETICS

Rate of Chemical Reaction



Rate of Chemical Reaction

The **rate of reaction** is the change in concentration of a reactant or productin unit time.

- Alternatively, the rate of reaction can also be expressed as

The rate of decrease in concentration of any one of the reactants.

The rate of increase in concentration of any one of the products.

- Consider a hypothetical reaction, assuming that the volume of the system remains constant.

$$R \rightarrow P$$

  One mole of the reactant R produces one mole of the product P.
- If $[R]_1$ and $[P]_1$ are the concentrations of R and P at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2, then

$$\Delta t = t_2 - t_1$$
$$\Delta[R] = [R]_2 - [R]_1$$
$$\Delta[P] = [P]_2 - [P]_1$$

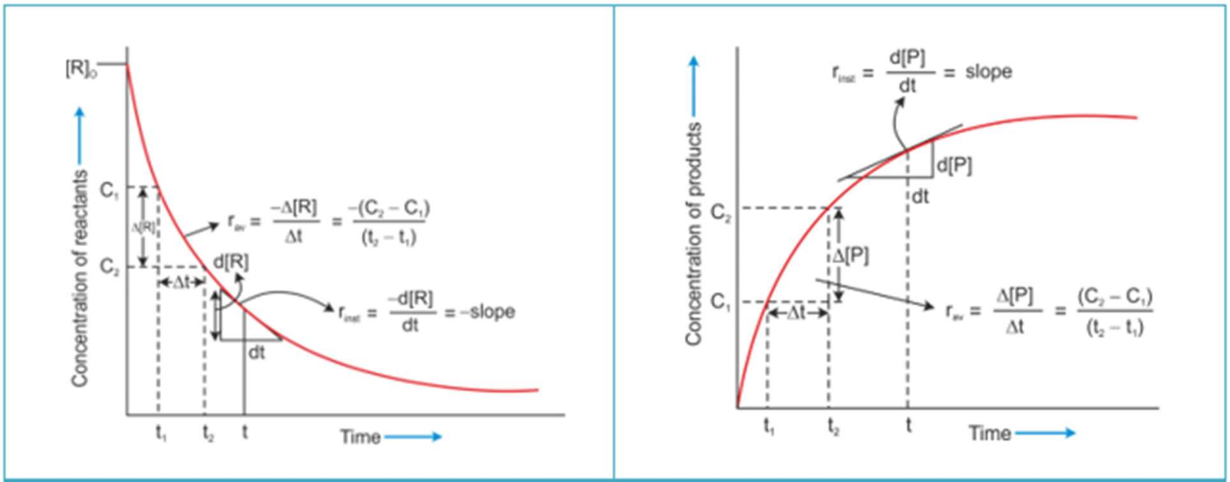
  The square brackets in the above expressions are used to express molar concentration.

$$\text{Rate of disappearance of R} = \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t} \_\_\_\_\_(1)$$

- $\Delta[R]$ is a negative quantity because the concentration of reactants is decreasing.

$$\text{Rate of appearance of P} = \frac{\text{Increase in concentration of P}}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t} \_\_\_\_\_(2)$$

- Equations 1 and 2 represent the average rate of a reaction, r_{av}.
  This average rate depends on the change in concentration of reactants or products and the timetaken for that change to occur.



Instantaneous and average rate of a reaction

Units of Rate of a Reaction

- From Equations 1 and 2, it is clear that the units of rate are concentration time^{-1}.
- For example, if concentration is in mol L^{-1} and time is in seconds, then the units are mol $L^{-1}s^{-1}$.
- In gaseous reactions, the concentration of gases is expressed in terms of their partial pressures;hence, the units of the rate equation will be atm s^{-1}.

Instantaneous Rate of Reaction

- Consider the hydrolysis of butyl chloride (C_4H_9Cl).

$$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$$

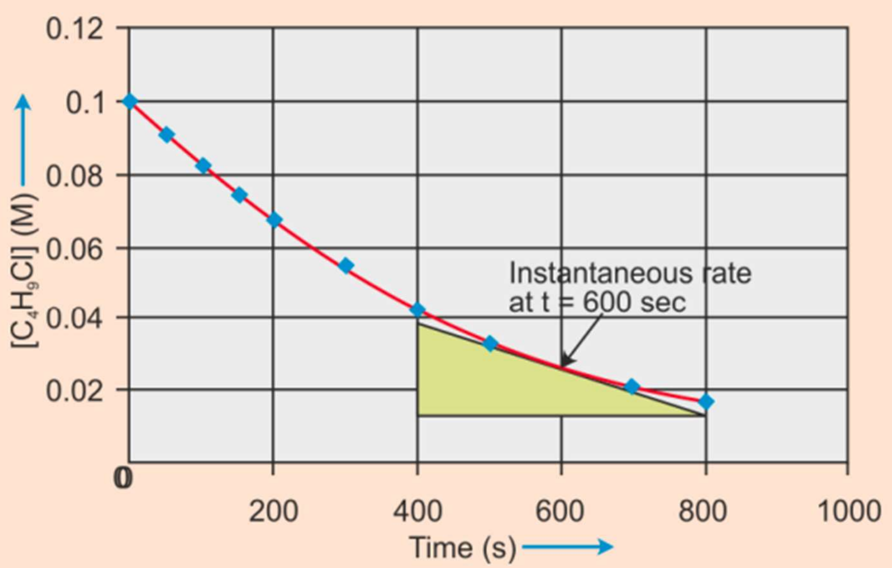
- We have provided the concentrations over different intervals of time below.

Time (s^{-1})	0	50	100	150	200	300	400	700	800
Concentration (mol L^{-1})	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439	0.0210	0.017

- We can determine the difference in concentration over different intervals of time, and thus, wedetermine the average rate by dividing Δ[R] by Δt.
- It can be seen from experimental data that the average rate falls from 1.90×10^{-4} mol $L^{-1}s^{-1}$ to 0.4×10^{-4} mol $L^{-1}s^{-1}$.
- However, the average rate cannot be used to predict the rate of reaction at a particular instant as itwould be constant for the time interval for which it is calculated.

- Hence, to express the rate at a particular moment of time, we determine the instantaneous rate.
- It is obtained when we consider the average rate at the smallest time interval, say dt, when Δt approaches zero.
  Therefore, for an infinitesimally small dt, the instantaneous rate is given by

$$r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$



Instantaneous rate of hydrolysis of butyl chloride(C_4H_9Cl)

- By drawing the tangent at time t on either of the curves for the concentration of R versus time t orconcentration of P versus time t and calculating the slope of the curve, we can determine the instantaneous rate of reaction.
- Hence, in this example, r_{inst} at 600 s is calculated by plotting the graph of the concentration of butylchloride as against time t.
- A tangent is drawn on the curve at a point t = 600 s.

$$\therefore r_{inst} \text{ at } 600\text{s} = \left[\frac{0.0165-0.037}{(800-400)}\right] \text{molL}^{-1} = 5.12\times10^{-5}\,\text{molL}^{-1}\text{s}^{-1}$$

$$\begin{aligned} \text{At } t&=250\text{s} & r_{inst} &= 1.22\times10^{-4}\,\text{molL}^{-1}\,\text{s}^{-1} \\ t&=350\text{s} & r_{inst} &= 1.0\times10^{-4}\,\text{molL}^{-1}\,\text{s}^{-1} \\ t&=450\text{s} & r_{inst} &= 6.4\times10^{-5}\,\text{molL}^{-1}\,\text{s}^{-1} \end{aligned}$$

- Now consider a reaction,

$$Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)$$

Here, the stoichiometric coefficients of the reactants and products are the same; hence, the rate of reaction is given as

$$\text{Rate of reaction} = -\frac{\Delta[Hg]}{\Delta t} = -\frac{\Delta[Cl_2]}{\Delta t} = \frac{\Delta[HgCl_2]}{\Delta t}$$

Therefore, we can say that from the above equation that the rate of disappearance of any of the reactants is the same as the rate of appearance of the products.

- Consider another reaction,

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

In this reaction, two moles of HI decompose to produce one mole each of H2 and I2, i.e. the stoichiometric coefficients of reactants or products are not equal to one; hence, we need to divide the rate of disappearance of any of the reactants or the rate of appearance of products by their respective stoichiometric coefficients.

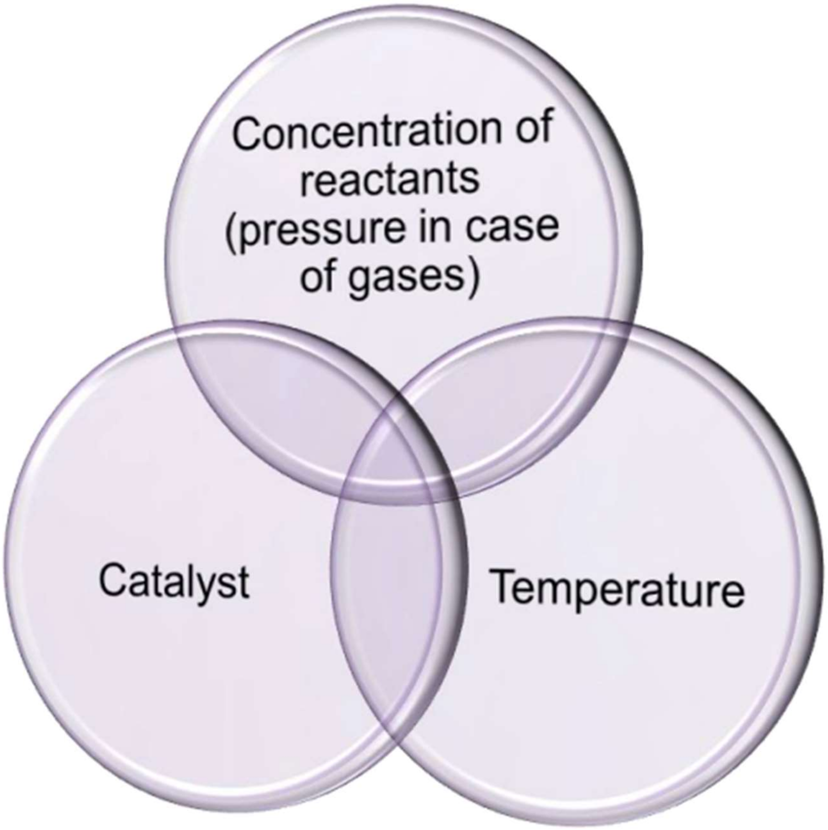
Because the rate of consumption of HI is twice the rate of formation of H2 or I2, to make them equal, the term Δ[HI] is divided by 2.

The rate of this reaction is given by

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

- For a gaseous reaction at constant temperature, concentration is directly proportional to the partial pressure of a species, and hence, the rate can be expressed as the rate of change in partial pressure of the reactant or the product.

Instantaneous Rate of Reaction



MIND MAP : LEARNING MADE SIMPLE — CHAPTER - 4

Chemical Kinetics

Rate Of Chemical Reaction
Change in concentration of reactants or products in unit time; Unit : mol $L^{-1} s^{-1}$ or atm s^{-1}

- **Average Rate:** Appearance of products or disappearance of reactants over a long time interval.
  $r_{av} = \frac{d[P]}{dt}$ = slope
  $r_{av} = \frac{-d[R]}{dt}$ = –slope
- **Instantaneous Rate:** Rate of change in concentration of reactant/product at a particular time
  $r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$
- **R → P:**
  - Rate of disappearance of R $= \frac{\text{Decease in concentration of R}}{\text{Time taken}} = \frac{-\Delta[R]}{\Delta t}$
  - Rate of appearance of P $= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{+\Delta[P]}{\Delta t}$
- **Factors Influencing:**
  Concentration : Higher the concentration of reactants, faster is the rate of reaction
  Temperature : Increases with increase in temperature. becomes almost double with 10°C rise.
  Presence of Catalyst : Increases with a catalyst.
  Surface Area : Greater is the surface area, faster is the rate of reaction.
  Activation Energy : Lower the activation energy, faster is the reaction.
- **Rate Law:** Expression in which reaction rate in given in terms of molar concentration of reactants with each term raised to power which may or may not be same as stoichiometric coefficient of reactants in a balanced chemical equation. $aA + bB \longrightarrow cC + dD$
  Rate = $K[A]^x[B]^y = \frac{d[R]}{dt}$
- **Rate Constant:** Rate of a reaction when concentration of each of the reactant in unity.

Order	Unit
0	$molL^{-1}s^{-1}$
1	s^{-1}
2	$mol^{-1}Ls^{-1}$

Order Of A Reaction
Sum of powers of concentration of the reactants in the rate law.

Molecularity Of A Reaction
Number of reacting species taking part in an elementary reaction colliding to bring out a reaction.

Collision Theory: Rate of reaction depends on the collision frequency and effective collisions.
- **Collision Frequency:** Number of collisions per unit volume of reaction mixture
  Rate = $Z_{AB} e^{-Ea/RT}$
- **Effective Collision:** Collision in which molecules collide with sufficient kinetic energy and proper orientation for breaking of bonds and formation of new bonds.
  Rate = $PZ_{AB}e^{-Ea/RT}$
  P is Steric or Probability factor
  E_a and proper orientation of the molecules determine the criteria for an effective collision.

Arrhenius Equation
$K = Ae^{-Ea/RT}$
$\log k = \log A - \frac{E_a}{2.303RT}$
$\log \frac{k2}{k1} = \frac{E_a}{2.303RT}\left[\frac{T_2-T_1}{T_1T_2}\right]$

Activation Energy, E_a
: Energy required to form an intermediate called activated complex (c)
E_a = Threshold energy - Average Kinetic energy of reacting molecules

Integrated Rate Equation
Integration of differential rate equation to give a relation between concentrations at different times and rate constant.

Order	Integrated Rate Law	Straight Plot	Units (K)
0	$kt = [R]_0 - [R]$	[R] vs t	mol $L^{-1}s^{-1}$
1	$kt = \ln\{[R]_0/[R]\}$	In[R] vs t	s^{-1}

Pseudo First Order Reaction
- Are not truly of first order but under certain conditions behave as first order reaction
- Acid hydrolysis of ethyl acetate
- Inversion of sugar

Half-life Of A Reaction
Time in which the concentration of a reactant is reduced to one half of its initial concentration
- 1st Order: $t_{1/2} = \frac{0.693}{K}$
- 0 Order: $t_{1/2} = \frac{[R]_0}{2K}$

Important Questions

Multiple Choice questions-

Question 1.A first order reaction has a half life period of 34.65 seconds. Its rate constant is

(a) 2×10^{-2} s^{-1}

(b) 4×10^{-4} s^{-1}

(c) 20 s^{-1}

(d) 2×10^{-4} s^{-1}

Question 2.If a graph is plotted between In k and 1/T for the first order reaction, the slope of the straight line so obtained is given by

(a) $-\frac{E_a}{R}$
(b) $\frac{E_a}{2.303R}$
(c) $\frac{2.303}{E_a.R}$
(d) $\frac{E_a}{2.303}$

Question 3.The unit of rate constant for a zero order reaction is

(a) mol $L^{-1}s^{-1}$

(b) s^{-1}

(c) L $mol^{-1}s^{-1}$

(d) L2$mol^{-2}s^{-1}$

Question 4.A catalyst increases the speed of a chemical reaction by

(a) increasing activation energy

(b) decreasing activation energy

(c) increasing reactant energy

(d) decreasing threshold energy

Question 5.The units of the rate constant for the second order reaction are:

(a) mol^{-1} litre s^{-1}

(b) mol $litre^{-2}$ s^{-1}

(c) s^{-1}

(d) mol $litre^{-1}$ s^{-1}

Question 6.The value of k for a reaction is 2.96 × 10-^{30} $s^{-1.}$ What is the order of the reaction?

(a) Zero

(b) 3

(c) 2

(d) 1

Question 7.A reaction is found to be of second order with respect to concentration of carbon monoxide. If concentration of carbon monoxide is doubled, the rate of reaction will

(a) triple

(b) increase by a factor of 4

(c) double

(d) remain unchanged

Question 8. If the concentrations are expressed in mol litre-1 and time in s, then the units of rate constant for the first-order reactions are

(a) mol $litre^{-1}$ s^{-1}

(b) mol^{-1} litre s^{-1}

(c) s^{-1}

(d) mol^2 $litre^{-2}$ s^{-1}

Question 9.The half life of a first order reaction having rate constant 200 s^{-1} is

(a) 3.465×10^{-2} s

(b) 3.465×10^{-3} s

(c) 1.150×10^{-2} S

(d) 1.150×10^{-3} S

Question 10.The rate of a reaction is $1.209 \times 10^{-4} L^2\ mol^{-2} s^{-1}$. The order of the reaction is:

(a) zero

(b) first

(c) second

(d) third

Very Short Question:

Question 1. Is rate of reaction always constant?

Question 2. Can order of reaction be zero? Give example.

Question 3. What do you understand by rate law expression?

Question 4. Is it possible to determine or predict the rate law theoretically by merely looking at the equation?

Question 5. Define the term chemical kinetics?

Question 6. Define – Rate of reaction and the factors affecting the rate of reaction.

Question 7. What is average rate of a reaction? How is it determined?

Question 8. What are the units of rate of a reaction?

Question 9. Identify the reaction order for from each of the following rate constant –

(a) $k = 2.3 \times 10^{-5} L\ mol - 1\ s^{-1}$

(b) $k = 3.1 \times 10^{-4} s^{-1}$

Question 10. Consider the equation $2NO(q)+2H_2(g)\rightarrow N_2(g)+2H_2O(g)$

The rate law for this equation is first order with respect to H_2 and second order with respect to NO. write the rate law for this reaction.

Short Questions:

Question 1 For the reaction A+B $\rightarrow$ C+D, the rate of reaction doubles when the concentration of A doubles, provided the concentration of B is constant. To what order does A enter into the rate expression?

Question 2. . A chemical reaction 2A $\Leftrightarrow$ 4B+C in gas phase occurs in a closed vessel. The concentration of B is found to be increased by $5\times10^{-3} mole\ L^{-1}$ in 10 second. Calculate (i) the rate of appearance of B (ii) the rate of disappearance of A?

Question 3. For the following reactions, write the rate of reaction expression in terms of reactants and products?

$4NH_3(g)+5O_2(g)4\rightarrow NO(g)+6H_2O(g)$

ii) $2N_2O_5\ 2NO_2+O_2$

Question 4. **.** The reaction $2N_2O_5(g)\rightarrow 2NO_2(g)+O_2(g)$ was studied and the following data were collected:

S.no (mol/L/min)	$[N_2O_5]\ mol\ L^{-1}$	**Rate of disappearance of $[N_2O_5]$(mol/L/min**
1.	1.13×10^{-2}	34×10^{-5}
2.	$0.84\ \times10^{-2}$	25×10^{-5}
3.	0.62×10^{-2}	18×10^{-5}

Determine

i) The order
ii) The rate law.
iii) Rate constant for the reaction.

Question 5. The following experimental data was collected for the reaction:

$Cl_2(g)+2NO(g)\rightarrow 2NOCl(g)$

Trial	**Intial conc. Of** $Cl_2(mol/L)$	**NO mol/L**	**Initial Rate,(mol/L/s)**
1	0.10	0.010	1.2×10^{-4}

2	0.10	0.030	10.8×10^{-4}
3	0.20	0.030	21.6×10^{-4}

Construct the rate equation for the reaction.

Question 6. Draw a graph for

a) Concentration of reactant against time for a zero order reaction.
b) Log Ro/ R against time for a first order reaction.

Question 7. In general it is observed that the rate of a chemical reaction doubles with every 10^0 rise in temperature. If this generalization holds for a reaction in the temperature range295K to 305K, what would be the activation energy for this reaction? $\left(R=8.314Jk^{-1}mol^{-1}\right)$

Question 8. The rate constant for a reaction is $1.5\times10^7 s^{-1}$ at 50^0C and $4.5\times10^7 s^{-1}$ at 100^0C. Calculate the value of activation energy for the reaction $R=8.314\ JK^{-1}mol^{-1}$?

Question 9. Plot a graph showing variation of potential energy with reaction. coordinate?

Question 10. The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?

Long Questions:

Question 1. . The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a

Question 2. The activation energy for the reaction $2HI_{(g)}\rightarrow H_2+I_{2(g)}$ is $209.5\,kJ\,mol^{-1}$ at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Question 3. From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

) $3NO(g)\rightarrow N_2O(g)\ Rate=k[NO]^2$

(ii) $H_2O_2(aq)+3I^-(aq)+H^+\rightarrow 2H_2O(l)+I_3^-\ Rate=k[H_2O_2][I^-]$

(iii) $CH_3CHO(g)\rightarrow CH_4(g)+CO(g)\ Rate=k[CH_3CHO]^{3/2}$

(iv) $C_2H_5Cl(g)\rightarrow C_2H_4(g)+HCl(g)\ Rate=k[C_2H_5Cl]$

Question 4. The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5\times10^{-4}\ mol^{-1} L\ s^{-1}$?

Question 5. The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by Rate = $k[CH_3OCH_3]^{3/2}$. The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e., $Rate = k\left(P_{CH_3OCH_3}\right)^{3/2}$ If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

Assertion and Reason Questions:

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: The rate ofreaction is always negative.

Reason: Minus sign used in expressing the rate shows that concentration of product is decreasing.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
b) Assertion and reason both are correct statements but reason is not correct explanation for assertionss.
c) Assertion is correct statement but reason is wrong statement.
d) Assertion is wrong statement but reason is correct statement.

Assertion: Kinetics explains the reaction mechanism.

Reason: Kinetics explains the formation of products.

Case Study Questions:

1. In a reaction, the rates of disappearance of different reactants or rates of formation of different products may not be equal but rate of reaction at any instant of time has the same value expressed in terms of any reactant or product. Further, the rate of reaction may not depend upon the stoichiometric coefficients of the balanced chemical equation. The exact powers of molar concentrations of reactants on which rate depends are found experimentally and expressed in terms of 'order of reaction'. Each reaction has a characteristic rate constant depends upon temperature. The units of the rate constant depend upon the order of reaction.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The rate constant of a reaction is found to be 3×10^{-3} mol^{-2} L^2 sec^{-1}. The order of the reaction is:

a) 0.5
b) 2
c) 3
d) 1

(ii) In the reaction, $A + 3B \rightarrow 2C$, the rate of formation of C is:

a) The same as rate of consumption of A.
b) The same as the rate of consumption of B.
c) Twice the rate of consumption of A.
d) 3232 times the rate of consumption of B.

(iii) Rate of a reaction can be expressed by following rate expression, Rate = $k[A]^2$ [B], if concentration of A is increased by 3 times and concentration of B is increased by 2 times, how many times rate of reaction increases?

a) 9 times
b) 27 times
c) 18 times
d) 8 times

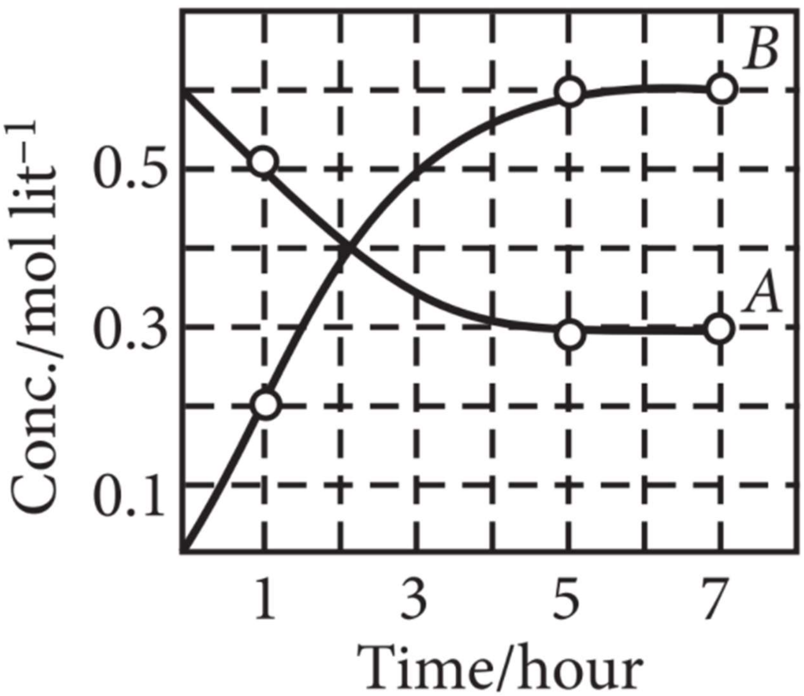
(iv) The rate of a certain reaction is given by, rate = $k[H^+]^n$.The rate increases 100 times when the pH changes from 3 to 1. The order (n) of the reaction is:

a) 2
b) 0
c) 1
d) 1.5

(v) In a chemical reaction A + 2B → products, when concentration of A is doubled, rate of the reaction increases 4 times and when concentration of B alone is doubled rate continues to be the same. The order of the reaction is:

a) 1
b) 2
c) 3
d) 4

2. The progress of the reaction, A ⇌ nB with time is represented in the following figure:



The following questions are multiple choice questions. Choose the most appropriate answer:

(i) What is the value of n?

a) 1
b) 2
c) 3
d) 4

(ii) Find the value of the equilibrium constant.

a) 0.6M
b) 1.2M
c) 0.3M
d) 2.4M

(iii) The initial rate of conversion of A will be:

a) 0.1 mol $L^{-1}hr^{-1}$
b) 0.2 mol $L^{-1}hr^{-1}$
c) 0.4 mol $L^{-1}hr^{-1}$
d) 0.8 mol $L^{-1}hr^{-1}$

(iv) For the reaction, if $\frac{d[B]}{dt} = 2 \times 10^{-4}$, value of $\frac{d[A]}{dt}$ will be:

a) 2×10^{-4}
b) 10^{-4}
c) 4×10^{-4}
d) 0.5×10^{-4}

(v) Which factor has no effect on rate of reaction?

a) Temperature.
b) Nature of reactant.
c) Concentration of reactant.
d) Molecularity.

Answers key

MCQ Answer:

1. Answer: (a) 2×10^{-2} s^{-1}
2. Answer: : (a) $-\frac{E_a}{R}$
3. Answer: (a) mol $L^{-1}s^{-1}$
4. Answer: (b) decreasing activation energy
5. Answer: (a) mol^{-1} litre s^{-1}
6. Answer: (d) 1
7. Answer: (b) increase by a factor of 4
8. Answer: (c) s^{-1}
9. Answer: (b) 3.465×10^{-3} s
10. Answer: (d) third

Very Short Answers:

1. No. rate of a reaction is not always constant. It depends on many factors such as concentration, temperature etc.

2. Yes, decomposition of ammonia on a hot platinum surface is a zero order of reaction at high pressure

3. Answer: The rate law is the expression in which rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

4. Answer: No, the rate law cannot be predicted by merely looking at the balanced chemical equation but must be determined experimentally.

5. Answer: The branch of chemistry that deals with the study of reaction rates and their mechanisms is called chemical Kinetics.

6. Answer: Rate of reaction can be defined as the change in concentration of a reactant or product per unit time. Factors affecting the rate of reaction are temperature, concentration of reactants and catalyst.

7. Answer: Average rate of a reaction is defined as the change in concentration of a reactant or a product per unit time. It can be determined by dividing the change in concentration of reactant or product by the time interval

   For the reaction: A $\rightarrow$ B Rav

   $= \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$

8. The units of rate of a reaction are Mol $L^{-1}S^{-1}$ In gaseous reaction the unit of rate of reaction is atom .

9. a) Since the units of rate constant are $Lmol^{-1}s^{-1}$ The reactions is of second order.
   b) Since the units of rate constant are s^{-1}, The reaction is of first order

10. The rate law will be $R = K[NO]^2[H_2]$

Short Answers:

1. Answer

. A+B $\rightarrow$ C+D

$Rate[A]^x$

Rate = 1 when A = 1 ———- 1)
Rate = 2 when A = 2————2)
Dividing equation 2) by 1)

$\frac{2}{1} \alpha \frac{(2)^x}{1^x}$

$2^1 \alpha (2)^x$

$\therefore x = 1$

The reaction is first order reaction.

2. Answer:

2A $\rightarrow$ 4B

$$-\frac{1}{2}\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

i) Rate of disappearance of B

$$= \frac{5\times10^{-3}}{10\ 5}\text{mol /L}^{-1} = 5\times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

$$\frac{-d[A]}{dt} = \frac{2}{4}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$$

ii) = $\frac{1}{2}\times5\times10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$ = 2.5 $\times10^{4}\ \text{mol L}^{-1}\ \text{s}^{-1}$

3. Answer:

In terms of reactant	In terms of products
i) $R_1 - \frac{-1}{4}\frac{\Delta[NH_3]}{\Delta t}$	$R_3 = \frac{1}{4}\frac{\Delta[NO]}{\Delta t}$
$R_2 = \frac{-1}{5}\frac{\Delta[O_2]}{\Delta t}$	$R_4 = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$

$$\frac{1}{4}R_1 = \frac{1}{5}R_2 = \frac{1}{4}R_3 = \frac{1}{6}R_4$$

$$-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

II) In terms of reactant	In terms of product
R1 = $-\frac{\Delta[N_2O_5]}{\Delta t}$	$R_2 = \frac{\Delta[NO_2]}{\Delta t}$

	$R_3 = \frac{\Delta[O_2]}{\Delta t}$

$$\frac{1}{2}R_1 = \frac{1}{2}R_2 = R_3 - \frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

4. Answer:

Let the order of reaction be x

$Rate = K[N_2O_5]^x$

i) From the data –

$34\times10^{-5} = (1.13\times 10^{-2})^x$ ————-1)

$25\times10^{-5} = (0.84\times 10^{-2})^x$ ————-2)

$18\times10^{-5} = (0.62\times10^{-2})^x$ ————-3)

Dividing 1) by 2)

$$\frac{34\times10^{-5}}{25\times10^{-5}} = \left(\frac{1.13\times10^{-2}}{0.84\times10^{-2}}\right)^x$$

(1.36) = $(1.35)^x$

X=1

The order of reaction with respect with respect to N_2O_5 is 1

ii) Rate law $R = K\ [N_2O_5]$

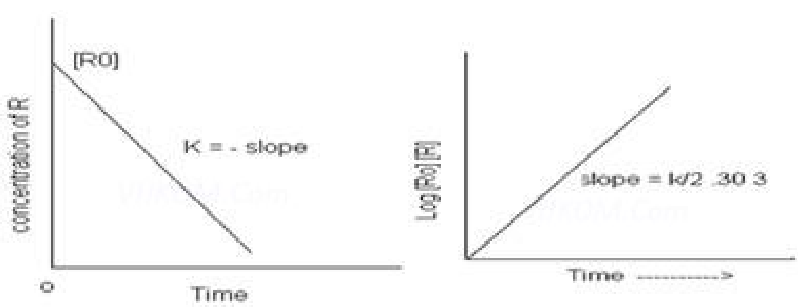
iii) Rate constant , K = $\frac{Rate}{[N_2O_5]}$ = $\frac{18\times10^{-5}\ \text{mol/L/min}}{0.62\times10^{-2}\ \text{mol/L}}$ = $0.29\ min^{-1}$

5. Answer :

Order of NO is 2

Rate law = $K\ [Cl_2]\ [NO]^2$

6. Answer



(a) (b)

7. **Answer:**

. $T_1 = 295K\ T_2 = 305K$

$$Ea = 2.303\,R\left[\frac{T_2T_1}{T_2 - T_1}\right]\left[\log\frac{k_2}{k_1}\right]$$

$K_2 = 2k_1$

$$E_a = 2.303 \times 8.314 \times \left[\frac{305 \times 295}{305 - 295}\right] \log\frac{2k_1}{k_1}$$

$= 2.303 \times 8.314 \times 8997.5K\,log2$

= 51855.2 J/mol (log2 = 0.3010)

8. **Answer:**

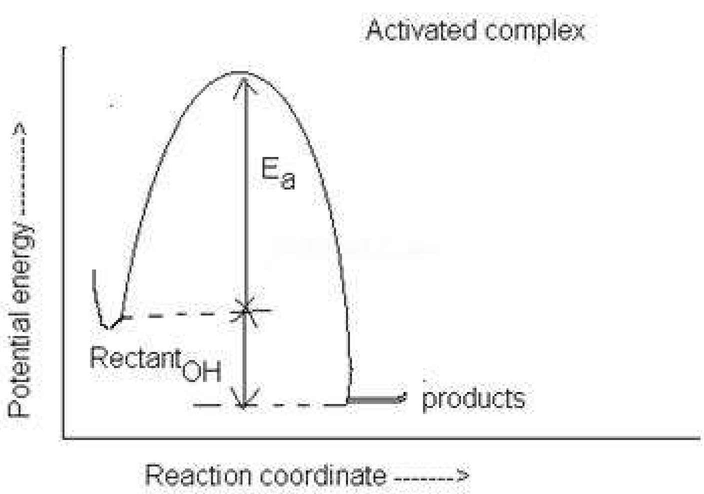
$$\log\frac{4.5\times10^7}{1.5\times10^7} = \frac{Ea}{2.303\times3.314}\left(\frac{373-323}{373\times323}\right)$$

$$\log 1.5 = \frac{Ea}{2.303\times3.314}\left(\frac{50}{373\times323}\right)$$

$$Ea = \left(\frac{2.303\times3.314\times373\times323}{50}\right)\times\log 1.5$$

$= 22\ KJ/mol$

9. **Answer :**



10.**Answer :**

The reaction $X \rightarrow Y$ follows second order kinetics.
Therefore, the rate equation for this reaction will be:

Rate = $k[X]^2$ (1)
Let X = a mol^{-1}, then equation (1) can be written as:
$Rate_1 = k.(a)_2$
= ka_2
If the concentration of X is increased to three times, then X = $3a\,mol\,L^{-1}$
Now, the rate equation will be:
Rate = $k(3a)_2$
$= 9(ka^2)$
Hence, the rate of formation will increase by 9 times.

Long Answers:

1. **Answer:**

It is given that $T1$ = 298 K
Therefore, $T_2 = (298+10)K$
= 308 K
We also know that the rate of the reaction doubles when temperature is increased by $10°$.
Therefore, let us take the value of $k_1 = k$ and that of $k_2 = 2k$
Also, $R = 8.314\,JK^{-1}\,mol^{-1}$
Now, substituting these values in the equation:

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

We get:

$$\log\frac{2k}{k} = \frac{E_a}{2.303\times8.314}\left[\frac{10}{298\times308}\right]$$

$$\log 2 = \frac{E_a}{2.303\times8.314}\left[\frac{10}{298\times308}\right]$$

$$E_a = \frac{2.303\times8.314\times298\times308\times\log 2}{10}$$

$$= 52897.78\,J\,mol^{-1}$$

$$= 52.9\,k\,J\,mol^{-1}$$

2. Answer:

In the given case:
$E_a = 209.5\,kJ\,mol^{-1} = 209500\,J\,mol^{-1}$
T = 581 K
$R = 8.314\,JK^{-1}\,mol^{-1}$
Now, the fraction of molecules of reactants having energy equal to or greater than

activation energy is given as:

$x = e^{-Ea/RT}$

In $x = -E_a / RT$

$$\log x = -\frac{E_a}{2.303\,RT}$$

$$\log x = \frac{209500\,J\,mol^{-1}}{2.303 \times 8.314\,J\,K^{-1}mol^{-1} \times 581} = 18.8323$$

Now, x = Anti log (18.8323)

= Anti log $\overline{19}.1677$

1.471×10^{-19}

3. Answer:

(i) Given rate = $k[NO]^2$

Therefore, order of the reaction = 2

Dimension of $k = \frac{Rate}{[NO]^2}$

$$= \frac{mol\,L^{-1}\,s^{-1}}{(mol\,L^{-1})^2}$$

$$= \frac{mol\,L^{-1}s^{-1}}{mol^2L^{-2}}$$

$$= L\,mol^{-1}s^{-1}$$

(ii) Given rate = $k[H_2O_2][I^-]$

Therefore, order of the reaction = 2

Dimension of $k = \frac{Rate}{[H_2O_2][I^-]}$

$$= \frac{mol\,L^{-1}s^{-1}}{(mol\,L^{-1})(mol\,L^{-1})}$$

$$= L\,mol^{-1}s^{-1}$$

(iii) Given rate = $k[CH_3CHO]^{3/2}$

Therefore, order of reaction = $\frac{3}{2}$

Dimension of $k = \frac{Rate}{[CH_3CHO]^{\frac{3}{2}}}$

$= \frac{mol\,L^{-1}\,s^{-1}}{(mol\,L^{-1})^{\frac{3}{2}}}$

$= \frac{mol\,L^{-1}s^{-1}}{mol^{\frac{3}{2}}L^{-\frac{3}{2}}}$

$= L^{\frac{1}{2}}\,mol^{-\frac{1}{2}}s^{-1}$

(iv) Given rate = $k[C_2H_5Cl]$

Therefore, order of the reaction = 1

Dimension of $k = \frac{Rate}{[C_2H_5Cl]}$

$= \frac{mol\,L^{-1}s^{-1}}{mol\,L^{-1}}$

$= s^{-1}$

4. Answer:

The decomposition of NH_3 on platinum surface is represented by the following equation.

$2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$

Therefore, $Rate = -\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt}$

However, it is given that the reaction is of zero order.

$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = k$

Therefore, $= 2.5\times10^{-4}\,mol\,L^{-1}s^{-1}$

Therefore, the rate of production of N_2 is

$\frac{d[N_2]}{dt} = 2.5\times10^{-4}\,mol\,L^{-1}s^{-1}$

And, the rate of production of H_2 is

$\frac{d[H_2]}{dt} = 3\times2.5\times10^{-4}\,mol\,L^{-1}s^{-1}$

$= 7.5\times10^{-4}\,mol\,L^{-1}s^{-1}$

5. Answer:

If pressure is measured in bar and time in minutes, then

Unit of rate = $bar\,min^{-1}$

$Rate = k\left(P_{CH_3OCH_3}\right)^{3/2}$

$$k = \frac{\text{Rate}}{\left(P_{CH_3OCH_3}\right)^{3/2}}$$

Therefore, unit of rate constants $(k) = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}}$

$= \text{bar}^{-1/2}\ \text{min}^{-1}$

Assertion and Reason Answers:

1. (d) Assertion is wrong statement but reason is correct statement.

Explanation:

The rate reaction is never negative. Minus sign used in expressing the rate only shows that the concentration of the reactant is decreasing.

2. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Explanation:

Kinetics deals with the reaction mechanism i.e., how the atoms rearrange themselves in the reactant molecules in a single step or a number of steps, finally leading to the product molecules.

Case Study Answers:

1. Answer :

i. (c) 3

Explanation:

Unit of k for n^{th} order = $(\text{mot } L^{-1})^{1-n}\ \text{sec}^{-1}$

Here, $k = 3 \times 10^{-3}\ \text{mol}^{-2}\ L^2\ \text{sec}^{-1}$

Unit of $k = \text{mol}^{-2}\ L^2\ \text{sec}^{-1} \Rightarrow (\text{mol } L^{-1})^{-2}\ \text{sec}^{-1}$

Comparing (i) and (ii) we get, $1 - n = -2 \Rightarrow n = 3$

ii. (c) twice the rate of consumption of A.

Explanation:

$$\text{Rate} = \frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt}$$

iii. (c) 18 times

Explanation:

Given, $R_1 = k[A]^2 [B]$

According to question, $R_2 = k[3A]^2 [2B]$

$= k \times 9 [A]^2 \times 2[B] = 18 \times k[A]^2 [B] = 18 R_1$

iv. (c) 1

Explanation:

Rate (r) = $k[H^+]^n$

When pH = 3 ; $[H^+] = 10^{-3}$

and when pH = 1 ; $[H^+] = 10^{-1}$

$$\therefore \frac{r_1}{r_2} = \frac{k(10^{-3})^n}{k(10^{-1})^n} \Rightarrow \frac{1}{100} = \left(\frac{10^{-3}}{10^{-1}}\right)^n (\because r_2 = 100r_1)$$

$$\Rightarrow (10^{-2})^1 = (10^{-2})^n \Rightarrow n = 1$$

v. (b) 2

Explanation:

Let the order of reaction w.r.t. A is x and w.r.t. B is y.

$$r_1 = k[A]^x[B]^y$$

$$r_2 = k[2A]^x[B]^y$$

$$r_3 = k[A]^x[2B]^y$$

$$\frac{r_1}{r_2} = \frac{k[A]^x[B]^y}{k[2A]^x[B]^y}$$

$$\Rightarrow \frac{1}{4} = \left(\frac{1}{2}\right)^x \Rightarrow \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^x \Rightarrow x = 2$$

Similarly, $\frac{r_1}{r_3} = \frac{k[A]^x[B]^y}{k[A]^x[2B]^y}$

$$\Rightarrow 1 = \left(\frac{1}{2}\right)^y \Rightarrow \left(\frac{1}{2}\right)^0 = \left(\frac{1}{2}\right)^y \Rightarrow y = 0$$

Hence the rate law equation is

Rate = $k[A]^2\,[B]^0 \Rightarrow$ Order of reaction = 2

2. Answer :

i. (b) 2

Explanation:

According to the figure,

in the given time of 4 hours (1 to 5) concentration of A falls from 0.5 to 0.3M,

while in the same time concentration of B increases from 0.2 to 0.6 M.

Decrease in concentration of A in 4 hours

= 0.5 - 0.3 = 0.2M

Increase in concentration of B in 4 hours

= 0.6 - 0.2 = 0.4M

Thus, increase in concentration of B in a given time is

twice the decrease in concentration of A. Thus, n = 2.

ii. (b) 1.2M

Explanation:

$$K = \frac{[B]^2}{[A]} = \frac{(0.6)^2}{0.3} = 1.2M$$

iii. (a) 0.1 mol $L^{-1}hr^{-1}$

Explanation:

From t = 0 to t = 1hr,

For A, dx = 0.6 - 0.5 = 0.1 mol L^{-1}

∴ Initial rate of conversion of $A = \frac{dx}{dt}$

$$= \frac{0.1 \text{ mol } L^{-1}}{1 hr} = 0.1 \text{ mol } L^{-1} hr^{-1}$$

iv. (b) 10^{-4}

Explanation:

$$A \rightleftharpoons 2B$$

$$-\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt}$$

$$= \frac{1}{2} \times 2 \times 10^{-4} = 10^{-4}$$

V. (d) Molecularity.

Explanation:

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction is called molecularity and it has no influence on the rate of reaction.