

Class: 12
Subject: Chemistry
Topic: Chemical kinetics
No. of Questions: 27

1. Why we prefer instantaneous rate of reaction over average rate of reaction?

Solution: The rate of reaction decreases continuously with time except for a zero order reaction. Therefore, average rate of reaction has no significance for the reaction. But instantaneous rate of reaction for a given instant of time does not change with time.

2. Define rate of a reaction.

Solution: Rate of a reaction may be defined as the change in the concentration of any one of the reactants or products per unit time.

3. Define specific rate constant.

Solution: It is defined as the rate of a chemical reaction when the concentration of each reactant appearing in the rate equation is taken as unity.

4. The following reaction was carried out in water. $\text{Cl}_2 + 2\text{I}^- \longrightarrow 2\text{Cl}^- + \text{I}_2$.

The initial concentration of I^- was $0.50 \text{ mol } \ell^{-1}$ and concentration after 10 minutes was $0.46 \text{ mole lit}^{-1}$. Calculate the rate of disappearance of I^- and rate of appearance of iodine.

Solution: $\Delta[\text{I}^-] = 0.46 - 0.50 = -0.04 \text{ mol } \ell^{-1}$
 $\Delta t = 10.0 - 0.0 = 10 \text{ min}$

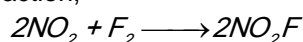
$$\begin{aligned} \text{Rate of disappearance of } \text{I}^- &= -\frac{\Delta[\text{I}^-]}{\Delta t} = \frac{-(-0.04)}{10} \\ &= 0.004 \text{ mol } \ell^{-1} \text{ min}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Rate of appearance of iodine} &= \frac{1}{2}(\text{Rate of disappearance of } \text{I}^-) \\ &= \frac{1}{2} \times 0.004 = 0.002 \text{ mol } \ell^{-1} \text{ min}^{-1} \end{aligned}$$

5. For the reaction $A + 2B \longrightarrow AB_2$, the rate constant is $1.26 \times 10^{-3} \text{ L mol}^{-1}\text{s}^{-1}$. What is the order of the reaction?

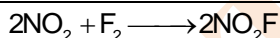
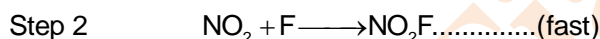
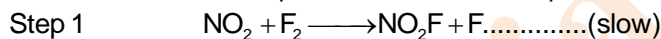
Solution: The units of rate constant is $\text{L mol}^{-1}\text{s}^{-1}$ or $(\text{mol L}^{-1})^{-1}\text{s}^{-1}$. Equate this with general expression of $(\text{mol L}^{-1})^{1-n}\text{s}^{-1}$.
 $(\text{mol L}^{-1})^{-1} \text{ s}^{-1} = (\text{mol L}^{-1})^{1-n} \text{ s}^{-1}$
 $\therefore -1 = 1 - n$ or $n = 2$
 The order of reaction = 2

6 For a reaction,

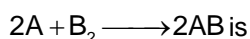


The experimental rate law is $r = k[\text{NO}_2][\text{F}_2]$. Propose the mechanism of the reaction.

Solution: The rate law is $r = k[\text{NO}_2][\text{F}_2]$ since rate law is proportional to single power of NO_2 and single power of F_2 , it implies that only one molecule of NO_2 and one molecule of F_2 are involved in the slow step. Thus the various steps are:



7. The experimental data for the reaction



Experiment	[A] mole/lit	[B ₂] mol/lit	Initial rate
1.	0.50	0.50	1.6×10^{-4}
2.	0.50	1.00	3.2×10^{-4}
3.	1.00	1.00	3.2×10^{-4}

Write the rate law equation.

Solution: Let the rate law equation be

$$r = k[\text{A}]^x [\text{B}_2]^y$$

Now,

$$r_1 = 1.6 \times 10^{-4} = k(0.50)^x (0.50)^y \dots\text{(i)}$$

$$r_2 = 3.2 \times 10^{-4} = k(0.50)^x (1.00)^y \dots\text{(ii)}$$

$$r_3 = 3.2 \times 10^{-4} = k(1.00)^x (1.00)^y \dots\text{(iii)}$$

Divide (ii) by (i)

$$\frac{r_2}{r_1} = \frac{k(0.50)^x (1.00)^y}{k(0.50)^x (0.50)^y} = \frac{3.2 \times 10^{-4}}{1.6 \times 10^{-4}}$$

$$\left(\frac{1.00}{0.50}\right)^y = 2 \Rightarrow 2^y = 2, y = 1$$

Now divide (iii) by (ii)

$$\frac{r_3}{r_2} = \frac{K(1.00)^x (1.00)^y}{K(0.50)^x (1.00)^y} = \frac{3.2 \times 10^{-4}}{3.2 \times 10^{-4}}$$

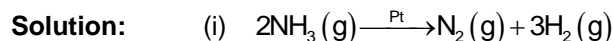
$$\left(\frac{1.00}{0.50}\right)^x = 1 \quad \text{or} \quad 2^x = 1$$

$$2^x = 1$$

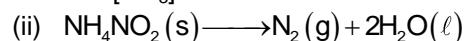
$$x = 0$$

$$\therefore \text{Rate law} = r = K[A]^0 [B_2]^1$$

8. Give any one example of
 (i) zero order reaction
 (ii) first order reaction

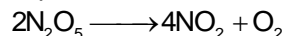


$$r = k[\text{NH}_3]^0$$



$$r = k[\text{NH}_4\text{NO}_2]$$

- 9 For decomposition of N_2O_5 in CCl_4 solution at 320 K.



Show that the reaction is of first order and also calculate the rate constant:

Time in min	10	15	20	25	∞
Vol. of O_2 Evolved (in ml)	6.30	8.95	11.40	13.50	34.75

Solution: If the reaction is of first order, it must obey the equation

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

In the above reaction, NO_2 remains in solution and oxygen is liberated and collected at different intervals of time.

Therefore

$$V_t \propto x, \quad V_\infty \propto a$$

Substituting these values in the first order equation.

$$K = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

$$\text{Time } t = 10 \quad K = \frac{2.303}{10} \log \frac{34.75}{34.75 - 6.30} = 0.0198$$

$$\text{Time } t = 15 \quad K = \frac{2.303}{15} \log \frac{34.75}{34.75 - 8.95} = 0.0198$$

$$\text{Time } t = 20 \quad K = \frac{2.303}{20} \log \frac{34.75}{34.75 - 11.40} = 0.0198$$

$$\text{Time } t = 25 \quad K = \frac{2.303}{25} \log \frac{34.75}{34.75 - 13.50} = 0.0198$$

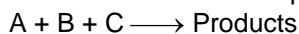
Since the value of K comes out to be constant, the reaction is therefore is of first order.

10 Differentiate between the rate of reaction and the rate constant.

Rate of reaction		Rate constant	
(i)	It is defined as the change in concentration of the reactant or product with time, each divided by its stoichiometric coefficient.	(i)	It is defined as the rate of chemical reaction when the concentration of each reactant appearing in the rate equation is taken as unity.
(ii)	It always has a unit of (conc)/time.	(ii)	Its units depends on the order of a reaction. For n^{th} order reaction the units of rate constant = $(\text{conc})^{1-n} \text{time}^{-1}$
(iii)	It depends on the initial concentration of the reactants.	(iii)	It is independent of the initial concentration of the reactants.

11 Define order of a reaction. Can it be a fractional value? If yes then give an example of a fractional order reaction.

Sol. The order of a reaction is defined as the sum of the exponents to which each concentration terms is raised in the experimentally derived rate equation. For example in the reaction

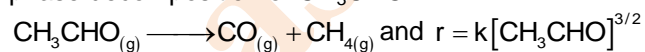


and the rate law expression is

$$r = k[A]^x [B]^y [C]^z$$

Then, overall order of reaction = $x + y + z$.

Order of a reaction can be fractional value. An example of a fractional order reaction is gas-phase decomposition of CH_3CHO .



12 Differentiate between order and molecularity of a reaction.

Order of a reaction		Molecularity of a reaction	
(i)	It is sum of the exponents to which the concentration terms in the rate law expression are raised to express observed rate of reaction.	(i)	In simple reactions, it is equal to the number of molecules of the reactants while in complex reactions, it is number of molecules involved in rate determining step.
(ii)	It need not be whole number –it can be fractional or zero also.	(ii)	Always a whole number.
(iii)	It can only be experimentally determined.	(iii)	It can be obtained by adding the molecules of the slowest step.
(iv)	It is for the overall reaction and no separate steps are written to obtain it.	(iv)	Overall molecularity of a complex reaction has no significance; only slowest step is significant.
(v)	It does not give an ideal of the mechanism of the reaction.	(v)	It explains the mechanism of the reaction.

13 How would you compare chemical reactions and the nuclear reactions?

Chemical Reactions		Nuclear Reactions	
(i)	This involves making and breaking of bonds in order to rearrange the atoms.	(i)	This involves the conversion of one element into another.
(ii)	Only electrons in the atomic orbitals are involved in the making and breaking of bonds.	(ii)	It involves protons, neutrons, electrons, and other elementary particles.
(iii)	It involves the absorption or release of relatively small amount of energy.	(iii)	These reactions are accompanied by absorption or release of tremendous amounts of energy.
(iv)	Rates of reaction are influenced by temperature, pressure, concentrations and catalyst.	(iv)	Rates of reaction normally are not affected by temperature, pressure, and catalyst.

14 Calculate the rate constant of a reaction at 293 K when the energy of activation is 103 KJ mol⁻¹ and the rate constant at 273 K is $7.87 \times 10^{-7} \text{ sec}^{-1}$.

Sol.

$$\log_{10} \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

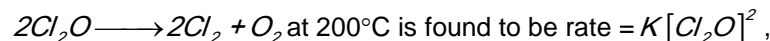
$K_1 = 7.87 \times 10^{-7} \text{ S}^{-1}$; $E_a = 103 \text{ KJ mol}^{-1}$
 $T_1 = 273 \text{ K}$, $T_2 = 293 \text{ K}$

$$\log_{10} \frac{K_2}{7.87 \times 10^{-7}} = \frac{103 \times 20}{2.303 \times 8.314 \times 293 \times 273 \times 10^{-3}}$$

$$\log_{10} \frac{K_2}{7.87 \times 10^{-7}} = 1.345$$

$$K_2 = 1.74 \times 10^{-5} \text{ sec}^{-1}$$

15 The rate law for the reaction,



(a) How would the rate change if $[\text{Cl}_2\text{O}]$ is reduced to one third of its original value?

(b) How should the $[\text{Cl}_2\text{O}]$ be changed in order to double the rate?

(c) How would the rate change if $[\text{Cl}_2\text{O}]$ is raised to three fold of its original value?

Sol. (a) Rate equation for the reaction

$$r = K[\text{Cl}_2\text{O}]^2$$

Let new rate be r' ; so

$$r' = K \left[\frac{[\text{Cl}_2\text{O}]}{3} \right]^2 = \frac{1}{9}r$$

(b) In order to have the rate = $2r$, let the concentration of Cl_2O be x .

$$\text{so } 2r = Kx^2 \quad \dots(i)$$

$$\text{we know that } r = K[\text{Cl}_2\text{O}]^2 \quad \dots(ii)$$

Dividing equation (i) and (ii)

$$\frac{2r}{r} = \frac{Kx^2}{K[\text{Cl}_2\text{O}]^2} \Rightarrow 2 = \frac{x^2}{[\text{Cl}_2\text{O}]^2}$$

$$x^2 = 2[\text{Cl}_2\text{O}]^2 \text{ or } x = \sqrt{2}[\text{Cl}_2\text{O}]$$

(c) New rate = $K[3\text{Cl}_2\text{O}]^2 = 9K[\text{Cl}_2\text{O}]^2 = 9r$ nine times of original rate.

16. Explain in brief the collision theory of reaction rates.

Sol. According to this theory, the reaction takes place as a result of the collision between the reactant molecules. The number of collisions per unit volume per unit time is known as collision frequency Z_{AB} . But all collisions are not effective. The collision which actually converts the reactants into products are called effective collisions. These collisions take the molecules to the top of the energy barrier and finally results in the formation of products.

There are two conditions for the effective collision:

(i) **Energy barrier:** The reactant molecules must possess the minimum energy known as threshold energy before they could react and form products.

(ii) **Orientation barrier:** The reactant molecules must be properly oriented in order to have an effective collision.

The rate constant is given by

$$k = PZ_{AB}e^{-E_a/RT}$$

Where Z_{AB} = collision frequency

P = orientation factor and $e^{-E_a/RT}$ = fraction of total collision which are effective.

17 What is the difference between ${}^0_{-1}e$ and ${}^0_{-1}\beta$?

Sol. The symbol ${}^0_{-1}e$ represents the electron in or from an atomic orbital. The symbol ${}^0_{-1}\beta$ represents an electron, that although physically identical to any other electron, comes from a nucleus and not from an atomic orbital.
 The emission of ${}^0_{-1}\beta$ involves the conversion of a neutron into a proton.

18 How are the radioactive decay series distinguished? Which one of the decay series is not natural but artificial?

Sol. A radioactive decay series is a sequence of nuclear reactions that ultimately result in the formation of stable isotope.
 There are four decay series distinguished by whether the mass number are
 (i) divided by four ($4n$ series) or
 (ii) divided by four with remainder equals to one ($4n + 1$)
 (iii) divided by four with remainder equals to two ($4n + 2$)
 (iv) divided by four with remainder equals to three ($4n + 3$)
 The ($4n + 1$) series is not natural but artificial series and it starts with ${}^{237}_{93}\text{Np}$ and ends with ${}^{209}_{83}\text{Bi}$.

19. Explain the following:
 (i) Mass defect (ii) Binding energy

Sol. (i) Mass defect is the difference between the actual mass of an isotope of an element and the sum of the masses of protons, neutrons and electrons present in it.
 (ii) Binding energy is the energy required to hold the nucleus together. Binding energy of a nucleus is generally quoted as energy in million volts (MeV) per nucleons.
 The binding energy per nucleon is a measure of the stability of the nucleus. The greater the binding energy per nucleon, the more stable is the nucleon.

20. Decomposition of N_2O_5 is expressed by the equation, $\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$

If during a certain time interval, the rate of decomposition of N_2O_5 is $1.8 \times 10^{-3} \text{ mol lit}^{-1} \text{ min}^{-1}$, what will be the rates of formation of NO_2 and O_2 during the same interval?

Sol. The rate expression for the decomposition of N_2O_5 is

$$\frac{-\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{2\Delta[\text{O}_2]}{\Delta t}$$

So $\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{2\Delta[\text{N}_2\text{O}_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3}$
 $= 3.6 \times 10^{-3} \text{ mol lit}^{-1} \text{ min}^{-1}$

and $\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{2} \times 1.8 \times 10^{-3}$
 $= 0.9 \times 10^{-3} \text{ mol lit}^{-1} \text{ min}^{-1}$

21. The conversion of molecules X to Y follows the second order of kinetics. If concentration of X is increased 3 times, how will it affect the rate of formation of Y.

Sol:
$$\begin{aligned} \text{Rate} &= k[A]^2 \\ &= k[3A]^2 \\ &= k[9a]^2 \end{aligned}$$

The rate of formation will become nine times.

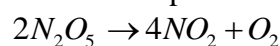
22. The rate law for a reaction is

$$\text{Rate} = K [A][B]^{3/2}$$

Can the reaction be an elementary process? Explain.

- Sol: No, an elementary process would have a rate law with orders equal its molecularities and therefore must be integral form.

23. If the decomposition of nitrogen oxide is represented as



follows a first order kinetics.

- (i) Calculate the rate constant for a 0.05 M solution if the instantaneous rate is 1.5×10^{-6} mol/l/s.

Sol:
$$\begin{aligned} \text{Rate} &= K[N_2O_5] \\ K &= \frac{\text{Rate}}{[N_2O_5]} \\ K &= \frac{1.5 \times 10^{-6}}{0.05} \\ K &= 3.0 \times 10^{-5} \end{aligned}$$

- (ii) What concentration of N_2O_5 would give a rate of 2.45×10^{-5} mol L⁻¹ S⁻¹

$$\begin{aligned} \text{Rate} &= \frac{2.45 \times 10^{-5}}{3.0 \times 10^{-5}} \\ &= 0.82 \text{ M} \end{aligned}$$

24. Write the difference between order and molecularity of reaction.

ORDER	MOLECULARITY
It is the sum of the powers of concentration terms in the rate law expression.	It is the number of reacting species undergoing simultaneous collision in a reaction.
It is determined experimentally	It is a theoretical concept
Order of reaction need not be a whole number	It is whole no. only
Order of reaction can be zero.	It can't be zero or fractional

25. A first order reaction takes 69.3 min for 50% completion. Set up an equation for determining the time needed for 80% completion.

Sol:
$$K = \frac{0.693}{T^{1/2}}$$

$$= \frac{0.693}{69.3} \text{ min}^{-1}$$

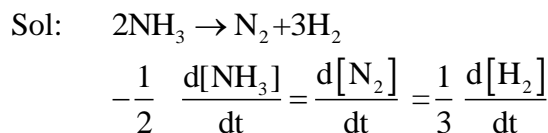
$$= 10^{-2} \text{ min}^{-1}$$

$$T = \frac{2.303}{K} \log \frac{[R_0]}{[R]}$$

$$T = 2.303/10^{-2} \log 5$$

$$T = 160.9 \text{ min}$$

26. The decomposition of NH_3 on platinum surface is zero order reaction.
 What are the rate of production of N_2 and H_2 ? The rate constant is $2.5 \times 10^{-4} \text{ mol}^{-1} \text{ sec}^{-1}$



$$\frac{-d[\text{NH}_3]}{dt} = \text{Rate} = k \times [\text{NH}_3]^0$$

$$2.5 \times 10^{-4} \text{ mol}^{-1} \text{ sec}^{-1}$$

$$\frac{d[\text{N}_2]}{dt} = \frac{-1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$= \frac{1}{2} \times 2.5 \times 10^{-4} \text{ molL}^{-1} \text{ sec}^{-1}$$

$$\frac{d[\text{H}_2]}{dt} = \frac{-3}{2} \frac{d[\text{NH}_3]}{dt} = k \times [\text{NH}_3]^0$$

$$= 3.75 \times 10^{-4} \text{ molL}^{-1} \text{ sec}^{-1}$$

$$\text{Rate} = \frac{-d[\text{NH}_3]}{dt} = k \times [\text{NH}_3]^0$$

$$2.5 \times 10^{-4} \text{ molL}^{-1} \text{ sec}^{-1}$$

$$\text{Rate of production of } \text{N}_2 = 2.5 \times 10^{-4} \text{ molL}^{-1} \text{ sec}^{-1}$$

27. Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Sol: We know that for a 1st order reaction,

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

It is given that $t_{1/2} = 60$ min

$$\begin{aligned}\therefore k &= \frac{0.693}{t_{1/2}} \\ &= \frac{0.693}{60}\end{aligned}$$

$$= 0.01155 \text{ Min}^{-1}$$

$$= 1.155 \text{ Min}^{-1}$$

$$\text{Or } k = 1.925 \times 10^{-4} \text{ s}^{-1}$$

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