Chapter 4

Chemical Kinetics and Nuclear Chemistry

Solutions (Set-1)

Very Short Answer Type Questions :

1. The reaction, $X + Y \longrightarrow Z$ has zero order. What is the rate equation?

Sol. $\text{Rate} = \frac{dx}{dt} = k[X]^0 [Y]^0 = k$

2. What is the rate-determining step of a reaction?

Sol. The slowest step is the rate determining step.

3. State any one condition under which a bimolecular reaction may be kinetically of first order.

Sol. A bimolecular reaction may become kinetically of first order if one of the reactants is present in excess.

4. Radioactive disintegration is which type of reaction?

Sol. The rate of disintegration of a radioactive substance is directly proportional to the amount of the substance present. Hence, it is a reaction of first order.

5. Define specific reaction rate.

Sol. Specific reaction rate is the rate of reaction when the molar concentration of each of the reactants is unity.

6. How does the value of rate constant vary with concentration of reactant?

Sol. For a particular reaction at a particular temperature, rate constant is constant and does not depend upon the concentrations of the reactants.

7. Burning of carbon is highly exothermic process, yet it does not start on its own. Explain.

Sol. Energy is required to cross the energy barrier.

8. The rate of reaction in the remaining mixture is not affected when a portion is removed for analysis.

Sol. Because rate of reaction is affected by change in concentration not amount.

9. Which is greater in magnitude threshold energy or activation energy?

Sol. Threshold energy.

10. Whether the value of activation energy is higher in exothermic reactions or endothermic reactions and why?

Sol. Cannot be predicted without mentioning the nature of reaction.

Short Answer Type Questions :

11. For a reaction, the rate law is : Rate = [A] $[B]^{1/2}$. Can this reaction be an elementary reaction?

Sol. For an elementary reaction, order of reaction should be equal to molecularity and further molecularity should be integral. For the given reaction, order of reaction = $\frac{3}{2}$. Since, molecularity cannot be fractional, therefore, for the given reaction, order is not equal to molecularity. Hence, given reaction cannot be an elementary reaction.

12. For $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$; $\text{rate} = \frac{k[H_2][Br_2]^{3/2}}{[HBr]}$.

What is the order of reaction? Write down unit of rate constant.

Sol. Order = $1 + \left(\frac{3}{2}\right) - 1 = \frac{3}{2}$

Hence, unit of $k = \left(\frac{L}{mol}\right)^{\frac{3}{2}-1}_{s^{-1}} = L^{1/2}\ mol^{-1/2}\ s^{-1}$

13. For the reaction,

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6,$$ write

(i) Rate of reaction

(ii) Rate law equation

(iii) Molecularity

(iv) Order of reaction

Sol. (i) Rate of reaction = $-\frac{d[C_{12}H_{22}O_{11}]}{dt} = +\frac{d[C_6H_{12}O_6\ (\text{glucose})]}{dt} = +\frac{d[C_6H_{12}O_6\ (\text{fructose})]}{dt}$

(ii) It is pseudo first order reaction :

$\therefore$ Rate = $k[C_{12}H_{22}O_{11}]$

(iii) Molecularity is 2.

(iv) Order is 1.

14. For the reaction, $3A \longrightarrow \text{Product}$, if the concentration of reactant A is increased four times, rate of reaction is doubled. Determine the order of reaction.

Sol. Rate = $k[A]^m$ ...(i)

Where m is the order of reaction.

Given, $2 \times \text{rate} = k[4A]^m$ ...(ii)

From equations (i) & (ii)

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

$$m = \frac{1}{2}$$

15. The rate law of a chemical reaction, $2NO + O_2 \longrightarrow 2NO_2$ is given as rate = $k[NO_2]^2\ [O_2]$. How will the rate of reaction change if the volume of reaction vessel is reduced to $\frac{1}{4}$th of its original value?

Sol. Rate = $k[NO]^2[O_2]$

Suppose a mole NO and b mole O_2 are present initially in a vessel of V litre.

$$\therefore \quad r_1 = k\left[\frac{a}{V}\right]^2\left[\frac{b}{V}\right]$$

If volume of vessel is reduced to $\frac{V}{4}$, then for same mole of NO and O_2.

$$r_2 = k\left(\frac{a}{\frac{V}{4}}\right)^2\left(\frac{b}{\frac{V}{4}}\right) = 64k\left[\frac{a}{V}\right]^2\left[\frac{b}{V}\right]$$

$r_2 = 64\ r_1$

i.e., rate will increase by 64 times.

16. Why the rate of a chemical reaction does not remain uniform throughout the reaction? Is it possible to have reaction with a uniform rate?

Sol. It is because rate of reaction depends on concentration which changes with passing of time.

A reaction of zero order proceeds at a uniform rate.

17. For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K, if k = $1.6 \times 10^6\ s^{-1}$ at 280 K (R = $8.31\ J\ K^{-1}\ mol^{-1}$)?

Sol. $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) = 0$$

$$\frac{k_2}{k_1} = 1$$

$k_2 = k_1 = 1.6 \times 10^6\ s^{-1}$

18. A first order reaction has rate constant of $10^{-2}\ s^{-1}$. Calculate the half life period of this reaction.

Sol. For a first order reaction, $t_{1/2} = \frac{0.693}{k}$

$k = 10^{-2}\ s^{-1}$

$$t_{1/2} = \frac{0.693}{10^{-2}} = 69.3\ s$$

19. The $t_{1/2}$ of a first order reaction is 60 minutes. What percentage will be left after 240 minutes?

Sol. $$k = \frac{2.303}{t}\log\frac{[A_0]}{[A_t]}$$

$$\frac{0.693}{60} = \frac{2.303}{240}\log\frac{100}{[A_t]}$$

$A_t = 6.25\ \%$

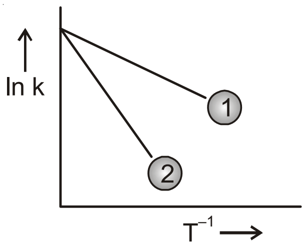
20. The rate constant for a first order reaction involving compound A was found to be 0.082 min^{-1}. When the initial concentration of A is 0.15 mol/L, how long will it take for the concentration of A to drop to 0.03 mole/L.

Sol. $k = 0.082\ \text{min}^{-1}$

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

$$t = \frac{2.303}{0.082}\log\frac{0.15}{0.03} = \frac{2.303}{0.082}\log 5 = \frac{2.303}{0.082}\times 0.694 = 19.6\ \text{min.}$$

21. The dependence of rate constant on temperature for two reactions is shown in the diagram.



Which reaction has the higher activation energy?

Sol. The temperature dependence of rate constant is expressed by Arrhenius equation as

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\text{Slope} = -\frac{E_a}{R}$$

Since reaction 2 has greater negative slope, it has higher activation energy.

22. If rate of a reaction gets doubled as temperature is increased from 27°C to 37°C, what is the activation energy of the reaction?

Sol. Arrhenius equation of two different temperatures is given as

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

$$\log 2 = \frac{E_a}{2.303\times 8.31}\left(\frac{10}{300\times 310}\right)$$

E_a = 53.6 kJ

23. What happens exactly at molecular level that leads to increase in rate of reaction as temperature is raised?

Sol. According to collision theory, reaction may take place only when the molecules collide with a kinetic energy at least equal to activation energy, otherwise, they simply bounce back. As temperature is increased, average kinetic energy increases and fraction of colliding molecules having energy greater than activation energy increases.

24. What is known as activation energy? How is the activation energy affected by

(i) The use of a catalyst and

(ii) A rise in temperature.

Sol. Activation energy is the extra energy which must be supplied to the reactants so that they can change into products.

(i) Catalyst lowers the activation energy.

(ii) There is almost no effect on activation energy with rise in temperature.

25. The rate of reaction, $2NO + Cl_2 \longrightarrow 2NOCl$ is doubled when concentration of Cl_2 is doubled and it becomes eight times when concentration of both NO and Cl_2 are doubled. Deduce the order of reaction.

Sol. The order is 1 w.r.t. Cl_2 because rate of reaction becomes double when concentration of Cl_2 is doubled. When concentration of both NO and Cl_2 is double, rate becomes eight times. It means that it becomes double due to $[Cl_2]$ and 4 times due to [NO].

$\therefore$ Order w.r.t. NO is 2

The overall order of reaction is 2 + 1 = 3.

26. Calculate the rate of reaction from the following rate law :

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

When the concentrations of A and B are 0.01 M and 0.02 M respectively and $k = 5.1 \times 10^{-3}\ L^2\ mol^{-2}\ s^{-1}$.

Sol. $\frac{-d[A]}{dt} = k[A]^1[B]^2$

Substituting the values of k, [A] and [B], we get

$$\begin{aligned}\text{Rate of reaction} &= 5.1 \times 10^{-3} \times (0.01)\,(0.02)^2\\ &= 5.1 \times 10^{-3} \times 10^{-2} \times 4 \times 10^{-4}\\ &= 20.4 \times 10^{-9}\\ &= 2.04 \times 10^{-8}\ \text{mol L}^{-1}\ \text{s}^{-1}\end{aligned}$$

27. $NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$, the experimentally determined rate expression below 400 K is

Rate = $k[NO_2]^2$

What mechanism can be suggested for above reaction?

Sol. As the rate is dependent on $[NO_2]^2$, there are two [NO] terms in the slow step of the reaction.

$$NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g) \quad \text{Slow}$$

$$NO_3(g) + CO(g) \longrightarrow CO_2(g) + NO_2(g) \quad \text{Fast}$$

Rate = $k[NO_2]^2$

28. What is meant by rate of reaction? Write the differential rate expressions for the following chemical reactions:

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

Sol. Relative rates of reaction are defined as change in concentration of reactant or product per unit time w.r.t. each reactant or product.

$$-\frac{1}{4}\frac{d[NH_3]}{dt} = -\frac{1}{5}\frac{d[O_2]}{dt} = +\frac{1}{4}\frac{d[NO]}{dt} = +\frac{1}{6}\frac{d[H_2O]}{dt}$$

29. Differentiate between reaction rate and reaction rate constant.

Sol. Points of difference between the two are given below :

	Reaction rate		**Reaction rate constant**
1.	It is defined as change in concentration of reactant per unit time.	1.	It is equal to rate of reaction when concentration of reactant is unity.
2.	Its unit is mol L^{-1} s^{-1}.	2.	Its unit depends on order of reaction.

30. The rate constant for a first order reaction is 0.0005 min^{-1}. Calculate its half life.

Sol. $t_{1/2} = \dfrac{0.693}{k}$

$$t_{1/2} = \frac{0.693}{0.0005}$$

$$t_{1/2} = \frac{693}{1000} \times \frac{10000}{5} = \frac{6930}{5} = 1386 \text{ min}$$

Long Answer Type Questions :

31. (a) The reaction, $2A + B + C \longrightarrow D + E$ is found to be first order in A, second order in B and zero order in C.

(i) Give the differential rate law for above reaction.

(ii) What is the effect on the rate when concentration of A, B and C, each is increased two times?

(b) Identify the reaction order, if the unit of rate constant is s^{-1}.

Sol. (a) (i) Rate law for above reaction is given by

$$r = \frac{dx}{dt} = k[A][B]^2[C]^0$$

(ii) On increasing the concentration of A, B and C, 2 times, then

$$r = \frac{dx}{dt} = k[2A]\ [2B]^2\ [2C]^0 = 2 \times 4k[A]\ [B]^2$$

$$r = 8k[A]\ [B]^2$$

i.e., the rate increases 8 times.

(b) Order or reaction is one.

32. (a) Write rate expression for the reaction, $A \longrightarrow \text{Product}$.

(b) For a reaction, $2A \longrightarrow A_2$ the rate of reaction becomes three times when the concentration of A is increased 27 times. What is the order of reaction?

(c) For a particular reaction, the rate of reaction does not change with time. What conclusion can you draw from this observation?

Sol. (a) Rate = $k[A]^n$ (If order of reaction is n)

(b) Order = $\dfrac{1}{3}$

(c) Zero order reaction.

33. (a) Can activation energy of a reaction be zero?

(b) Can a catalyst changes the E_a of a reaction? Explain.

(c) Predict the value of rate constant (K) if temperature approaches infinite. Is the value physically reasonable?

Sol. (a) In the Arrhenius equation rate constant, $k = Ae^{-E_a/RT}$, where E_a is the activation energy. R is gas constant, T is temperature on kelvin scale and A is the frequency factor. When E_a is zero then every collision between the reactant molecules lead to the formation of product. This is not possible. Therefore, activation energy E_a, cannot be equal to zero.

(b) Sometimes, the catalyst may appear in the rate law expression. This is due to the reason that the catalyst may be reactant in the slow step and may be released in the subsequent steps. For example, for the acidic hydrolysis of methyl acetate,

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

The rate law expression is, Rate = $k[CH_3COOCH_3][H^+]$.

(c) $k = Ae^{-E_a/RT}$

If $T \to \infty$ then k = A

Which is not reasonable.

34. (a) Express the relationship between the rate of production of iodine and hydrogen in the reaction

$$2HI \longrightarrow H_2 + I_2$$

(b) What is the rate and order of a reaction if the mechanism is

$$2NO + H_2 \longrightarrow N_2 + H_2O_2 \text{ (Slow)}$$

$$H_2O_2 + H_2 \longrightarrow 2H_2O \text{ (Fast)}$$

(c) How does rate constant is related to concentration of the reactants?

Sol. (a) $+\frac{d[I_2]}{dt} = +\frac{d[H_2]}{dt}$

(b) Rate of the reaction would be determined by the slower step.

$r = k[NO]^2[H_2]$

Order of reaction = 3

(c) Rate constant does not depend upon the concentration of reactants.

35. (a) The reaction, $2NO_2 \longrightarrow 2NO + O_2$ has an activation energy of 110 kJ mol^{-1}. At 400°C, the rate constant is 7.8 mol^{-1} L s^{-1}. What is the value of rate constant at 430°C?

(b) The activation energy for the decomposition of hydrogen iodide at 581 K is 209 kJ mol^{-1}. Calculate the fraction of molecules having energy equal to or greater than activation energy.

Sol. (a) We know,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\frac{k_2}{7.8} = \frac{110000}{2.303 \times 8.314}\left(\frac{703 - 673}{673 \times 703}\right)$$

$$\log\frac{k_2}{7.8} = 0.3643$$

$$\frac{k_2}{7.8} = 2.31$$

$k_2 = 2.31 \times 7.8$

$= 18.0 \text{ mol}^{-1} \text{ L s}^{-1}$

(b) Fraction of the molecules having energy equal to or greater than activation energy.

$$\frac{k}{A} = e^{-E_a/RT}$$

$$\log\frac{k}{A} = \frac{-E_a}{2.303RT}$$

$$= \frac{-209500}{2.303 \times 8.314 \times 581}$$

$= -18.8323$

$$\boxed{\frac{k}{A} = 1.471 \times 10^{-19}}$$

36. The rate law for the reaction,

$$2Cl_2O \longrightarrow 2Cl_2 + O_2$$

at 200°C is found to be : Rate = $k[Cl_2O]^2$

(a) How would the rate change if $[Cl_2O]$ is reduced to one third of its original value?

(b) How many times the $[Cl_2O]$ be changed in order to double the rate?

Sol. (a) $r = k[Cl_2O]^2$

Let the new rate = r′, so

$$r' = k\left[\frac{Cl_2O}{3}\right]^2 = \frac{1}{9}k[Cl_2O]^2 = \frac{1}{9}r$$

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

So, $2r = kx^2$ ...(i)

We know that, $r = k[Cl_2O]^2$ ...(ii)

Dividing equation (i) & (ii)

$$\frac{2r}{r} = \frac{kx^2}{k[Cl_2O]^2}$$

$$2 = \frac{x^2}{[Cl_2O]^2}$$

$x^2 = 2[Cl_2O]^2$

$x = \sqrt{2}[Cl_2O]$ ⇒ hence $\sqrt{2}$ times

37. A first order reaction is 20% complete in 10 minutes. Calculate the time taken for the reaction to go to 80% completion.

Sol. Applying first order equation

$$k = \frac{2.303}{t}\log\left(\frac{100}{100-20}\right)$$

$$k = \frac{2.303}{10}\log\frac{100}{80} = 0.0223\ \text{min}^{-1}$$

Again applying first order equation for 80% completion

$$t = \frac{2.303}{k}\log\left(\frac{100}{100-80}\right)$$

$$t = \frac{2.303}{0.0223}\log\frac{100}{20}$$

t = 72.18 min

38. Rate of a reaction, $A + B \longrightarrow \text{Product}$, is given as a function of different initial concentrations of A and B.

[A] (mol L^{-1})	**[B] (mol L^{-1})**	**Initial rate (mol L^{-1} min^{-1})**
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to A and with respect to B.

Sol. Let the rate of reaction be

Rate = $k[A]^x\ [B]^y$

From the data given, it is clear that by doubling the concentration of A, the rate also becomes double when B is kept constant. Thus, the rate is directly proportional to concentration of A.

Rate $\propto$ [A], *i.e.*, x = 1

Or the order of reaction w.r.t. A is 1.

When the concentration of A is kept constant and the concentration of B is doubled, the rate does not change, *i.e.*, y = 0 or the order of reaction w.r.t. B is zero.

Thus, reaction rate,

$$-\frac{dx}{dt} = k[A]$$

39. For the reaction, $2A + B \longrightarrow 2C + 3D$, the rate of change in concentration of C is 1.0 mol L^{-1} s^{-1}. Calculate the rate of reaction and rates of change in concentration of A, B, C and D.

Sol. Rate of reaction = $-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{3}\frac{d[D]}{dt}$

Given, $\frac{d[C]}{dt} = 0.1\ \text{mol L}^{-1}\ \text{s}^{-1}$

$\therefore$ Rate of reaction = $\frac{1}{2}\times\frac{d[C]}{dt}$ = $\frac{1}{2}\times 1.0$ = 0.5 mol L^{-1} s^{-1}

$$\frac{-d[A]}{dt}=\frac{d[C]}{dt}=1.0 \text{ mol } L^{-1} s^{-1} \Rightarrow \frac{d[A]}{dt}=-1.0 \text{ mol } L^{-1} s^{-1}$$

$$\frac{-d[B]}{dt}=\frac{1}{2}\frac{d[C]}{dt} = \frac{1}{2}\times 1.0 = 0.5 \text{ mol } L^{-1} s^{-1} \Rightarrow \frac{d[B]}{dt}=-0.5 \text{ mol } L^{-1} s^{-1}$$

$$\frac{d[D]}{dt}=\frac{3}{2}\frac{d[C]}{dt} = \frac{3}{2}\times 1.0 = 1.5 \text{ mol } L^{-1} s^{-1}$$

40. The rate law for the following reaction : $\text{Ester} + H^+ \longrightarrow \text{Acid} + \text{Alcohol}$, is $\frac{dx}{dt}=k[\text{ester}][H_3O^+]^0$.

What would be the effect on rate if :

(a) Concentration of ester is doubled?

(b) Concentration of H^+ ion is doubled?

Sol. As given the rate law for the reaction

(a) $r_1 = k[\text{ester}]^1 [H_3O^+]^0$

$r_1 = k[a]^1 [b]^0$

Where a and b are initial concentrations of ester and H_3O^+.

If concentration of ester is doubled *i.e.*, [Ester] = 2a, by keeping $[H_3O^+]$ constant, then suppose rate becomes r_2

$r_2 = k[2a]^1 [b]^0$

$\frac{r_1}{r_2}=\frac{1}{2}$ or $r_2 = 2r_1$

(b) $r_1 = k[a]^1 [b]^0$

If concentration of H_3O^+ (*i.e.*, b) is doubled, *i.e.*, $[H_3O^+]$ = 2b, by keeping [ester] = a then suppose rate becomes r_3,

$r_3 = [a]^1 [2b]^0$

$\frac{r_1}{r_3}=1$ or $r_1 = r_3$

41. For the reaction, $2A + B + \underset{\text{excess}}{C} \longrightarrow \text{Product}$,

(i) What is rate law for the reaction?

(ii) What are units of rate and rate constant of reaction?

(iii) On increasing the concentration of A two times, of B three times and of C four times, what is the effect on the rate of reaction?

Sol. (i) Rate = $k[A]^x [B]^y [C]^z$

Since, C is in excess, thus z = 0 and x = 2, y = 1

$\therefore$ Rate = $[A]^2 [B]^1 [C]^0$

Order = 2 + 1 + 0 = 3

(ii) Unit of rate of reaction = mol L^{-1} $time^{-1}$

Since, the reaction is of third order.

∴ Unit of rate constant = mol^{-2} L^2 $time^{-1}$

(iii) $r = k[A]^2 [B]^1 [C]^0$

$r_1 = k[2A]^2 [3B]^1 [4C]^0$

$r_1 = 12\ r$

Therefore, rate of reaction will increase by 12 times.

42. In a first order reaction time taken for initial concentration of a substance to become half, is 100 seconds, then

(a) Calculate the rate constant of reaction.

(b) Calculate the time required to reduce the concentration of reaction to 0.0125 M from 0.05 M.

Sol. (a) For a first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3}\ s^{-1}$$

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

$$t = \frac{2.303}{6.93 \times 10^{-3}}\log\frac{0.05}{0.0125}$$

t = 2000 s

43. In a reaction with initially 0.12 M, the concentration of reactant is reduced to 0.06 M in 10 hour and to 0.03 M in 20 hour.

(i) What is the order of reaction?

(ii) What is the rate constant?

Sol. Applying first order kinetics,

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

For case I : $$k = \frac{2.303}{10}\log\frac{0.12}{0.06} = 0.069\ hr^{-1}$$

For case II : $$k = \frac{2.303}{20}\log\frac{0.12}{0.03} = 0.069\ hr^{-1}$$

∴ Reaction is of 1st order and rate constant k = 0.069 hr^{-1}.

44. Write the rate law expression and find the rate constant for

$[A]_0$	$[B]_0$	Initial rate (mol L^{-1} s^{-1})
0.1	0.2	0.05
0.2	0.2	0.10
0.1	0.1	0.05

Sol. Let the rate law for the reaction is

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

$0.05 = k[0.1]^m\ [0.2]^n$ ...(i)

$0.10 = k[0.2]^m\ [0.2]^n$ ...(ii)

$0.05 = k[0.1]^m\ [0.1]^n$ ...(iii)

Solving these equations,

$m = 1,\ n = 0$

Thus, rate = $k[A]^1\ [B]^0$

Putting the values given

$0.05 = k[0.1]^1$

$k = 0.5\ s^{-1}$

45. Four experiments were conducted to discover how the initial rate of consumption of BrO_3^- ion in the reaction :

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+ \longrightarrow 3Br_2(aq) + 3H_2O(g)$$

Varies as the concentration of reactants are changed.

Exp. No.	Initial concentration			Initial rate (mol $L^{-1}\ s^{-1}$)
	$[BrO_3^-]$	$[Br^-]$	$[H^+]$	
1.	0.10	0.10	0.10	1.2×10^{-3}
2.	0.20	0.10	0.10	2.4×10^{-3}
3.	0.10	0.30	0.10	3.6×10^{-3}
4.	0.20	0.10	0.15	5.4×10^{-3}

Find (a) rate law (b) rate constant (c) rate when each of BrO_3^-, Br^- and H^+ is 0.2 M.

Sol. (a) Rate law can be derived as

$$\text{Rate} = k[BrO_3^-]\ [Br^-]\ [H^+]^2$$

Hence, overall order of the reaction is 4.

(b) $$k = \frac{\text{Rate}}{[BrO_3^-]\ [Br^-]\ [H^+]^2} = \frac{1.2 \times 10^{-3}}{(0.1)^4} = 12\ L^3\ mol^{-3}\ s^{-1}$$

(c) Rate = $12(0.2)^4 = 19.2 \times 10^{-3}$ mol $L^{-1}\ s^{-1}$

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Chapter 4

Chemical Kinetics and Nuclear Chemistry

Solutions (Set-2)

[Order and Molecularity]

1. For a reaction $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

Given :

$$-\frac{d(N_2O_5)}{dt} = k_1[N_2O_5]$$

$$\frac{d(NO_2)}{dt} = k_2[N_2O_5]$$

$$\frac{d(O_2)}{dt} = k_3[N_2O_5]$$

The relation between k_1, k_2 and k_3 are

(1) $2k_1 = k_2 = 4k_3$ (2) $k_1 = k_2 = k_3$ (3) $2k_1 = 4k_2 = k_3$ (4) $\frac{1}{2}k_1 = k_2 = \frac{1}{4}k_3$

Sol. Answer (1)

For the reaction,

$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$$

We can express the rate as,

$$\frac{-d[N_2O_5]}{dt} = \frac{1}{2} \cdot \frac{d[NO_2]}{dt} = \frac{1}{(1/2)} \cdot \frac{d[O_2]}{dt}$$

$$\Rightarrow K_1[N_2O_5] = \frac{1}{2} K_2[N_2O_5] = 2K_3[N_2O_5]$$

Hence, we can write

$$K_1 = \frac{K_2}{2} = 2K_3$$

$$\Rightarrow 2K_1 = K_2 = 4K_3.$$

2. The reaction: $A_2 + B_2 \longrightarrow 2AB$, is bound to obey the following mechanism

$$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A+A \text{ (fast)}$$

$$A + B_2 \xrightarrow{k_2} AB + B \text{ (slow)}$$

$$A + B \longrightarrow AB \text{ (fast)}$$

The order of overall reaction is

(1) 3 (2) 2 (3) 2.5 (4) 1.5

Sol. Answer (4)

$$\frac{k_1}{k_{-1}} = \frac{[A]^2}{[A_2]} \Rightarrow [A] = \sqrt{\frac{k_1}{k_{-1}}[A_2]}$$

Rate = $k_2[A]$ $[B]$ (r.d.s.)

$$= k_2 \times \sqrt{\frac{k_1}{k_{-1}}[A_2]} \times [B_2]$$

$$= k_2 \times \sqrt{\frac{k_1}{k_{-1}}} \times [A_2]^{1/2}\ [B_2]$$

$\Rightarrow$ Order of reaction = $\frac{1}{2} + 1 = 1.5$

3. The rate law for the reaction

$AB + CD\ (aq) \longrightarrow AD + CB$

is given by R = k[AB]. The rate of reaction will be

(1) Unaffected by increasing temperature of the reaction

(2) Halved on reducing the concentration of CD to one-half

(3) Increasing on increasing the concentration of CD

(4) Halved on reducing the concentration of AB to one-half

Sol. Answer (4)

The rate law is given

R = K[AB]

$\therefore$ When concentration of [AB] is reduced to half, the rate also becomes half .

4. The concentration of a reactant in a solution falls from 0.2 M to 0.1 M in 2 hours and to 0.05 M in 4 hours. The order of reaction is

(1) Zero (2) Two (3) One (4) Half

Sol. Answer (3)

Same % decay in same time. So, it indicates that reaction is of first order.

[Integrated Rate Equation and Rate Law]

5. Rate constant of a first order reaction is 6.93×10^{-3} min^{-1}. If we start with 10 mol/L. It is reduced to 1.25 mol/L in

(1) 100 minute (2) 200 minute (3) 30 minute (4) 300 minute

Sol. Answer (4)

Given, $k = 6.93 \times 10^{-3}\ \text{min}^{-1}$

$[A]_0 = 10\ \text{M};\ [A]_t = 1.25\ \text{M}$

Hence, for 1st order reaction we can write

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]_t} = \frac{1}{\left(6.93 \times 10^{-3}\right)} \ln \left(\frac{10}{1.25}\right)$$

$$\therefore \quad t = \frac{10^3}{6.93} \times \ln (8) = \frac{3 \ln 2 \times 10^3}{6.93}$$

$$\Rightarrow \quad t = \frac{3 \times 0.693 \times 10}{6.93} = \frac{3 \times 10^3}{1000} \times \frac{693}{693} \times 100$$

$\therefore \quad t = 300$ minutes

6. The reaction $A + 2B + C \rightarrow 2D + E$ is found to be 1, 2 and zero order with respect to A, B and C respectively. What will be the final rate, if concentration of each reactant is doubled?

(1) 2 times (2) 4 times (3) 8 times (4) 16 times

Sol. Answer (3)

The given reaction is

$A + 2B + C \rightarrow 2D + E$

Order = 1 w.r.t. A; 2 w.r.t. B and zero w.r.t. C

Initially $\dfrac{dx}{dt} = k\,[A]\,[B]^2$

Now when concentration is doubled

$$\left(\frac{dx}{dt}\right)' = k(2)\,[A]\,(2)^2\,[B]^2$$

$$\left(\frac{dx}{dt}\right)' = 8k\,[A]\,[B]^2 \qquad \therefore \left(\frac{dx}{dt}\right)' = 8\left(\frac{dx}{dt}\right)$$

The rate of reaction increases by 8 times.

7. A substance having initial concentration 'a' mole/L reacts according to zero order reaction. The time taken for completion of reaction is

(1) $\dfrac{2a}{k}$ (2) $\dfrac{a}{k}$ (3) $\dfrac{a}{2k}$ (4) $\dfrac{k}{a}$

Sol. Answer (2)

Initial concentration is $[A]_0 = a$ M

Reaction follows zero-order kinetics

$x = kt$

Here, $x = a \Rightarrow t = \frac{x}{k} = \frac{a}{k}$

8. Which of the following is an incorrect statement?

(1) Half life of second order reaction decreases with increase in concentration of reactant

(2) Half life of first order is independent of concentration of the reactant

(3) The unit of rate constant of zero order is equal to unit of rate

(4) The unit of frequency factor 'A' in Arrhenius equation is the unit of half life of the reaction

Sol. Answer (4)

For second order reactions $t_{1/2} = \frac{1}{K[A]_0}$

$\therefore$ Half life decrease with increase in concentration of reactants.

For 1^{st} order, $t_{1/2} = \frac{\ln 2}{k}$ and is independent of concentration.

For zero order,

$\frac{dx}{dt} = K$ (both are same)

9. For a hypothetical reaction x + y = A + B, Rate = $k[x]^{5/2}[y]^{-1/2}$ on doubling the concentration of x and y the rate will become

(1) 2 times (2) 4 times (3) 8 times (4) Remains same

Sol. Answer (2)

Rate given is

Rate = $K[x]^{5/2}[y]^{-1/2}$

On doubling the concentration of x and y

Rate = $K(2)^{5/2}(2)^{-1/2}[x]^{5/2}[y]^{-1/2} = K \cdot (2)^{\frac{5}{2}-\frac{1}{2}}[x]^{5/2}[y]^{-1/2} = K.(2)^2[x]^{5/2}[y]^{-1/2} = 4K[x]^{5/2}[y]^{-1/2}$

Hence, rate becomes 4 times.

10. A reaction : aA $\longrightarrow$ product. Follows zero order the concentration of A with respect to time(t) is given as

(1) $[A]_0 = [A] - kt$ (2) $[A] = [A]_0 - kt$ (3) $[A] = [A]_0 + kt$ (4) $[A] = [A]_0 - \frac{kt}{a}$

Sol. Answer (2)

aA $\rightarrow$ product

$R = -\frac{1}{a}\frac{d[A]}{dt} = k$ (zero order)

Integrating, we get: $(A)_t = (A)_0 - akt$

11. The half life period of a radioactive substance is 69.3 minutes. In how much time will it be disintegrated 80% of its original amount?

(1) 80 minutes (2) 100 minutes (3) 140 minutes (4) 161 minutes

Sol. Answer (4)

For radioactive disintegration

$$t_{1/2} = 69.3 \text{ min. } N_t = \frac{20}{100} N_0 = \frac{N_0}{5}$$

$$\therefore \quad \lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{69.3} = 0.01 \text{ min}^{-1}.$$

Applying I-order reaction

$$t = \frac{1}{(0.01)} \ln\left(\frac{5N_0}{N_0}\right) = \frac{\ln 5}{(0.01)}$$

$$\therefore \quad \text{Time taken (t)} = \frac{2.303 \times 0.7}{(0.01)}$$

$\Rightarrow$ t = 161 minutes

12. For a reaction $2N_2O_5 \longrightarrow 4NO_{2(g)} + O_{2(g)}$, the rate and rate constant are 1.02×10^{-4} mol L^{-1} s^{-1} and 3.4×10^{-5} s^{-1} respectively. The concentration of N_2O_5 at this time will be

(1) 1.732 mol/L (2) 3 mol/L (3) 1.02×10^{-4} mol/L (4) 3.2×10^{5} mol/L

Sol. Answer (2)

The given reaction is $2N_2O_5 \rightarrow 4NO_2 + O_2$

$R = 1.02\times10^{-4}$ m/s; $K = 3.4\times10^{-5}s^{-1}$.

Reactions follows I-order kinetics as units of K is s^{-1}

Rate = K $[N_2O_5]$

$\Rightarrow$ $1.02 \times 10^{-4} = (3.4 \times 10^{-5})\,[N_2O_5]$

$$\therefore \quad [N_2O_5] = \frac{1.02\times10^{-4}}{\left(3.4\times10^{-5}\right)} = \frac{1.02\times10}{3.4} = 3\text{ M}$$

13. A gas phase reaction $R \rightarrow A + B + C + D$ is of first order. The initial pressure was x_0 where pressure after 10 minutes was y. The correct expression for rate constant k is

(1) $k = \frac{2.303}{10} \log \frac{4x_0}{3x_0 - y}$ (2) $k = \frac{2.303}{10} \log \frac{2x_0}{3x_0 - y}$

(3) $k = \frac{2.303}{10} \log \frac{3x_0}{4x_0 - y}$ (4) $k = \frac{2.303}{10} \log \frac{4x_0}{4x_0 - y}$

Sol. Answer (3)

The gas phase reaction is

	R	$\rightarrow$	A	+	B	+	C	+	D
t = 0	x_0		0		0		0		0
t = t	$x_0 - P$		P		P		P		P

$\therefore\ x_0 - P + 4P = y \Rightarrow x_0 + 3P = y$

$\therefore\ 3P = (y - x_0) \Rightarrow P = \left(\frac{y - x_0}{3}\right)$

Applying I-order kinetics equation

$$K = \frac{1}{10} \ln \frac{x_0}{x_0 - P}$$

$$\therefore\ K = \frac{2.303}{10} \log \frac{x_0}{x_0 - \left(\frac{y - x_0}{3}\right)}$$

$$\therefore\ K = \frac{2.303}{10} \log \frac{3\,x_0}{3\,x_0 - y + x_0}$$

$$\therefore\ K = \frac{2.303}{10} \log \frac{3\,x_0}{4\,x_0 - y}$$

14. For the reaction $2NO + Br_2 \longrightarrow 2NOBr$, the following mechanism has been given

$NO + Br_2 \rightleftharpoons NOBr_2$

$NOBr_2 + NO \xrightarrow{\text{Slow}} 2NOBr$

Hence rate law is

(1) $K[NO]^2\ [Br_2]$ (2) $K[NO]\ [Br_2]$ (3) $K[NOBr_2]\ [NO]$ (4) $K[NO]\ [Br_2]^2$

Sol. Answer (1)

Mechanism given is

$$NO + Br_2 \overset{K_c}{\rightleftharpoons} NOBr_2$$

$$NOBr_2 + NO \xrightarrow[\text{slow}]{K} 2NOBr$$

From II- reaction, $\frac{dx}{dt} = K\,[NOBr_2]\,[NO]$ …(i)

$$K_c = \frac{[NOBr_2]}{[NO][Br_2]}$$

$[NOBr_2] = K_c\,[NO][Br_2]$ …(ii)

Substituting eq. (ii) in eq. (i), we get,

$$\frac{dx}{dt} = KK_c\,[NO]^2\,[Br_2] \text{ or } \frac{dx}{dt} = K'\,[NO]^2\,[Br_2]$$

15. For a reaction

$A + B \longrightarrow C + D$

the rate = $k[A]^{-1/2}\,[B]^{3/2}$. On doubling the concentration of A and B. The rate will be

(1) 4 times (2) 2 times (3) 3 times (4) Same

Sol. Answer (2)

The rate law for the reaction

$A + B \rightarrow C + D$ is given by

Rate = $K\,[A]^{-1/2}\,[B]^{3/2}$

When [A] and [B] becomes twice

$$R' = K(2)^{-}\ K(2)^{-\frac{1}{2}}\,[A]^{-\frac{1}{2}}\,2^{\frac{3}{2}}\,[B]^{\frac{3}{2}}$$

$$= K\ (2)^{-\frac{1}{2}+\frac{3}{2}}\ [A]^{-1/2}\,[B]^{3/2}$$

$$= K\ (2)^{2/2}\ [A]^{-1/2}\,[B]^{3/2}$$

$$R' = 2K\ [A]^{-1/2}\,[B]^{3/2}$$

$\therefore$ $R' = 2$ (rate)

Hence, the rate becomes 2 times.

[Numericals on 1st Order]

16. Half life of a chemical reaction at a particular concentration is 50 minutes. When the concentration of the reactant is doubled, the half life becomes 100 minutes, then the order of reaction is

(1) Zero (2) First (3) Second (4) Third

Sol. Answer (1)

Half life for zero order reaction is given by the expression

$$t_{1/2} = \frac{a}{2K}$$

When ‘a’ was doubled, Half-life also doubles. Hence, the reaction follows zero order kinetics.

17. In the first order reaction $t_{99.9\%}$ is 60 minute. $t_{50\%}$ of the reaction would be nearly

(1) 360 minute (2) 600 minute (3) 6 minute (4) 60 minute

Sol. Answer (3)

Let the initial concentration = a

Reaction follows I-order kinetics

$$K = \frac{1}{(60)}\ \ln\left\{\frac{a}{a-\frac{99.9}{100}a}\right\} = \frac{1}{(60)}\ \text{in}\left(\frac{100a}{100a-99.9a}\right)$$

$$= \frac{1}{(60)}\ \ln\left(\frac{100a}{0.1a}\right)$$

$$= \frac{1}{(60)}\ \ln\left\{\frac{1000a}{a}\right\} = \frac{\ln(1000)}{60}$$

$\therefore$ For 50% decomposition we can write

$$t = \frac{\ln 2}{K} = \frac{60(\ln 2)}{\ln(1000)}$$

$\therefore$ t = (60) (0.3)

$$\therefore \quad t = \frac{60\log 2}{\log(1000)} = \frac{60\log 2}{\log(10^3)}$$

$$\therefore \quad t = \frac{60\log 2}{3} = 20 \log 2$$

$\therefore$ t = 20 × 0.3 = 6 minute

18. For a first order reaction $t_{0.75}$ is 138.6 seconds. Its specific rate constant (in s^{-1}) is

(1) 10^{-2} (2) 10^{-4} (3) 10^{-5} (4) 10^{-6}

Sol. Answer (1)

T = 138.6 s

For 75% decomposition we can write

$$K = \frac{1}{t}\ \ln\left\{\frac{a}{a-\frac{75\,a}{100}}\right\} = \frac{1}{t}\ \ln\left(\frac{100a}{100a-75a}\right)$$

$$\therefore \quad K = \frac{1}{t}\ln\left\{\frac{100\,a}{25\,a}\right\} = \left\{\frac{\ln 4}{138.6}\right\}$$

$$\therefore \quad K = \frac{2.303\times 2\times 0.3010}{138.6} = 0.01 = 10^{-2}s^{-1}$$

19. For the following reaction

$$A(g) \longrightarrow B(g) + C(g)$$

The initial pressure was P_0 while pressure after time 't' was P_t. The rate constant k will be given by

(1) $k = \frac{2.303}{t}\log\frac{P_0}{P_t}$ (2) $k = \frac{2.303}{t}\log\frac{P_0}{P_0 - 2P_t}$

(3) $k = \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}$ (4) $k = \frac{2.303}{t}\log\frac{P_0}{P_0 - P_t}$

Sol. Answer (3)

The given reaction is

	A(g)	→	B(g)	+	C(g)
At t = 0	P_0		0		0
t = t	$P_0 - P$		P		P

$\therefore$ $P_t = P_0 - P + P + P = P_0 + P$

$\therefore$ $P = (P_t - P_0)$

Hence, applying I-order kinetics equation

$$K = \frac{1}{t}\ \ln\left\{\frac{P_0}{P_0 - P}\right\} = \frac{1}{t}\ \ln\left\{\frac{P_0}{P_0 - (P_t - P_0)}\right\}$$

$$\Rightarrow \frac{1}{t}\ \ln\left\{\frac{P_0}{2P_0 - P_t}\right\} = \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}$$

20. In the first order reaction, x $\longrightarrow$ y; the concentration of 'x' changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction (mol/L/min) when concentration of x is 0.01 M, would be

(1) 3.47×10^{-5} (2) 3.47×10^{-4} (3) 5.8×10^{-4} (4) 5.8×10^{-6}

Sol. Answer (2)

$[X]_0 = 0.1$ M; $[X]_t = 0.025$ M

t = 40 minute.

$$\therefore \quad K = \frac{1}{40} \ln\left(\frac{0.1}{0.025}\right) = \frac{\ln 4}{40}$$

Rate of reaction = K[X]

$$= \left\{\frac{\ln 4}{40}\right\} \times (0.01) \Rightarrow \frac{2\ln 2}{40} \times (0.01)$$

$$= \frac{2 \times 0.693 \times 0.01}{40} = 3.47 \times 10^{-4} \text{ m/s}$$

21. The gaseous reaction A (g) $\rightarrow$ 2B (g) + C (g) obeys first order kinetics. If the initial P = 90 mm and pressure after 10 minutes = 180 mm. The velocity constant k of the reaction is

(1) $1.15 \times 10^{+3}$ s^{-1} (2) $2.30 \times 10^{+3}$ s^{-1} (3) 3.45×10^{-3} s^{-1} (4) 1.15×10^{-3} s^{-1}

Sol. Answer (4)

	$A(g) \rightarrow$	$2B(g)$ +	$C(g)$
t = 0	P_0	0	0
t = t	$P_0 - P$	2P	P

$\therefore \quad P_t = 0; = P_0$; $P_t = P_0 - P + P + 2P$

$P_t = P_0 + 2P$

After 10 min; P_t = 180 mm Hg

$180 = 90 + 2P \Rightarrow 90 = 2P$

P = 45 mmHg

$\therefore$ Applying I-order kinetics:

$$\therefore \quad K = \frac{1}{10} \ln\left\{\frac{90}{90-45}\right\} = \frac{\ln 2}{10}$$

$$K = \frac{0.693}{60 \times 10} = \frac{0.693}{600} = 1.15 \times 10^{-3} \text{ s}^{-1}$$

[Arrhenius Equation]

22. Select the correct statement regarding activation energy.

(1) Activation energy may be greater than heat of reaction

(2) Activation energy is less than threshold energy

(3) Rate of reaction is inversely proportional to the activation energy

(4) All of these

Sol. Answer (4)

According to Arrhenius equation,

$$K = A.e^{\frac{-E_a}{Rt}}$$

The rate constant is inversely related to activation energy. It is energy required to make it equal to threshold level and it can be greater than ΔH for the reaction.

23. The temperature coefficient of most of the reactions lie between

(1) 2 and 4 (2) 3 and 4 (3) 1 and 2 (4) 2 and 3

Sol. Answer (4)

Temperature coefficient for the reaction is given by

$$T_c = \frac{K_T + 10}{K_T} = 2 \text{ and } 3$$

24. The plot of log k versus $\frac{1}{T}$ of a first order is linear with a

(1) Positive slope and zero intercept

(2) Positive slope and non-zero intercept

(3) Negative slope and non-zero intercept

(4) Negative slope and zero intercept

Sol. Answer (3)

According to Arrhenius logarithmic form,

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

Log K versus $\frac{1}{T}$ graph gives straight line having intercept = log A

$$\text{And slope (m)} = \frac{-E_a}{2.303R}$$

Since $E_a > 0$; $m < 0$

⇒ Slope is negative having non-zero intercept.

25. The rate constant, the activation energy and Arrhenius parameter of a chemical reaction at 25°C are K, E_a and A respectively. The value of rate constant as $T \to \infty$ is

(1) E_a (2) $E_a \times A$ (3) $A - E_a$ (4) A

Sol. Answer (4)

$$K = A.e^{\frac{-E_a}{RT}}$$

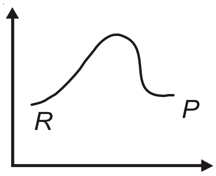
When $T \to \infty$, $K = \frac{A}{e^0} = A$

∴ as $T \to \infty$; K = A.

26. When the activation energies of forward and backward reactions are equal, then

(1) $\Delta H = 0, \Delta S = 0$ (2) $\Delta H = \infty, \Delta S = 0$ (3) $\Delta G = 0, \Delta H = 0$ (4) Only $\Delta H = 0$

Sol. Answer (4)



For $(E_a)_f = (E_a)_b$, $\Delta H = 0$

But $\Delta S \neq 0$

$\Rightarrow$ $\Delta G \neq 0$ also

[Nuclear Chemistry]

27. The position of element RaC in the periodic table is

$${}_{88}Ra^{226} \xrightarrow{-\alpha} {}_{86}Rn \xrightarrow{-\alpha} RaA \xrightarrow{-\beta} RaB \xrightarrow{-\alpha} RaC$$

(1) 13th group & 6th period (2) 16th group & 3rd period

(3) 15th group & 7th period (4) 15th group & 6th period

Sol. Answer (4)

$${}^{226}_{88}Ra \rightarrow {}_2He^4 + {}^{222}_{86}Rn$$

$${}^{222}_{86}Rn \rightarrow {}^{218}_{84}RaA + {}_2He^4$$

$${}^{218}_{84}RaA \rightarrow {}^{218}_{85}RaB + {}_{-1}\beta^0$$

$${}^{218}_{85}RaB \rightarrow {}_2He^4 + {}^{214}_{83}RaC$$

Element RaC will be lying in 15th group and 6th in period.

28. The radiation from a naturally occurring radioactive substance as seen after deflection by a magnetic field in one direction are

(1) α rays (2) β rays

(3) Both (1) & (2) (4) Either α or β-rays

Sol. Answer (4)

Since α and β-rays are +vely and –vely charged particles, hence, they will be deflected by magnetic field in one direction.

29. When ${}_{92}U^{235}$ is converted to ${}_{82}Pb^{207}$, 'x' number of α-particles and 'y' number of β-particles are released. Then 'x' and 'y' respectively are

(1) 7, 4 (2) 4, 7 (3) 7, 5 (4) 5, 7

Sol. Answer (1)

(i) ${}_{92}U^{235} \longrightarrow {}_{82}Pb^{207} + 7\,{}_2He^4 + 4\,{}_{-1}e^0$

30. One gram atom of $_{79}Au^{198}$ ($t_{1/2}$ = 65 hours) decays by β-emission to produce stable nuclide of Hg. How much Hg will be present after 260 hours?

(1) $\frac{1}{16}$ g atom (2) $\frac{1}{32}$ g atom (3) $\frac{15}{16}$ g atom (4) $\frac{16}{15}$ g atom

Sol. Answer (3)

No. of grams atom, t = 0 of Au is equal to 1

After 260 hours ($t_{1/2}$ = 65 hours)

$$\lambda = \frac{\ln 2}{65}$$

$$\therefore \quad \Rightarrow \frac{\ln 2}{65} = \frac{1}{260}\ln\left\{\frac{1}{x}\right\}$$

$$\frac{260 \ln 2}{65} = \ln\left(\frac{1}{x}\right)$$

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

$$\therefore \quad \frac{1}{x} = 2^4 \text{ or } x = \frac{1}{2^4} = \frac{1}{16} \text{ g atoms}$$

$$\therefore \quad \text{No. of gram atoms after 260 hrs} = 1 - \frac{1}{16} = \frac{15}{16}$$

31. 1.0 g atom of an α-emitting isotope ($t_{1/2}$ = 10 days) is sealed in a container. The volume of gas accumulated in the container at STP after 10 days would be

(1) 1.0 L (2) 44.8 L (3) 11.2 L (4) 22.4 L

Sol. Answer (3)

$[N_0]$ = 1 g atoms

$\therefore$ Since it is a-emitting.

Isotope it produces $_2He^4$ (1/2 mole)

$$\therefore \quad \text{Volume of gas liberated at STP} = 22.4 \times \frac{1}{2} = 11.2 \text{ L}$$

32. There are two radio nuclei A and B. A is α-emitter and B is a β-emitter, their decay constant are in the ratio of 1 : 2. What should be the number of atoms of A & B at time t = 0, so that probability of getting α and β-particles are same at time t = 0?

(1) 2 : 1 (2) 1 : 2 (3) 1 : 4 (4) 4 : 1

Sol. Answer (1)

$\text{Rate}_1 = \lambda_1 N_1$ …(i)

$\text{Rate}_2 = \lambda_2 N_2$ …(ii)

According to question,

$\text{Rate}_1 = \text{Rate}_2$

$\lambda_1 N_1 = \lambda_2 N_2$

$$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1} = \frac{2}{1}$$

33. The activity of a radioactive sample reduced from 20 Ci to 1.25 Ci in 2000 years. The half life of the sample and its decay constant are respectively

(1) 4000 years and $1.1 \times 10^{-3}\ y^{-1}$ (2) 500 years and $1.1 \times 10^{-2}\ y^{-1}$

(3) 500 years and $1.386 \times 10^{-3}\ y^{-1}$ (4) 1000 years and $1.386 \times 10^{-3}\ y^{-1}$

Sol. Answer (3)

The activity of radioactive sample decreases from 20 to 1.25

t = 2000 yrs.

$$\lambda = \frac{1}{2000} \ln\left(\frac{20}{1.25}\right) = \frac{\ln 16}{2000}$$

$\Rightarrow \lambda = 1.386 \times 10^{-3}\ y^{-1}$

$\therefore$ Half life is

$$t_{1/2} = \frac{\ln 2}{\ln 16} \times 2000 = \frac{\ln 2}{4 \ln 2} \times 2000 = 500 \text{ years.}$$

34. The amount of U-235 required per day to run a power house of capacity 15 MW (efficiency of nuclear reactor 75%. Assume energy liberated by fission of 1 U-235 atom is 200 MeV) is

(1) 15.8 g (2) 28.1 g (3) 21.1 g (4) None of these

Sol. Answer (3)

1 watt = $1\ J\ s^{-1}$

Capacity of power house = $15 \times 10^6\ J\ s^{-1}$

1 day = 86400 s

$\therefore$ For 1 day (86400 sec) energy required

$= 86400 \times 15 \times 10^6\ J$

$= 1.296 \times 10^{12}\ J$

200 MeV $= 200 \times 10^6 \times 1.6 \times 10^{-19} = 3.2 \times 10^{-11}\ J$

$\because$ 3.2×10^{-11} J energy produced by 1 atom of U-235.

$\therefore$ 1.296×10^{12} J energy will be produced $= \dfrac{1.296 \times 10^{12} \times 1}{3.2 \times 10^{-11}} = 4.05 \times 10^{22}$ atoms

Mass of 4.05×10^{22} atoms $= \left(\dfrac{4.05 \times 10^{22}}{6.023 \times 10^{23}}\right) \times 235 = 15.80$ g

Since efficiency is 75% hence actual mass required $= 15.8 \times \dfrac{100}{75} = 21.06$ g

35. The half life for decay of a radio active isotope is 14 hrs. Determine the fraction of radio isotope remaining undecayed after 30 hours

(1) 4.456 (2) 0.227 (3) 0.256 (4) 0.358

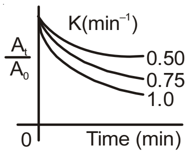
Sol. Answer (2)

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{14}$$

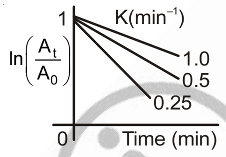
$$\frac{N_t}{N_0} = e^{-\lambda t} = e^{-\left(\frac{\ln 2}{14}\right)\times 30} = 0.227$$

[Miscellaneous]

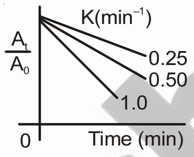
36. For a 1st order reaction of the form $A \xrightarrow{\Delta} P$ correct representation of graph is/are



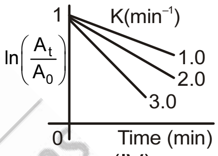
(I)



(II)



(III)



(IV)

(1) (I) & (II) (2) (I) & (III) (3) (II) & (III) (4) (I) only

Sol. Answer (4)

$$K = \frac{2.303}{t}\log_{10}\frac{A_0}{A_t}$$

$$\Rightarrow \quad Kt = \ln\frac{A_0}{A_t}$$

$$\Rightarrow \quad -Kt = \ln\frac{A_t}{A_0}$$

$$\Rightarrow \quad \frac{A_t}{A_0} = e^{-K.t.}$$

37. The rate constant for the formation of NOBr at 127°C is 2 × 10^4 times that of the NOBr at 27°C. The activation energy of the reaction is (approx.)

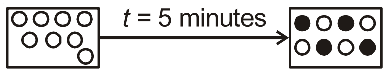
(1) 98.8 kJ/mole (2) 150.00 kJ/mole (3) 200.00 kJ/mole (4) 50.0 kJ/mole

Sol. Answer (1)

$$\log_{10}\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log_{10}\left(\frac{2\times 10^4 \times K}{K}\right) = \frac{E_a}{2.303\times 8.314\times 10^{-3}}\left[\frac{1}{300} - \frac{1}{400}\right]$$

E_a = 98.8 kJ/mole

38. 

represents the conversion of reactants to products in 5 minutes time in a first order reaction is given above. [Concentrations of reactant (O) and product (●) are represented in mole.L^{-1}]. What is time taken to convert 99.9% of reactants to products?

(1) 15 minute
(2) 25 minute
(3) 50 minute
(4) 75 minute

Sol. Answer (3)

Given, $t_{1/2}$= 5 minutes

$t_{99.9\%} = 10\ t_{1/2} = 10 \times 5 = 50$ minutes

39. For a general R-order reaction (B → C), with initial concentration of reactant 'a' and rate constant 'k', the expression for time for 75% completion of reaction is

(1) $\frac{1}{(R-1)}\left[\frac{2^{R-1}-2}{a^{R-1}}\right]\cdot\frac{1}{k}$

(2) $\frac{1}{(R-1)}\left[\frac{2^{2R-2}-1}{a^{R-1}}\right]\cdot\frac{1}{k}$

(3) $\frac{1}{(R-2)}\left[\frac{2^{2R-2}-2}{a^{R-1}}\right]\cdot\frac{1}{k}$

(4) $\frac{1}{(R-2)}\left[\frac{2^{2R-2}-1}{a^{2R-1}}\right]\cdot\frac{1}{k}$

Sol. Answer (2)

Rate = $K[A]^R$

$$K = \frac{1}{(R-1)t}\left[\frac{1}{(a-x)^{R-1}} - \frac{1}{a^{R-1}}\right]$$

$$K = \frac{1}{(R-1)t_{75\%}}\left[\frac{1}{(a-\frac{3a}{4})^{R-1}} - \frac{1}{a^{R-1}}\right]$$

$$t_{75\%} = \frac{1}{(R-1)K}\left[\frac{1}{\left(\frac{a}{4}\right)^{R-1}} - \frac{1}{a^{R-1}}\right]$$

$$t_{75\%} = \frac{2^{2R-2}-1}{(R-1)K\cdot a^{R-1}}$$

40. Consider the reaction

Reaction-I P → Q First order reaction, Rate constant K_1, Activation energy = x_1.

Reaction-II Y → Z First order reaction, Rate constant K_2. Activation energy = x_2.

Both reactions occurs in different container.

In reaction-I, rate constant becomes 10 times to initial rate constant when temperature increases T to 3T while in reaction-II, rate constant becomes 10 times to initial rate constant when temperature increases T to 2T. The correct statements is (given x_1 and x_2 both are positive value and temperature independent. T = 300 K and value of Arrhenius parameter(A) of both reactions is same]

(1) $x_1 > x_2$

(2) $x_2 = x_1$

(3) If initially [P] = [Y] = 1 M at 300 K then rate of 1st reaction (P → Q) is more than 2nd reaction (Y → Z)

(4) Both (1) & (3)

Sol. Answer (3)

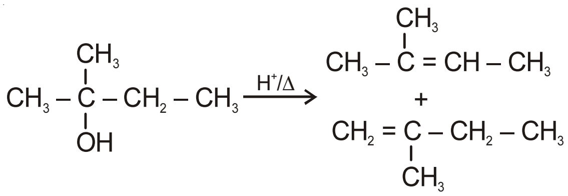
For reaction I: $E_a = 2.303 \times 1.5\ RT$

For reaction II: $E_a = 2.303 \times 2\ RT$

So, $x_2 > x_1$,

Initially rate = K, $K_1 > K_2$

41.



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2-CH_3 \xrightarrow{H^+/\Delta} \begin{matrix} CH_3-\overset{CH_3}{C}=CH-CH_3 \\ + \\ CH_2=\underset{CH_3}{C}-CH_2-CH_3 \end{matrix}$$

The above reaction can represent

(1) Consecutive reaction

(2) Parallel reaction

(3) Simultaneous reaction

(4) Both (2) & (3)

Sol. Answer (4)

It represents parallel (or) simultaneous reactions.

42. Given

$A_{(g)} \longrightarrow B_{(g)}$ (Zero order reaction with rate constant K_1)

$C_{(g)} \longrightarrow D_{(g)}$ (Zero order reaction with rate constant K_2)

If both reactions start at same time and initially concentration of A is 10 times of C. If half life of both reactions is same then which statement is correct?

(1) $K_2 = 10\ K_1$

(2) $K_1 = 10\ K_2$

(3) Completion time of both reactions is different

(4) $K_1 = K_2$

Sol. Answer (2)

43. Reaction

Reaction :1. $A \longrightarrow B$, Rate constant at T°C is K sec^{-1}, Activation energy of reaction is Y.

Reaction : 2. $C \longrightarrow D$, Rate constant at T°C is K sec^{-1}, Activation energy of reaction is Z.

Both reactions start at the same time in different containers at temperature T°C. Given that Y > Z, Y and Z both have positive value. If the temperature of both reactions is increased to 2T, then rate constant for reaction 1 and 2 becomes k_1 and k_2 respectively. Then the correct statement is

(1) $k_1 = k_2$

(2) $k_1 > k_2$

(3) $k_1 < k_2$

(4) Can't be predicted

Sol. Answer (2)

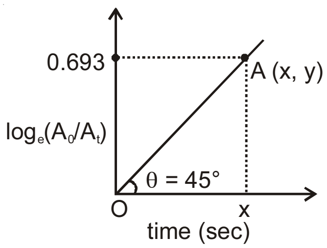
$$\log\left(\frac{K'}{K}\right) = \frac{E_a}{2.303R}\left(\frac{T'-T}{T'T}\right)$$

K′ Rate constant at T′

K Rate constant at T

The reaction which has more value of E_a is more sensitive against temperature.

44. A first order reaction $Q \rightarrow P$ is taking place in a vessel



If $A_0 \rightarrow$ Initial molar concentration of Q

$A_t \rightarrow$ Molar concentration of Q at time t

Here x represent

(1) Half life of reaction

(2) Time in which 90% of reaction is complete

(3) Time in which 99% of reaction is complete

(4) Time in which 99.9% of reaction is complete

Sol. Answer (1)

$\log_e(A_0/A_t) = 0.693;$ at time = x sec.

$A_t = A_0/2$

$\Rightarrow$ x represents half life

45. $P \longrightarrow Q;$ $K = 693 \times 10^{-3}\ s^{-1}$

The time in which concentration of P change from 2 M to 0.25 M is [Given $\log_e 2 = 0.693$]

(1) 1 second (2) 2 second (3) 3 second (4) 4 second

Sol. Answer (3)

Reaction is first order.

$$\therefore\ t_{1/2} = \frac{0.693}{0.693} = 1\,\text{second}$$

$$2\,M \xrightarrow{t_{1/2}} 1\,M \xrightarrow{t_{1/2}} 0.5\,M \xrightarrow{t_{1/2}} 0.25\,M$$

i.e., 3 second

46. Consider the reaction

$KClO_3 + 6\,FeSO_4 + 3H_2SO_4 \rightarrow KCl + 3Fe_2(SO_4)_3 + 3H_2O$

If concentration of $FeSO_4$ decreases from 0.9 M to 0.3 M in 10 second, the rate of formation of KCl is in the above reaction would be (In M sec^{-1}).

(1) 0.06 (2) 0.6 (3) 0.01 (4) 0.1

Sol. Answer (3)

Rate of formation of KCl = $\frac{1}{6}$ rate of consumption of $FeSO_4$.

47. Rate constant of a reaction is 10^{-2} mol L^{-1} s^{-1}. The rate of this reaction (in Ms^{-1}) when concentration of reactant is 10^{-3} M

(1) 10^{-5} (2) 10^{-3} (3) 10^{-2} (4) 10

Sol. Answer (3)

This reaction is zero order so rate = K

48. For a reaction rate law is

$$\text{rate} = \frac{1+K_1[A]^3}{K_2[A]}$$

Here A is reactant and value of K_1 and $K_2 > 1$

Select the correct statement.

(1) When concentration of A is very large as compared to 1, unit of rate constant is Ms^{-1}

(2) When concentration of A is very large as compared to 1, unit of rate constant is s^{-1}

(3) When concentration of A is very large as compared to 1, unit of rate constant is $M^{-1}s^{-1}$

(4) When concentration of A is very large as compared to 1, unit of rate constant is M

Sol. Answer (3)

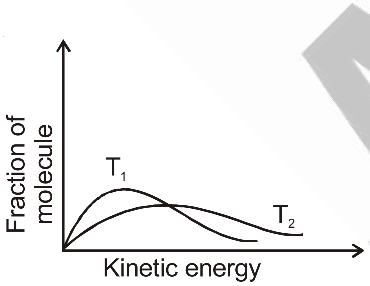
$$r = \frac{1+K_1[A]^3}{K_2[A]}$$

When [A] >> 1

$$r = \frac{K_1[A]^3}{K_2[A]} = K'[A]^2$$

So unit is M^{-1} s^{-1}

49.



Two curves are given in the graph at two different temperatures. If total area under both curve is same. The correct relation between T_1 and T_2

(1) $T_1 > T_2$ (2) $T_1 = T_2$ (3) $T_1 < T_2$ (4) $T_1 = 3T_2$ always

Sol. Answer (3)

Fact

50. For a reaction, rate constant is 0.693 s^{-1} at temperature 27°. If activation energy of this reaction is 2.303 × 600 R, then calculate half life (approx.) of this reaction at temperature 327°C [Assume no change in concentration due to change in temperature]

(1) 0.1 s (2) 1 s (3) 10 s (4) 100 s

Sol. Answer (1)

Arrhenius equation, $\log\left(\frac{k_2}{k_1}\right) = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$

$\log\left(\frac{k_2}{k_1}\right) = 1, k_2 = 10k_1$

$\Rightarrow k_2 = 6.93 \text{ sec}^{-1}$

$t_{1/2} = \frac{0.693}{6.93 \text{ sec}^{-1}} = 0.1 \text{ second}$

51. For which reaction half life of reaction is independent on initial concentration of reactant?

(1) Zero order (2) 1st order (3) 2nd order (4) 3rd order

Sol. Answer (2)

Fact

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