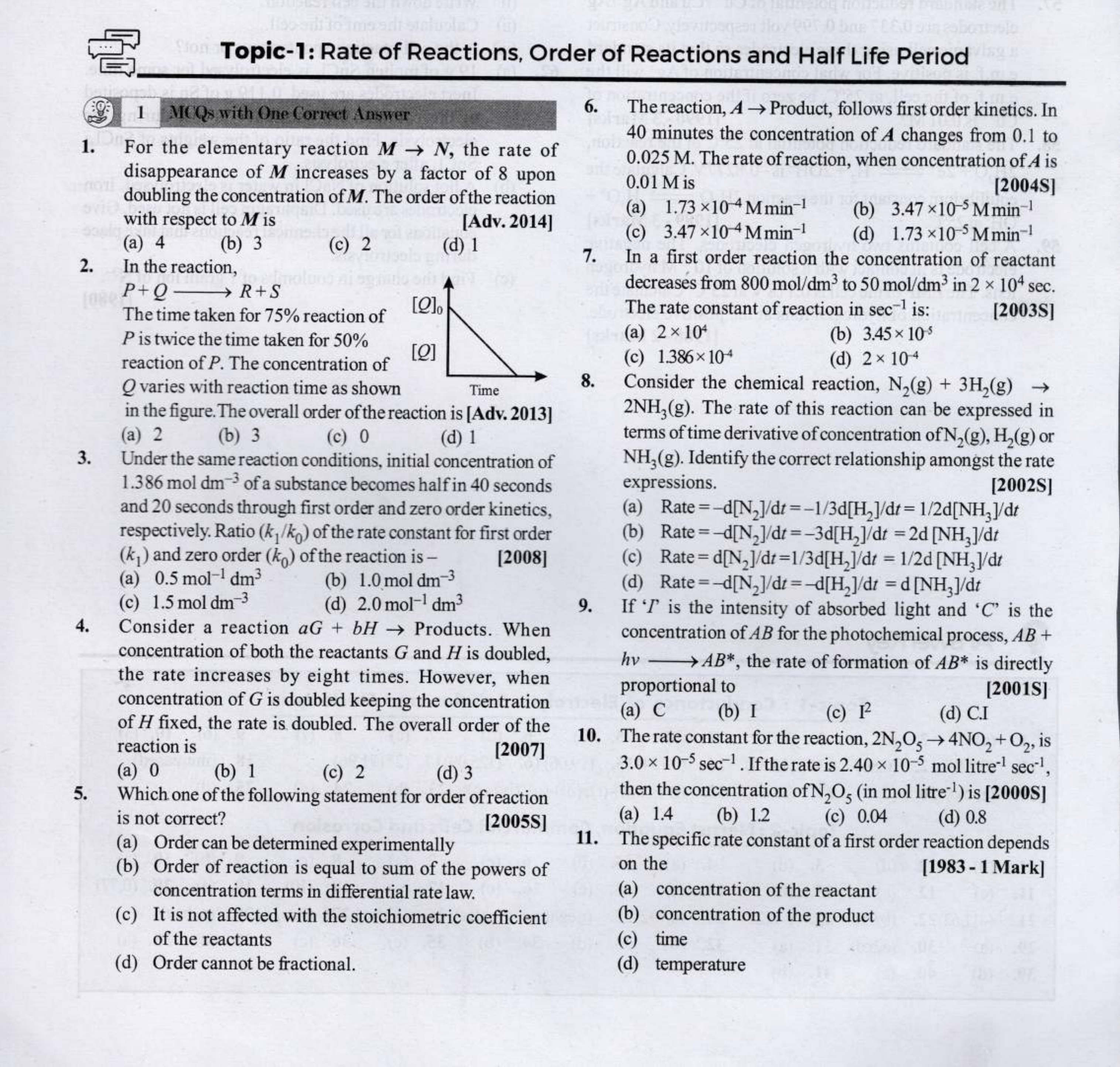
Chapter - Chemical Kinetics and Nuclear Chemistry



Topic-1: Rate of Reactions, Order of Reactions and Half Life Period

1 MCQs with One Correct Answer

1. For the elementary reaction $M \rightarrow N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is **[Adv. 2014]**

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

2. In the reaction,

$P + Q \longrightarrow R + S$

The time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is **[Adv. 2013]**

(a) 2 (b) 3 (c) 0 (d) 1

3. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio (k_1/k_0) of the rate constant for first order (k_1) and zero order (k_0) of the reaction is – **[2008]**

(a) 0.5 $mol^{-1}\,dm^3$ (b) 1.0 mol dm^{-3}
(c) 1.5 mol dm^{-3} (d) 2.0 $mol^{-1}\,dm^3$

4. Consider a reaction $aG + bH \rightarrow$ Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is **[2007]**

(a) 0 (b) 1 (c) 2 (d) 3

5. Which one of the following statement for order of reaction is not correct? **[2005S]**

(a) Order can be determined experimentally
(b) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.
(c) It is not affected with the stoichiometric coefficient of the reactants
(d) Order cannot be fractional.

6. The reaction, $A \rightarrow$ Product, follows first order kinetics. In 40 minutes the concentration of A changes from 0.1 to 0.025 M. The rate of reaction, when concentration of A is 0.01 M is **[2004S]**

(a) $1.73 \times 10^{-4}\,M\,min^{-1}$ (b) $3.47 \times 10^{-5}\,M\,min^{-1}$
(c) $3.47 \times 10^{-4}\,M\,min^{-1}$ (d) $1.73 \times 10^{-5}\,M\,min^{-1}$

7. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant of reaction in sec^{-1} is: **[2003S]**

(a) 2×10^4 (b) 3.45×10^{-5}
(c) 1.386×10^{-4} (d) 2×10^{-4}

8. Consider the chemical reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions. **[2002S]**

(a) Rate $= -d[N_2]/dt = -1/3\,d[H_2]/dt = 1/2\,d[NH_3]/dt$
(b) Rate $= -d[N_2]/dt = -3d[H_2]/dt = 2d\,[NH_3]/dt$
(c) Rate $= d[N_2]/dt = 1/3\,d[H_2]/dt = 1/2\,d\,[NH_3]/dt$
(d) Rate $= -d[N_2]/dt = -d[H_2]/dt = d\,[NH_3]/dt$

9. If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photochemical process, $AB + h\nu \longrightarrow AB^*$, the rate of formation of AB^* is directly proportional to **[2001S]**

(a) C (b) I (c) I^2 (d) C.I

10. The rate constant for the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, is $3.0 \times 10^{-5}\,sec^{-1}$. If the rate is 2.40×10^{-5} mol $litre^{-1}\,sec^{-1}$, then the concentration of N_2O_5 (in mol $litre^{-1}$) is **[2000S]**

(a) 1.4 (b) 1.2 (c) 0.04 (d) 0.8

11. The specific rate constant of a first order reaction depends on the **[1983 - 1 Mark]**

(a) concentration of the reactant
(b) concentration of the product
(c) time
(d) temperature

12. The rate constant of a reaction depends on
(a) temperature **[1981 - 1 Mark]**
(b) initial concentration of the reactants
(c) time of reaction
(d) extent of reaction

2 Integer Value Answer

13. A sample initially contains only U-238 isotope of uranium. With time, some of the U-238 radioactively decays into Pb-206 while the rest of it remains undisintegrated. **[Adv. 2024]**

When the age of the sample is P × 10^8 years, the ratio of mass of Pb-206 to that of U-238 in the sample is found to be 7. The value of P is ______.

[Given: Half-life of U-238 is 4.5×10^9 years; $\log_e 2 = 0.693$]

14. Consider the following reaction,

$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

which follows the mechanism given below: **[Adv. 2024]**

$$2NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g) \quad \text{(fast equilibrium)}$$

$$N_2O_2(g) + H_2(g) \xrightarrow{k_2} N_2O(g) + H_2O(g) \quad \text{(slow reaction)}$$

$$N_2O(g) + H_2(g) \xrightarrow{k_3} N_2(g) + H_2O(g) \quad \text{(fast reaction)}$$

The order of the reaction is ______

15. In dilute aqueous H_2SO_4, the complex diaquodioxalatoferrate(II) is oxidized by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is **[Adv. 2015]**

16. An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\left[\frac{t_{1/8}}{t_{1/10}}\right] \times 10$?

($\log_{10} 2 = 0.3$) **[2012]**

17. The concentration of R in the reaction $R \rightarrow P$ was measured as a function of time and the following data is obtained:

[R] (molar)	1.0	0.75	0.40	0.10
t(min.)	0.0	0.05	0.12	0.18

The order of reaction is **[2010]**

3 Numeric / New Stem Based Questions

18. Consider the kinetic data given in the following table for the reaction $A + B + C \rightarrow$ product. **[Adv. 2019]**

Experiment No.	[A] (mol dm^{-3})	[B] (mol dm^{-3})	[C] (mol dm^{-3})	Rate of reaction (mol dm^{-3})
1	0.2	0.1	0.1	6.0×10^{-5}
2	0.2	0.2	0.1	6.0×10^{-5}
3	0.2	0.1	0.2	1.2×10^{-4}
4	0.3	0.1	0.1	9.0×10^{-5}

The rate of the reaction for $[A] = 0.15$ mol dm^{-3}, $[B] = 0.25$ mol dm^{-3} and $[C] = 0.15$ mol dm^{-3} is found to be $Y \times 10^{-5}$ mol dm^{-3} s^{-1}. The value of Y is ______

19. The decomposition reaction

$2N_2O_5(g) \xrightarrow{\Delta} 2N_2O_4(g) + O_2(g)$ is started in a closed cylinder under isothermal isochoric condition at an initial pressure of 1 atm. After $Y \times 10^3$ s, the pressure inside the cylinder is found to be 1.45 atm. If the rate constant of the reaction is 5×10^{-4} s^{-1}, assuming ideal gas behaviour, the value of Y is __ **[Adv. 2019]**

20. The rate of a first-order reaction is 0.04 mol litre^{-1} s^{-1} at 10 minutes and 0.03 mol litre^{-1} s^{-1} at 20 minutes after initiation. Find the half-life of the reaction. **[2001 - 5 Marks]**

21. The gas phase decomposition of dimethyl ether follows first order kinetics.

$$CH_3 - O - CH_3(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minutes. Initially, only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minutes? Assume ideal gas behaviour. **[1993 - 4 Marks]**

4 Fill in the Blanks

22. For the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is 0.001 kg h^{-1}. The rate of conversion of H_2 under the same condition is .... kg h^{-1}. **[1994 - 1 Mark]**

23. The hydrolysis of ethyl acetate in .... medium is a .... order reaction. **[1986 - 1 Mark]**

24. The rate of chemical change is directly proportional to .... **[1985 - 1 Mark]**

5 True / False

25. For a first order reaction, the rate of the reaction doubles as the concentration of the reactant (s) doubles. **[1986 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

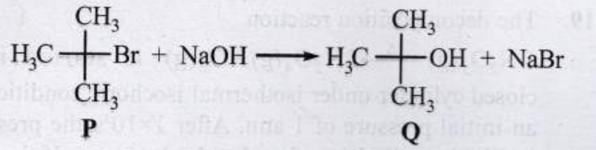
26. For the following reaction $2X + Y \xrightarrow{k} P$

the rate of reaction is $\frac{d[P]}{dt} = k[X]$. Two moles of X are mixed with one mole of Y to make 1.0 L of solution. At 50 s, 0.5 mole of Y is left in the reaction mixture. The correct statement(s) about the reaction is(are)

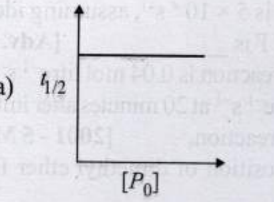
(Use: ln 2 = 0.693) **[Adv. 2021]**

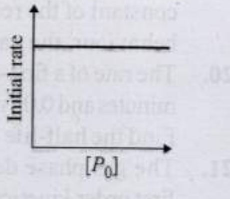
(a) The rate constant, k, of the reaction is 13.86×10^{-4} s^{-1}.
(b) Half-life of X is 50s.
(c) At 50 s, $-\frac{d[X]}{dt} = 13.86 \times 10^{-3}$ mol L^{-1}s^{-1}.
(d) At 100 s, $-\frac{d[Y]}{dt} = 3.46 \times 10^{-3}$ mol L^{-1}s^{-1}.

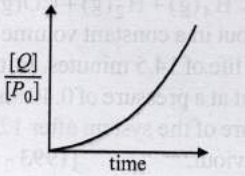
27. Which of the following plots is(are) correct for the given reaction?
($[P]_0$ is the initial concentration of **P**) **[Adv. 2020]**

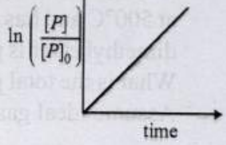

$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-Br + NaOH \longrightarrow H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH + NaBr$$

P **Q**

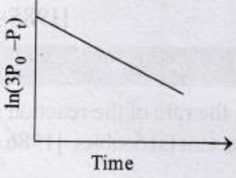
(a)


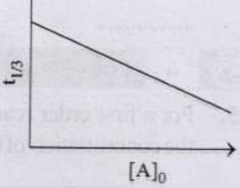
(b)


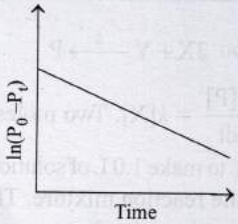
(c)


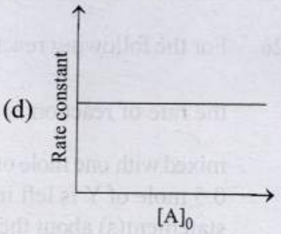
(d)


28. For a first order reaction $A(g) \rightarrow 2B(g) + C(g)$ at constant volume and 300 K, the total pressure at the beginning ($t = 0$) and at time t are P_0 and P_t, respectively. Initially, only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach 1/3rd of its initial value. The correct option(s) is (are) (Assume that all these gases behave as ideal gases) **[Adv. 2018]**

(a)


(b)


(c)


(d)


29. For the first order reaction **[2011]**

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

(a) the concentration of the reactant decreases exponentially with time

(b) the half-life of the reaction decreases with increasing temperature

(c) the half-life of the reaction depends on the initial concentration of the reactant

(d) the reaction proceeds to 99.6% completion in eight half-life duration

30. The following statement(s) is (are) correct: **[1999 - 3 Marks]**

(a) A plot of $\log K_p$ versus $1/T$ is linear

(b) A plot of $\log [X]$ versus time is linear for a first order reaction, $X \rightarrow P$

(c) A plot of P versus $1/T$ is linear at constant volume

(d) A plot of P versus $1/V$ is linear at constant temperature

31. For a first order reaction, **[1998 - 2 Marks]**

(a) the degree of dissociation is equal to $(1-e^{-kt})$

(b) a plot of reciprocal concentration of the reactant vs. time gives a straight line.

(c) the time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction

(d) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}

32. The rate law for the reaction : **[1988 - 1 Mark]**

$$RCl + NaOH(aq.) \rightarrow ROH + NaCl$$

is given by, Rate = k_1 [RCl]. The rate of the reaction will be

(a) doubled on doubling the concentration of sodium hydroxide.

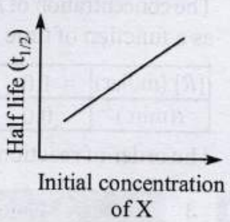
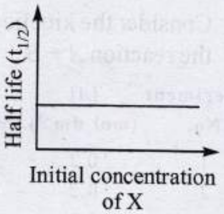
(b) halved on reducing the concentration of alkyl halide to one half.

(c) increased on increasing the temperature of the reaction.

(d) unaffected by increasing the temperature of the reaction.

7 Match the Following

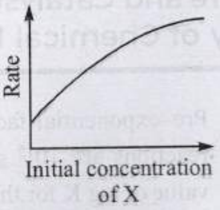
33. Match the rate expressions in LIST-I for the decomposition of X with the corresponding profiles provided in LIST-II. Xs and k are constants having appropriate units. **[Adv. 2022]**

LIST-I	LIST-II
(I) rate = $\frac{k[X]}{X_s + [X]}$ under all possible initial concentrations of X	(P) 
(II) rate = $\frac{k[X]}{X_s + [X]}$ where initial concentrations of X are much less than X_s.	(Q) 

(III) rate $= \dfrac{k[X]}{X_s + [X]}$

where initial concentrations of X are much higher than X_s.

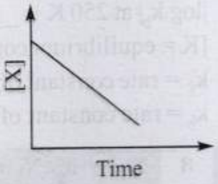
(R)



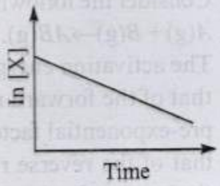
(IV) rate $= \dfrac{k[X]^2}{X_s + [X]}$

where initial concentration of X are much higher than X_s.

(S)



(T)



(a) I → P; II → Q; III → S; IV → T
(b) I → R; II → S; III → S; IV → T
(c) I → P; II → Q; III → Q; IV → R
(d) I → R; II → S; III → Q; IV → R

10 Subjective Problems

34. At constant temperature and volume, X decomposes as **[2005 - 4 Marks]**

$2X(g) \longrightarrow 3Y(g) + 2Z(g)$; P_X is the partial pressure of X.

Observation No.	Time (in minute)	P_X (in mm of Hg)
1	0	800
2	100	400
3	200	200

(i) What is the order of reaction with respect to X?
(ii) Find the rate constant.
(iii) Find the time for 75% completion of the reaction.
(iv) Find the total pressure when pressure of X is 700 mm of Hg.

35. For the given reactions, $A + B \rightarrow$ Products, following data were obtained. **[2004 - 2 Marks]**

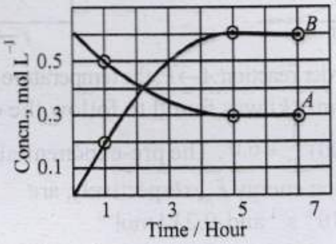
	$[A_0]$	$[B_0]$	R_0 (mol L^{-1} s^{-1})
1.	0.1	0.2	0.05
2.	0.2	0.2	0.10
3.	0.1	0.1	0.05

(a) Write the rate law expression
(b) Find the rate constant

36. The vapour pressure of the two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask, 10 moles of (A) is mixed with 12 moles of (B). However, as soon as (B) is added, (A) starts polymerizing into a completely insoluble solid. The polymerization follows first-order kinetics. After 100 minutes, 0.525 mole of a solute is dissolved which arrests the polymerization completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate of constant of the polymerization reaction. Assume negligible volume change on mixing and polymerization and ideal behaviour for the final solution. **[2001 - 10 Marks]**

37. The rate constant for an isomerisation reaction, $A \rightarrow B$ is 4.5×10^{-3} min^{-1}. If the initial concentration of A is 1 M, calculate the rate of the reaction after 1 h. **[1999 - 4 Marks]**

38. The progress of the reaction, $A \rightleftharpoons nB$, with time, is presented in figure given below. Determine



(i) the value of n
(ii) the equilibrium constant, K and
(iii) the initial rate of conversion of A. **[1994 - 3 Marks]**

39. The decomposition of N_2O_5 according to the equation :
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ **[1991 - 6 Marks]**
is a first order reaction. After 30 min. from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.

40. A first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed in the product? What is the half life of this reaction? **[1987 - 5 Marks]**

41. While studying the decomposition of gaseous N_2O_5, it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameters can be obtained from this observation? **[1985 - 2 Marks]**

42. Rate of a reaction $A + B \rightarrow$ products, is given below as a function of different initial concentrations of A and B : **[1982 - 4 Marks]**

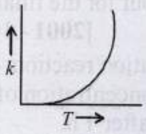
$[A]$ (mol/l)	$[B]$ (mol/l)	Initial rate (mol/l/min)
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

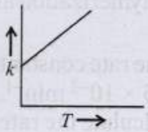
Determine the order of the reaction with respect to A and with respect to B. What is the half-life of A in the reaction?

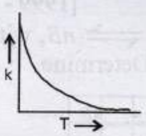
Topic-2: Effect of Temperature and Catalyst on Rate of Reactions, Collosion Theory of Chemical Reactions

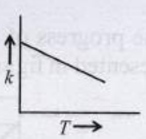
1 MCQs with One Correct Answer

1. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is **[2010]**

(a)


(b)


(c)


(d)


2. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation $\log k = -(2000)\frac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a, respectively, are **[2009]**

(a) $1.0 \times 10^6\ s^{-1}$ and $9.2\ kJ\ mol^{-1}$
(b) $6.0\ s^{-1}$ and $16.6\ kJ\ mol^{-1}$
(c) $1.0 \times 10^6\ s^{-1}$ and $16.6\ kJ\ mol^{-1}$
(d) $1.0 \times 10^6\ s^{-1}$ and $38.3\ kJ\ mol^{-1}$

3. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} s^{-1}$, $104.4\ kJ\ mol^{-1}$ and $6.0 \times 10^{14}\ s^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is, **[1996 - 1 Mark]**

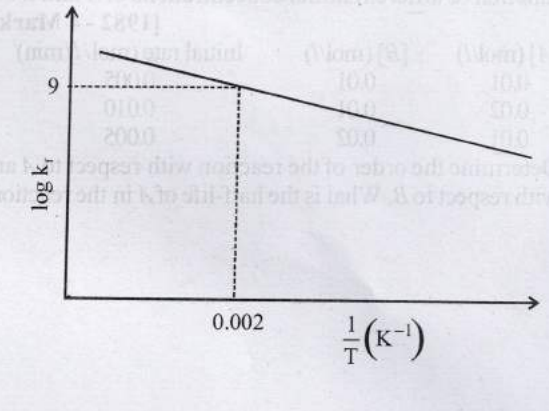
(a) $2.0 \times 10^{18}\ s^{-1}$
(b) $6.0 \times 10^{14}\ s^{-1}$
(c) infinity
(d) $3.6 \times 10^{30}\ s^{-1}$

4. A catalyst is a substance which **[1983 - 1 Mark]**

(a) increases the equilibrium concentration of the product
(b) changes the equilibrium constant of the reaction
(c) shortens the time to reach equilibrium
(d) supplies energy to the reaction

2 Integer Value Answer

5. The plot of $\log k_f$ versus $1/T$ for a reversible reaction $A(g) \rightleftharpoons P(g)$ is shown. **[Adv. 2023]**



Pre–exponential factors for the forward and backward reactions are $10^{15}\ s^{-1}$ and $10^{11}\ s^{-1}$, respectively. If the value of log K for the reaction at 500 K is 6, the value of $|\log k_b|$ at 250 K is ______.
[K = equilibrium constant of the reaction
k_f = rate constant of forward reaction
k_b = rate constant of backward reaction]

3 Numeric / New Stem Based Questions

6. Consider the following reversible reaction,
$A(g) + B(g) \rightarrow AB(g)$.
The activation energy of the backward reaction exceeds that of the forward reaction by $2RT$ (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of $\Delta G°$ (in J mol^{-1}) for the reaction at 300 K is ______.
(Given; $\ln(2) = 0.7$, $RT = 2500$ J mol^{-1} at 300 K and G is the Gibbs energy) **[Adv. 2018]**

7. A hydrogenation reaction is carried out at 500 K. If same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1}. **[2000 - 3 Marks]**

8. At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C. **[1995 - 4 Marks]**

9. In the Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are 4×10^{13} sec^{-1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life period be ten minutes? **[1990 - 3 Marks]**

4 Fill in the Blanks

10. In the Arrhenius equation, $k = A \exp(-E_a/RT)$, A may be termed as the rate constant at .... **[1997 - 1 Mark]**

5 True / False

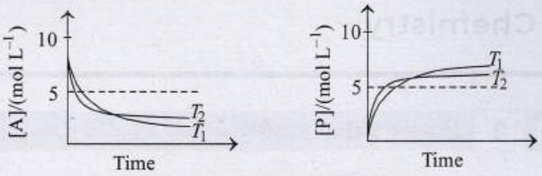
11. The rate of an exothermic reaction increases with increasing temperature. **[1990 - 1 Mark]**

12. Catalyst does not affect the energy of activation in a chemical reaction. **[1989 - 1 Mark]**

13. Catalyst makes a reaction more exothermic. **[1987 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

14. For a reaction, $A \rightleftharpoons P$, the plots of $[A]$ and $[P]$ with time at temperatures T_1 and T_2 are given below. **[Adv. 2018]**



If $T_2 > T_1$, the correct statement(s) is (are)
(Assume ΔH° and ΔS° are independent of temperature and ratio of $\ln K$ at T_1 to $\ln K$ at T_2 is greater than $\frac{T_2}{T_1}$. Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

(a) $\Delta H^\circ < 0, \Delta S^\circ < 0$ (b) $\Delta G^\circ < 0, \Delta H^\circ > 0$
(c) $\Delta G^\circ < 0, \Delta S^\circ < 0$ (d) $\Delta G^\circ < 0, \Delta S^\circ > 0$

15. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is(are) **[Adv. 2017]**

(a) The activation energy of the reaction is unaffected by the value of the steric factor
(b) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation
(c) Since $P = 4.5$, the reaction will not proceed unless an effective catalyst is used
(d) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

16. According to the Arrhenius equation, **[Adv. 2016]**

(a) a high activation energy usually implies a fast reaction.
(b) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy.
(c) higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant.
(d) the pre–exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

17. A catalyst : **[1984 - 1 Mark]**

(a) increases the average kinetic energy of reacting molecules
(b) decreases the activation energy
(c) alters the reaction mechanism
(d) increases the frequency of collisions of reacting species

9 Assertion and Reason Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
(c) If Statement -1 is correct but Statement -2 is incorrect.
(d) If Statement -1 is incorrect but Statement -2 is correct.

18. **Statement-1 :** For each ten degree rise of temperature the specific rate constant is nearly doubled.

Statement-2 : Energy-wise distribution of molecules in a gas is an experimental function of temperature.

[1989 - 2 Marks]

10 Subjective Problems

19. The rate constant of a reaction is $1.5 \times 10^7\ s^{-1}$ at 50°C and $4.5 \times 10^7\ s^{-1}$ at 100°C. Evaluate the Arrhenius parameters A and E_a. **[1998 - 5 Marks]**

20. The rate constant for the first order decomposition of a certain reaction is described by the equation

$$\log(k) = 14.34 - \frac{1.25 \times 10^4\,K}{T}$$ **[1997 - 5 Marks]**

(i) What is the energy of activation for this reaction?
(ii) At what temperature will its half-life period be 256 minutes?

21. From the following data for the reaction between A and B. **[1994 - 5 Marks]**

	[A], mol lit^{-1}	[B], mol lit^{-1}	Initial rate mole lit^{-1} s^{-1} at	
			300 K	320 K
I	2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
II	5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	–
III	1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	–

Calculate

(i) the order of the reaction with respect to A and with respect to B,
(ii) the rate constant at 300K
(iii) the energy of activation, and
(iv) the pre-exponential factor

22. A first order reaction $A \rightarrow B$, requires activation energy of 70kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature. **[1993 - 4 Marks]**

23. Two reactions (i) $A \rightarrow$ products, (ii) $B \rightarrow$ products, follows first order kinetics. The rate of the reaction : (*i*) is doubled when the temperature is raised from 300K to 310K. The half life for this reaction at 310K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction, (*ii*) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300K.

[1992 - 3 Marks]

24. A first order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C. Calculate the reaction rate constant at 27°C and the energy of activation of the reaction in kJ/mole. **[1988 - 3 Marks]**

Topic-3: Nuclear Chemistry

1 MCQs with One Correct Answer

1. Bombardment of aluminium by α-particle leads to its artificial disintegration in two ways, (i) and (ii) as shown. Products X, Y and Z respectively are, **[2011]**

$$\begin{tikzcd}
{}^{27}_{13}\mathrm{Al} \arrow[r, "(ii)"] \arrow[d, "(i)"'] & {}^{30}_{15}\mathrm{P}+Y \arrow[d] \\
{}^{30}_{14}\mathrm{Si}+X & {}^{30}_{14}\mathrm{Si}+Z
\end{tikzcd}$$

(a) proton, neutron, positron
(b) neutron, positron, proton
(d) proton, positron, neutron
(d) positron, proton, neutron

2. A positron is emitted from ${}^{23}_{11}\mathrm{Na}$. The ratio of the atomic mass and atomic number of the resulting nuclide is **[2007]**
(a) 22/10 (b) 22/11 (c) 23/10 (d) 23/12

3. ${}^{23}\mathrm{Na}$ is the more stable isotope of Na. Find out the process by which ${}^{24}_{11}\mathrm{Na}$ can undergo radioactive decay **[2003S]**
(a) β^- emission (b) α emission
(c) β^+ emission (d) K electron capture

4. The number of neutrons accompanying the formation of ${}^{139}_{54}\mathrm{Xe}$ and ${}^{94}_{38}\mathrm{Sr}$ from the absorption of a slow neutron by ${}^{235}_{92}\mathrm{U}$, followed by nuclear fission is, **[1999 - 2 Marks]**
(a) 0 (b) 2 (c) 1 (d) 3

5. ${}^{27}_{13}\mathrm{Al}$ is a stable isotope, ${}^{29}_{13}\mathrm{Al}$ is expected to disintegrate by **[1996 - 1 Mark]**
(a) α-emission (b) β-emission
(c) positron emission (d) proton emission

6. The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduced to : **[1986 - 1 Mark]**
(a) $\frac{1}{2}$ g (b) $\frac{1}{4}$ g (c) $\frac{1}{8}$ g (d) $\frac{1}{16}$ g

7. The radiations from a naturally occurring radioactive substance, as seen after deflection by a magnetic field in one direction, are : **[1984 - 1 Mark]**
(a) definitely alpha rays
(b) definitely beta rays
(c) both alpha and beta rays
(d) either alpha or beta rays

8. If uranium (mass number 238 and atomic number 92) emits an α-particle, the product has mass no. and atomic no. **[1981 - 1 Mark]**
(a) 236 and 92 (b) 234 and 90
(c) 238 and 90 (d) 236 and 90

2 Integer Value Answer

9. A closed vessel with rigid walls contains 1 mol of ${}^{238}_{92}\mathrm{U}$ and 1 mol of air at 298 K. Considering complete decay of ${}^{238}_{92}\mathrm{U}$ to ${}^{206}_{82}\mathrm{Pb}$, the ratio of the final pressure to the initial pressure of the system at 298 K is **[Adv. 2015]**

10. The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table? **[2012]**

$${}^{63}_{29}\mathrm{Cu}+{}^{1}_{1}\mathrm{H}\rightarrow 6\,{}^{1}_{0}n+{}^{4}_{2}\alpha+2\,{}^{1}_{1}\mathrm{H}+X$$

11. The number of neutrons emitted when ${}^{235}_{92}\mathrm{U}$ undergoes controlled nuclear fission to ${}^{142}_{54}\mathrm{Xe}$ and ${}^{90}_{38}\mathrm{Sr}$ is **[2010]**

12. The total number of α and β particles emitted in the nuclear reaction ${}^{238}_{92}\mathrm{U}\rightarrow {}^{214}_{82}\mathrm{Pb}$ is **[2009]**

3 Numeric / New Stem Based Questions

13. ${}^{238}_{92}\mathrm{U}$ is known to undergo radioactive decay to form ${}^{206}_{82}\mathrm{Pb}$ by emitting alpha and beta particles. A rock initially contained 68×10^{-6} g of ${}^{238}_{92}\mathrm{U}$. If the number of alpha particles that it would emit during its radioactive decay of ${}^{238}_{92}\mathrm{U}$ to ${}^{206}_{82}\mathrm{Pb}$ in three half-lives is $Z\times10^{18}$, then what is the value of Z? **[Adv. 2020]**

14. One of the hazards of nuclear explosion is the generation of ${}^{90}\mathrm{Sr}$ and its subsequent incorporation in bones. This nuclide has a half-life of 28.1 years. Suppose one microgram was absorbed by a new-born child, how much ${}^{90}\mathrm{Sr}$ will remain in his bones after 20 years? **[1995 - 2 Marks]**

4 Fill in the Blanks

15. A radioactive nucleus decays emitting one alpha and two beta particles; the daughter nucleus is .... of the parent. **[1989 - 1 Mark]**

16. The number of neutrons in the parent nucleus which gives ${}^{14}_{7}\mathrm{N}$ on beta emission is .... **[1985 - 1 Mark]**

17. An element ${}^{A}_{Z}M$ undergoes an α-emission followed by two successive β-emissions. The element formed is .... **[1982 - 1 Mark]**

5 True / False

18. In β-emission from a nucleus, the atomic number of the daughter element decreases by one. **[1990 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

19. In the decay sequence, **[Adv. 2019]**

$$^{238}_{92}\text{U} \xrightarrow{-x_1} {}^{234}_{90}\text{Th} \xrightarrow{-x_2}$$

$$^{234}_{91}\text{Pa} \xrightarrow{-x_2} {}^{234}\text{Z} \xrightarrow{-x_4} {}^{230}_{90}\text{Th}$$

x_1, x_2, x_3 and x_4 are particles/radiation emitted by the respective isotopes. The correct option(s) is (are)

(a) Z is an isotope of uranium
(b) x_1 will deflect towards negatively charged plate
(c) x_3 is γ-ray
(d) x_2 is β-ray

20. A plot of the number of neutrons (N) against the number of protons (P) of stable nuclei exhibits upward deviation from linearity for atomic number, $Z > 20$. For an unstable nucleus having N/P ratio less than 1, the possible mode(s) of decay is (are) **[Adv. 2016]**

(a) β^-–decay (β emission)
(b) orbital or K–electron capture
(c) neutron emission
(d) β^+–decay (positron emission)

21. In the nuclear transmutation **[Adv. 2013]**

$$^{9}_{4}\text{Be} + X \longrightarrow {}^{8}_{4}\text{Be} + Y$$

(X, Y) is (are)

(a) (γ, n) (b) (p, D) (c) (n, D) (d) (γ, p)

22. Decrease in atomic number is observed during **[1998 - 2 Marks]**

(a) alpha emission (b) beta emission
(c) positron emission (d) electron capture.

23. Nuclear reactions accompanied with emission of neutron(s) are : **[1988 - 1 Mark]**

(a) $^{27}_{13}\text{Al} + {}^{4}_{2}\text{H} \rightarrow {}^{30}_{15}\text{P}$

(b) $^{12}_{6}\text{C} + {}^{1}_{1}\text{H} \rightarrow {}^{13}_{7}\text{N}$

(c) $^{30}_{15}\text{P} \rightarrow {}^{30}_{14}\text{Si} + {}^{0}_{1}\text{e}$

(d) $^{241}_{96}\text{Am} + {}^{4}_{2}\text{He} \rightarrow {}^{244}_{97}\text{Bk} + {}^{0}_{1}\text{e}$

8 Comprehension/Passage Based Questions

Several short-lived radioactive species have been used to determine the age of wood or animal fossils. One of the most interesting substances is $_6\text{C}^{14}$ (half-life 5760 years) which is used in determining the age of carbon-bearing materials (*e.g.* wood, animal fossils, *etc.*). Carbon-14 is produced by the bombardment of nitrogen atoms present in the upper atmosphere with neutrons (from cosmic rays).

$$_7\text{N}^{14} + {}_0\text{n}^1 \longrightarrow {}_6\text{C}^{14} + {}_1\text{H}^1$$

Thus carbon-14 is oxidised to CO_2 and eventually ingested by plants and animals. The death of plants or animals put an end to the intake of C^{14} from the atmosphere. After this the amount of C^{14} in the dead tissues starts decreasing due to its disintegration as per the following reaction :

$$_6\text{C}^{14} \longrightarrow {}_7\text{N}^{14} + {}_{-1}\beta^0$$

The C^{14} isotope enters the biosphere when carbon dioxide is taken up in plant photosynthesis. Plants are eaten by animals, which exhale C^{14} as CO_2. Eventually, C^{14} participates in many aspects of the carbon cycle. The C^{14} lost by radioactive decay is constantly replenished by the production of new isotopes in the atmosphere. In this decay-replenishment process, a dynamic equilibrium is established whereby the ratio of C^{14} to C^{12} remains constant in living matter. But when an individual plant or an animal dies, the C^{14} isotope in it is no longer replenished, so the ratio decreases as C^{14} decays. So, the number of C^{14} nuclei after time *t* (after the death of living matter) would be less than in a living matter. The decay constant can be calculated using the following formula,

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

The intensity of the cosmic rays have remain the same for 30,000 years. But since some years the changes in this are observed due to excessive burning of fossil fuel and nuclear tests.

24. Why do we use the carbon dating to calculate the age of the fossil? **[2006 - 5M, –2]**

(a) Rate of exchange of carbon between atmosphere and living is slower than decay of C^{14}
(b) It is not appropriate to use C^{14} dating to determine age
(c) Rate of exchange of C^{14} between atmosphere and living organism is so fast that an equilibrium is set up between the intake of C^{14} by organism and its exponential decay
(d) none of the above

25. What should be the age of the fossil for meaningful determination of its age? **[2006 - 5M, –2]**

(a) 6 years
(b) 6000 years
(c) 60,000 years
(d) can be used to calculate any age

26. A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the respective places then **[2006 - 5M, –2]**

(a) The age of the fossil will increase at the place where explosion has taken place and $T_1 - T_2 = \frac{1}{\lambda}\ln\frac{C_1}{C_2}$
(b) The age of the fossil will decrease at the place where explosion has taken place and $T_1 - T_2 = \frac{1}{\lambda}\ln\frac{C_1}{C_2}$
(c) The age of fossil will be determined to be same
(d) $\frac{T_1}{T_2} = \frac{C_1}{C_2}$

9 Assertion and Reason/Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason).** Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.

(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.

(c) If Statement -1 is correct but Statement -2 is incorrect.

(d) If Statement -1 is incorrect but Statement -2 is correct.

27. **Statement-1 :** The plot of atomic number (y-axis) versus number of neutrons (x-axis) for stable nuclei shows a curvature towards x-axis from the line of 45° slope as the atomic number is increased.

Statement-2 : Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides. **[2008]**

28. **Assertion :** Nuclide $^{30}_{13}$Al is less stable than $^{40}_{20}$Ca **[1998 - 2 Marks]**

Reason : Nuclides having odd number of protons and neutrons are generally unstable.

10 Subjective Problems

29. Complete and balance the following reactions.

(*i*) $_{92}Th^{234} \longrightarrow .... + 7\ _2He^4 + 6\ _{-1}\beta^0$ **[2004 - 1 Mark]**

(*ii*) $_{92}U^{235} + {_0}n^1 \longrightarrow .... + {_{52}}Te^{137} + {_{40}}Zr^{92}$ **[2005 - 1 Mark]**

(*iii*) $_{34}Se^{86} \longrightarrow 2\ _{-1}e^0 + ...$ **[2005 - 1 Mark]**

30. ^{64}Cu (half-life = 12.8 h) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes. **[2002 - 5 Marks]**

31. $^{238}_{92}$U is radioactive and it emits α and β particles to form $^{206}_{82}$Pb. Calculate the number of α and β particles emitted in this conversion. An ore of $^{238}_{92}$U is found to contain $^{238}_{92}$U and $^{206}_{82}$Pb in the weight ratio of 1:0.1. The half-life period of $^{238}_{92}$U is 4.5×10^9 years. Calculate the age of the ore. **[2000 - 5 Marks]**

32. Write a balanced equation for the reaction of ^{14}N with α-particle. **[1997 - 1 Mark]**

33. ^{227}Ac has a half-life of 21.8 years with respect to radioactive decay. The decay follows two parallel paths, one leading to ^{227}Th and the other to ^{223}Fr. The percentage yields of these two daughter nuclides are 1.2 and 98.8 respectively. What are the decay constants (λ) for each of the separate paths? **[1996 - 2 Marks]**

34. The nucleidic ratio, $^3_1$H to $^1_1$H in a sample of water is 8.0×10^{-18} : 1. Tritium undergoes decay with a half life period of 12.3 years. How many tritium atoms would 10.0 g of such a sample contain 40 years after the original sample is collected? **[1992 - 4 Marks]**

35. An experiment requires minimum beta activity product at the rate of 346 beta particles per minute. The half life period of $^{99}_{42}$Mo, which is a beta emitter is 66.6 hours. Find the minimum amount of $^{99}_{42}$Mo required to carry out the experiment in 6.909 hours. **[1989 - 5 Marks]**

36. $^{234}_{90}$Th disintegrates to give $^{206}_{82}$Pb as the final product. How many alpha and beta particles are emitted during this process? **[1986 - 2 Marks]**

37. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half life of 5770 years. What is the rate constant (in years^{-1}) for the decay? What fraction would remain after 11540 years? **[1984 - 3 Marks]**

Answer Key

Topic-1 : Rate of Reactions, Order of Reactions and Half Life Period

1. (b) **2.** (d) **3.** (a) **4.** (d) **5.** (d) **6.** (c) **7.** (c) **8.** (a) **9.** (b) **10.** (d)
11. (d) **12.** (a) **13.** (143) **14.** (3) **15.** (8) **16.** (9) **17.** (0) **18.** (6.75) **19.** (2.30) **20.** (24.14)
21. (0.749) **22.** (1.765×10^4kg/hr) **23.** (acidic, pseudo first)
24. (Product of active masses of reactants at that time) **25.** (True) **26.** (b, c, d) **27.** (a) **28.** (a, d)
29. (a,b,d) **30.** (a,b,d) **31.** (a, d) **32.** (b, c) **33.** (a)

Topic-2 : Effect of Temperature and Catalyst on Rate of Reactions, Collosion Theory of Chemical Reactions

1. (a) **2.** (d) **3.** (b) **4.** (c) **5.** (5) **6.** (–8500) **7.** (100) **8.** (20.34) **9.** (311.35)
10. (Very high temperature) **11.** (True) **12.** (False) **13.** (False) **14.** (a, c) **15.** (a, b)
16. (b,c,d) **17.** (b, c) **18.** (a)

Topic-3 : Nuclear Chemistry

1. (a) **2.** (c) **3.** (a) **4.** (d) **5.** (b) **6.** (d) **7.** (d) **8.** (b) **9.** (9) **10.** (8)
11. (3) **12.** (8) **13.** (1.20) **14.** (0.061) **15.** (Isotope) **16.** (8) **17.** ($^{A-4}_{Z}M$) **18.** (False)
19. (a,b,d) **20.** (b,d) **21.** (a,b) **22.** (a,c,d) **23.** (a,d) **24.** (c) **25.** (b) **26.** (a) **27.** (a) **28.** (c)

Hints & Solutions

Topic-1: Rate of Reactions, Order of Reactions and Half Life Period

1. **(b)** $M \rightarrow N$
$r = k[M]^x$
when concentration $= 2M$; rate $= 8r$, thus
$8r = k[2M]^x$
$8 = (2)^x$
$x = 3$

2. **(d)** For P, if $t_{50\%} = x$ then $t_{75\%} = 2x$
This is true only for first order reaction.
So, order with respect to P is 1.
Further, the graph shows that concentration of Q decreases with time. So, rate with respect to Q, remains constant. Hence, it is zero order wrt Q.
So, overall order is $1 + 0 = 1$

3. **(a)** The values of rate constants k_0, k_1 for zero order and first order reaction, respectively, are given by the following equation:

$$k_0 = \frac{A_{rs}}{2 \times t_{1/2}}$$ [where A_{rs} = initial concentration, and $t_{1/2}$ = half-life period]

and $k_1 = \dfrac{0.693}{t_{1/2}}$

substituting various given values, we get

$$k_0 = \frac{1.386\ \text{mol litre}^{-1}}{2 \times 20\ \text{sec}} \quad \text{... (i)}$$

and $$k_1 = \frac{0.693}{40\ \text{sec}} \quad \text{... (ii)}$$

Dividing (ii) by (i), we get

$$\frac{k_1}{k_0} = \frac{0.693}{40} \times \frac{2 \times 20}{1.386}\ \text{mol}^{-1}\ \text{litre}$$

$$= \frac{0.693}{1.386}\ \text{mol}^{-1}\ \text{litre} = 0.5\ \text{mol}^{-1}\ \text{litre}$$

$= 0.5\ \text{mol}^{-1}\ \text{dm}^3$ [1 litre $= 1\text{dm}^3$]

Thus, the correct answer is (a).

4. **(d)** Overall order = sum of orders w.r.t each reactant.
Let the order be x and y for G and H respectively

Exp.No.	$[G]$mole litre^{-1}	$[H]$mole litre^{-1}	rate (mole litre^{-}time^{-1})
1	a	b	r
2	$2a$	$2b$	$8r$
3	$2a$	b	$2r$

Applying $r = k[G]^x[H]^y$ we get, $x = 1, y = 2$
$\because$ For (1) and (3), the rate is doubled when conc. of G is doubled keeping that of H constant *i.e.*, rate $\propto [G]$ $\therefore x = 1$
From (2) and (3), $y = 2$ $\therefore$ Overall order is 3.

5. **(d)** Order of a reaction can be fractional. Rest of all are true.
Order of a reaction can be determined experimentally

6. **(c)** For first order reaction,
Rate $= k$ [conc. of reactant]
Since 0.1 M of A changes to 0.025 M in 40 minutes,
$t_{1/2}$ of reaction $= 40/2 = 20$ minutes

$$\text{Rate of reaction of } A = k[A] = \frac{0.693}{t_{1/2}} \times [A] = \frac{0.693}{20} \times 0.01$$
$= 3.47 \times 10^{-4}\ \text{M min}^{-1}$

7. **(c)** $$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$$

$$\therefore\ k = \frac{2.303}{2 \times 10^4}\log\frac{800}{50} = 1.386 \times 10^{-4}\text{s}^{-1}$$

8. **(a)** Individual rates of reactants and products become equal when each of these is divided by their respective stoichiometric coefficient. With time, concentration of reactants decreases and is represented by negative sign whereas concentration of products increases and is represented by positive sign.
The given reaction is

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$\therefore$ Correct relationship amongst the rate expression is shown in (a).

9. **(b)** The rate of photochemical process varies with the intensity of absorption.
Since, greater the intensity of absorbed light, more photons will fall at a point, and further, each photon causes one molecule to undergo reaction.

10. **(d)** Find the order of reaction and then use appropriate equation.
As unit of k is sec^{-1}, reaction is of **first order**,

$$r = k[N_2O_5];\ \therefore\ [N_2O_5] = \frac{2.4 \times 10^{-5}}{3 \times 10^{-5}} = 0.8\ \text{mol/L}$$

11. **(d)** It is a characteristic constant of a particular reaction at a given temperature. It does not depend upon initial concentration of the reactants, time of reaction and extent of reaction.

12. **(a)** It is a constant of a particular reaction at a given temperature. It does not depend upon initial concentration of the reactants, time of reaction and extent of reaction.

13. (143) Life of sample → t year

$[A]_0 \propto$ Initial mole of U-238

$[A]_t \propto$ Final mole of U-238

$$\frac{[A]_0}{[A]_t} = \frac{\frac{1}{238}+\frac{7}{206}}{\frac{1}{238}}$$

$$= \frac{0.0042+0.0340}{0.0042}$$

$$= 9.1$$

$$\Rightarrow \frac{2.303}{t}\log\frac{[A]_0}{[A]_t} = \frac{2.303}{t}\log(9.1) = k$$

$$\text{Now, } k = \frac{\ln^2}{t_{1/2}} = \frac{0.693}{4.5\times10^9} = 1.54\times10^{-10}$$

$$\Rightarrow \frac{2.303}{t}\log(9.1) = 1.54\times10^{-10}$$

$$\Rightarrow t = 1.434\times10^{10} = 143\times10^8 \text{ years} \Rightarrow P = 143$$

14. (3) Rate of reaction is determined by slowest step as:

$$\Rightarrow r = k_2[N_2O_2][H_2] \qquad ...(1)$$

Now concentration for intermediate $[N_2O_2]$ can be written as:

$$\frac{k_1}{k_{-1}} = \frac{[N_2O_2]}{[NO]^2}$$

$$\Rightarrow [N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2 \qquad ...(2)$$

From equation (1) and (2) we get,

$$r = \frac{k_2k_1}{k_{-1}}[NO]^2[H_2]$$

Overall order of reaction = 2 + 1 + 3

15. (8) $8H^+ + 5[Fe(H_2O)_2(Ox)_2]^{2-} + MnO_4^- \rightarrow Mn^{2+} + 5[Fe(H_2O)_2(Ox)_2]^- + 4H_2O$

$$\text{Rate} = \frac{1}{8}\frac{d[H^+]}{dt} = \frac{d[MnO_4^-]}{dt}$$

$$\text{Hence, } \frac{\text{rate of } [H^+] \text{decay}}{\text{rate of } [MnO_4^-] \text{ decay}} = 8$$

16. (9) $t_{1/8} = \frac{2.303\log 8}{k} = \frac{2.303\times3\log 2}{k}$

$$t_{1/10} = \frac{2.303}{k}\log 10 = \frac{2.303}{k}$$

$$\left[\frac{t_{1/8}}{t_{1/10}}\right]\times10 = \frac{\left(\frac{2.303\times3\log 2}{k}\right)}{\left(\frac{2.303}{k}\right)}\times10 = 9$$

17. (0)

Δx	$1-0.75$	$1-0.4$	$1-0.1$
Δt	0.05	0.12	0.18
$\frac{\Delta x}{\Delta t}$	5	5	5

Since, rate = $\Delta x/\Delta t$ is constant for different concentration values, order of reaction is zero.

18. (6.75)

Rate of the reaction = $K[A]^x[B]^y[C]^z$

Compairing experiment 1 with 2 we get that, $y = 0$

Compairing experiment 1 with 3 we get that, $z = 1$

Compairing experiment 1 with 4 we get that, $x = 1$

putting values of x, y, z in rate equation for experiment 1.

$6\times10^{-5} = K\times(0.2)^1\times(0.1)^1\times(0.1)^0$

$K = 3\times10^{-3}$

Now, for the given concentration of A, B and C, rate of reaction will be,

Rate = $3\times10^{-3}\times0.15\times1\times0.15 = 6.75\times10^{-5}$

Therefore, value of Y = 6.75.

19. (2.30) $2N_2O_5(g) \xrightarrow{\Delta} 2N_2O_4(g) + O_2(g)$

Given rate constant of the reaction = $5\times10^{-4}\text{sec}^{-1}$

Thus, it is a first order reaction.

$$\frac{1}{2}\frac{dP_{N_2O_5}}{dt} = K_{\text{overall}}P_{N_2O_5}$$

$$\Rightarrow \frac{dP_{N_2O_5}}{dt} = 2K_{\text{overall}}P_{N_2O_5}$$

$$\begin{array}{lll} 2N_2O_5(g) \rightarrow & 2N_2O_4(g) + & O_2(g) \\ 1-x & x & x/2 \end{array}$$

$t = Y\times10^3$ sec.

$$1+\frac{x}{2} = 1.45$$

$x = 0.90$ atm

For a first order reaction,

$$t = \frac{2.303}{K}\log\frac{[P]_o}{[P]}$$

$$t = \frac{2.303}{2K}\log\frac{[P]_o}{[P]}$$

$$Y\times10^3 = \frac{2.303}{2\times5\times10^{-4}}\log\frac{1}{0.1}$$

$$Y = \frac{23.03}{10} = 2.30$$

20. (24.14)

$r_1 = kc_1$ and $r_2 = kc_2$

Since, rate of first order reaction is directly proportional to the concentration of its reactant,

$$\therefore \frac{r_1}{r_2} = \frac{c_1}{c_2} = \frac{0.04}{0.03}$$

According to first order reaction

$$k = \frac{2.303}{t_{20} - t_{10}} \log \frac{c_1}{c_2}$$

On substituting the various values

$k = 0.0287\ \text{min}^{-1}$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287} = 24.14\ \text{min}$$

21. (0.749)

$CH_3-O-CH_3(g) \rightarrow CH_4(g) + CO(g) + H_2(g)$

Given $t_{1/2} = 14.5$ min, initial pressure $= 0.40$ atm, $t = 12$ min.

$$\text{Now, } k = \frac{0.693}{14.5} = 4.78 \times 10^{-2}\ \text{min}^{-1}$$

Writing first order equation and substituting the given values, we get

$$4.78 \times 10^{-2} = \frac{2.303}{12\ \text{min.}} \log \frac{0.4}{0.4 - x}$$

which gives $x = 0.175$ atm

Since, volume and temp. are constant, final pressure :

$$\begin{array}{cccc} CH_3-O-CH_3(g) & \rightarrow CH_4(g) & + CO(g) & + H_2(g) \\ 0.4 & & & \\ 0.4 - 0.175 & 0.175 & 0.175 & 0.175 \end{array}$$

Hence, total pressure $= 0.4 - 0.175 + 3 \times 0.175 = 0.749$ atm

22. 1.765×10^{-4} kg/hr;

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

Rate of reaction $= \frac{1}{3}$ [Rate of disappearance of H_2] $= \frac{1}{2}$ [Rate of appearance of NH_3]

$$\text{or} \quad \frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt} \Rightarrow \frac{d[H_2]}{dt} = \frac{3}{2}\frac{d[NH_3]}{dt}$$

$$\frac{d[NH_3]}{dt} = 0.01\ \text{kg/hr} = \frac{0.001}{17} \times 1000 = \frac{1}{17}\ \text{mole/hr}$$

$$\therefore \frac{d[H_2]}{dt} = \frac{1}{17} \times \frac{3}{2} = \frac{3}{34}\ \text{mole/hr} = \frac{3}{34} \times \frac{2}{1000}\ \text{kg/hr}$$

$$= \mathbf{1.765 \times 10^{-4}\ kg/hr.}$$

23. acidic, Pseudo first

24. Product of active masses of reactants at that time

25. True : The rate of reaction of first order is directly proportional to the concentration of reacting substance.

26. (b,c, d) Rate $= \frac{dP}{dt} = k[X]^1$

$2X + Y \rightarrow P$

$$\begin{array}{llll} t = 0 & 2\ \text{mol} & 1\ \text{mol} & \\ t = 50\text{s} & 1\ \text{mol} & 0.5\ \text{mol} & 0.5\ \text{mol} \end{array}$$

$$-\frac{1}{2}\frac{d[X]}{dt} = \frac{d[P]}{dt} = k[X]^1$$

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

$$2k = \frac{\ln 2}{50} \quad \Rightarrow \quad k = \frac{\ln 2}{100} = 6.93 \times 10^{-3}\ \text{s}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{2k} = \frac{\ln 2 \times 50}{\ln 2} = 50\ \text{sec}$$

$$\text{At 50 sec } \frac{-d[X]}{dt} = 2k \times (1)^1 = \frac{\ln 2}{50}$$

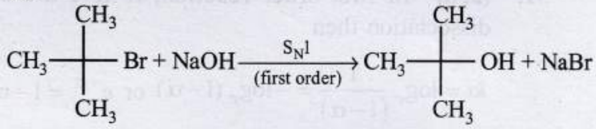
$$= 13.86 \times 10^{-3}\ \text{mol L}^{-1}\text{s}^{-1}$$

$$\text{At 100 sec } -\frac{1}{2}\frac{d[X]}{dt} = \frac{-d[Y]}{dt}$$

$$\Rightarrow -\frac{d[Y]}{dt} = \frac{\ln 2}{100} \times \frac{1}{2}\left\{\frac{-d[Y]}{dt} = k[X]^1\right\}$$

$$\frac{d[Y]}{dt} = 3.46 \times 10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

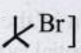
27. (a)



$$(CH_3)_3C-Br + NaOH \xrightarrow[\text{(first order)}]{S_N1} (CH_3)_3C-OH + NaBr$$

At time t = 0 P_0 0

At time t P $P_0 - P$

rate $= k\big[$  $\big] \quad \Rightarrow \quad \ln\frac{P_0}{P} = kt;\quad t_{1/2} = \frac{0.693}{k}$

$$\ln\frac{P}{P_0} = -kt;\ \frac{[Q]}{[P]_0} = \frac{[P_0]-[P]}{[P_0]} = 1 - \frac{[P]}{[P_0]} = 1 - e^{-kt}$$

28. (a, d)

$$A(g) \xrightarrow{\text{First order}} 2B(g) + C(g) \quad V = \text{constant}, T = 300\text{K}$$

$$\begin{array}{llll} t = 0 & P_0 & & \\ t = t_{1/3} & \left(P_0 - \frac{2P_0}{3}\right) & \frac{4P_0}{3} & \frac{2P_0}{3} \\ t = t & P_0 - x & 2x & x \end{array}$$

So, $P_t = P_0 - x + 2x + x = P_0 + 2x$

or $2x = P_t - P_0$

$$t = \frac{1}{k}\ln\frac{P_0}{(P_0 - x)}$$

$$\text{or} \quad t = \frac{1}{k}\ln\frac{P_0}{P_0 - \frac{(P_t - P_0)}{2}} = \frac{1}{k}\ln\frac{2P_0}{2P_0 - P_t + P_0}$$

$$\text{or} \quad kt = \ln\frac{2P_0}{3P_0 - P_t},\ kt = \ln 2P_0 - \ln(3P_0 - P_t)$$

$$\text{or} \quad \ln(3P_0 - P_t) = -kt + \ln 2P_0$$

Graph between $\ln(3P_0 - P_t)$ vs 't' is a straight line with negative slope.

Since, rate constant is a constant quantity and independent of initial concentration.

So, graph (a) and (d) are correct.

29. **(a, b, d)** For first order reaction

$$[A] = [A]_0 e^{-kt}$$

Hence, concentration of $[NO_2]$ decreases exponentially.

Also, $t_{1/2} = \frac{0.693}{K}$. Which is independent of concentration and $t_{1/2}$ decreases with the increase of temperature.

$$t_{99.6} = \frac{2.303}{K} \log\left(\frac{100}{0.4}\right)$$

$$t_{99.6} = \frac{2.303}{K}(2.4) = 8 \times \frac{0.693}{K} = 8t_{1/2}$$

30. **(a, b, d)** The relevant expressions are as follows.

Choice (a) $\log K_p = -\frac{\Delta H}{R}\frac{1}{T} + I$

Choice (b) $\log [X] = \log [X]_0 + kt$

Choice (c) $P/T =$ constant (V constant)

Choice (d) $PV =$ constant (T constant).

31. **(a, d)** In first order reaction, if α is the degree of dissociation then

$$kt = \log_e \frac{1}{(1-\alpha)} = -\log_e (1-\alpha) \text{ or } e^{-kt} = 1-\alpha$$

$$\therefore\ \alpha = 1 - e^{-kt}$$

The Arrhenius equation is, $k = Ae^{-E_a/RT}$

Plot of reciprocal concentration of the reactant vs time is linear. Dimensions of pre-exponential factor 'A' are equivalent to dimensions of k, which is T^{-1} for a first order reaction.

32. **(b, c)** As rate $= k$ [RCl], so it is first order reaction. On decreasing the concentration of RCl to half, the rate will also be halved. Rate will also increase with temperature.

33. **(a)** $\text{Rate} = \frac{k[X]}{X_s + [X]} = \frac{k}{\frac{X_s}{[X]} + 1} = k\frac{1}{\frac{X_s}{[X]} + 1}$

(I) When $[X]_0 \longrightarrow \infty$; Rate $= k \Rightarrow$ Rate is independent of substrate's concentration.

$\therefore$ Order of reaction $= 0$

(I) → (P), (S)

(II) When $[X]_0 << X_s$ $\therefore$ Rate $= k\,\frac{[X]}{X_s}$

$\Rightarrow$ This implies Order of the reaction $= 1$.

(II) → (Q), (T)

(III) $[X]_0 >> X_s$; $[X] + X_s \approx [X]$

$\text{Rate} = \frac{k[X]}{[X]} = k \Rightarrow$ This implies Order of the reaction $= 0$.

(III) → (P), (S)

(IV) $\text{Rate} = \frac{k[X]^2}{X_s + [X]}$

$[X] >> X_s$; Rate $= k[X] \Rightarrow$ This implies Order of the reaction $= 1$.

(IV) → (Q), (T)

34. (i) From the given data, it is evident that the $t_{1/2}$ (half-life period) for the decomposition of X (g) is constant (100 minutes) therefore, the order of reaction is **one**.

(ii) Rate constant, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = \mathbf{6.93 \times 10^{-3}\ min^{-1}}$

(iii) Time taken for 75% completion of reaction

$= 2t_{1/2} = 2 \times 100 = 200$ minutes

(iv)
$$\begin{array}{lcccc} & 2X & \longrightarrow & 3Y & + & 2Z \\ \text{Initial pressure} & 800 & & 0 & & 0 \\ \text{After time } t & (800-2P) & & 3P & & 2P \end{array}$$

when the pressure of X is 700 mm of Hg then,

$800 - 2P = 700$

$2P = 100$; $P = 50$ mm of Hg

Total pressure $= 800 - 2P + 3P + 2P = 800 + 150$

$= \mathbf{950\ mm\ of\ Hg}$

35. (a) From the rate law expression, $R_0 = k[A_0]^a [B_0]^b$ and from the table it is clear that :

(i) when the concentration of $[A_0]$ is doubled, keeping $[B_0]$ constant (see readings 1 and 2), the rate also doubles *i.e.* rate is directly proportional to $[A_0]$ or $a = 1$.

(ii) when the concentration of $[B_0]$ is reduced, keeping $[A_0]$ constant (see readings 1 and 3), the rate remains constant. *i.e.* rate is independent of $[B_0]$ or $b = 0$

Thus, rate equation becomes $\mathbf{R_0 = k[A_0]}$

(b) $k = \frac{R_0}{[A_0]} = \frac{0.05}{0.10} = \mathbf{0.5\ sec^{-1}}$

36. Let the number of moles of A left after 100 min $= x$

Total number of moles after 100 min $= x + 12 + 0.525$

$P_{\text{mix}} = p_A + p_B$

$$= \left(\frac{x}{12+x} \times 300\right) + \left(\frac{12}{12+x} \times 500\right) = \frac{6000 + 300x}{12+x}$$

According to Raoult's law

$$\frac{\left(\frac{6000+300x}{12+x}\right) - 400}{\frac{6000+300x}{12+x}} = \frac{0.525}{x + 12 + 0.525}$$

On solving we get, $x = 9.9$

Now according to first order kinetics,

$$k = \frac{2.303}{100} \log \frac{10}{9.9} = \mathbf{1.005 \times 10^{-4}\ min^{-1}}$$

37. $A \rightarrow B$; $k = 4.5 \times 10^{-3}\ \text{min}^{-1}$; $[A]_0 = 1\text{M}$

For first order reaction, $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$

Find $(a-x)$ at $t = 60$ min.

$$4.5 \times 10^{-3} = \frac{2.303}{60} \log \frac{1}{(a-x)} \quad \therefore\ (a-x) = 0.7634$$

Thus, rate after 60 minute $= k(a-x) = 4.5 \times 10^{-3} \times 0.7634$

$= \mathbf{3.4354 \times 10^{-3}\ M\ min^{-1}}$

38. (i) According to Fig. in the given time of 4 hours (1 to 5) concentration of A falls from 0.5 to 0.3 M, while in the same time concentration of B increases from 0.2 M to 0.6 M.

Decrease in concentration of A in 4 hours

$= 0.5 - 0.3 = 0.2$ M

Increase in concentration of B in 4 hours

$= 0.6 - 0.2 = 0.4$ M

Thus increase in concentration of B in a given time is twice the decrease in concentration of A. Thus $\boldsymbol{n = 2}$.

(ii) $K = \dfrac{[B^2]_{\text{eq.}}}{[A]_{\text{eq.}}} = \dfrac{(0.6)^2}{0.3} = \mathbf{1.2\ M}$

(iii) Initial rate of conversion of A

= Change in conc. of A during 1 hour

$= \dfrac{0.6 - 0.5}{1} = \mathbf{0.1\ mole\ litre^{-1}\ hour^{-1}}$

39.

$$\begin{array}{cccl} 2N_2O_5(g) & \longrightarrow\ 4NO_2(g) & +\ O_2(g) & \\ a & 0 & 0 & t=0 \\ a-x & 2x & x/2 & t=30\text{ min} \\ 0 & 2a & a/2 & \text{final} \end{array}$$

$2a + a/2 = 584.5$ mm Hg

$a = 584.5 \times \dfrac{2}{5}$ mm Hg

$a = 233.8$ mm Hg

Therefore, initial pressure of $N_2O_5 = 233.8$ mm Hg

Total pressure after 30 min

$= 284.5 \text{ mm Hg} = 233.8 - x + 2x + \dfrac{x}{2}$

or $233.8 + \dfrac{3x}{2} = 284.5$ or $x = 33.8$ mm Hg

Hence pressure of N_2O_5 after 30 min.

$= 233.8 - 33.8 = 200$ mm Hg

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)} = \frac{2.303}{30}\log\frac{233.8}{200}$$

$$k = \frac{2.303}{30} \times 0.0679 = \mathbf{5.2 \times 10^{-3}\ min^{-1}}$$

40. For a first order reaction we know that

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

Here, $t = 10 \times 60 \times 60$ sec. and let $a = 1$, then substituting the values, we get

$$1.5 \times 10^{-6} = \frac{2.303}{10 \times 3600}\log\frac{1}{(1-x)}$$

$$\frac{1.5 \times 10^{-6} \times 10 \times 3600}{2.303} = \log\frac{1}{(1-x)}$$

$$0.0234 = \log\frac{1}{(1-x)}$$

Taking antilog, $1.055 = \dfrac{1}{(1-x)}$

or $1.055 - 1.055x = 1 \Rightarrow x = \dfrac{(1.055-1)}{1.055} = 0.052$

Thus, **5.2%** of the initial concentration has changed into product.

Again we know that

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-6}} = 462000 \text{ second} = \mathbf{128.33\ hours}$$

41. Assuming that the decomposition of N_2O_5 is a **first order reaction,** then

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)} = \frac{2.303}{t}\log\frac{P_0}{P}$$

or $\log P = \dfrac{-kt}{2.303} + \log P_0$

Thus $\log P$ vs time graph is linear with slope $= \dfrac{-k}{2.303}$ if the given reaction is of first order which is in accordance with the given statement. Thus, the reaction obeys first order reaction.

42. From data (i) and (ii), it is obvious that when the concentration of B is kept constant (0.01 mol litre^{-1}) and the concentration of A is doubled (0.01 to 0.02 mol litre^{-1}), the rate of reaction is also doubled (0.005 to 0.010 mol litre^{-1} min^{-1}). Hence, **the order of reaction with respect to A is 1**. Similarly, from data (i) and (iii) it is obvious that when the concentration of A is kept constant (0.01 mol litre^{-1}) and the concentration of B doubled (0.01 to 0.02 mol litre^{-1}), the rate of reaction remains constant (0.005 mol litre^{-1} min^{-1}). This shows that the **order of reaction with respect to B is zero.**

Now we know that the rate of reaction, $A + B \rightarrow$ Products, is given by

Rate $r = k[A]^1[B]^0 \Rightarrow r = k[A]$

$$\therefore\ k = \frac{r}{[A]} = \frac{0.005}{0.01} = 0.5 \text{ min}^{-1}$$

$[\because r = 0.005 \text{ mol}/l/\text{m and } [A] = 0.01 \text{ mol}/l]$

For a first order reaction :

We know that $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{0.5}$ $[\because k = 0.5 \text{ min}^{-1}]$

$= \mathbf{1.386\ minutes}$

Topic-2: Effect of Temperature and Catalyst on Rate of Reactions, Collosion Theory of Chemical Reactions

1. **(a)** As per Arrhenius equation $(k = Ae^{-E_a/RT})$, the rate constant increases exponentially with temperature.

2. **(d)** $\log k = \log A - \dfrac{E_a}{2.303RT}$ ....(1)

Also given $\log k = 6.0 - (2000)\dfrac{1}{T}$ ....(2)

On comparing equations, (1) and (2)

$\log A = 6.0 \Rightarrow A = 10^6 \text{s}^{-1}$ and $\dfrac{E_a}{2.303\,R} = 2000$;

$\Rightarrow E_a = 2000 \times 2.303 \times 8.314 = 38.29 \text{ kJ mol}^{-1}$

3. **(b)** The Arrhenius equation is : $k = A \exp(-E_a/RT)$
As $T \to \infty, \exp(-E_a/RT) \to 1$. Hence, $k = A$
where A, the Arrhenius parameter, is $6.0 \times 10^{14} \text{ s}^{-1}$
'A' is also known as frequency factor

4. **(c)** A catalyst decreases the activation energy of the reactants and thus shortens time of reaction. So (c) is the correct option.

5. **(5)** $\text{Log k}_\text{f} = 9$ at 500K (given)

$\therefore \text{k}_\text{f} = 10^9$

$$\log \text{k}_\text{b} = \frac{(\text{E}_\text{a})_\text{b}}{2.303\text{R}}.\frac{1}{\text{T}} + \log \text{A}_\text{b}$$

$$\text{k}_{\text{eq}} = 10^6 = \frac{10^9}{\text{k}_\text{b}} \Rightarrow \text{k}_\text{b} = 10^3$$

$$\therefore 3 = \frac{-(\text{E}_\text{a})_\text{b}}{2.303\text{R}}.\frac{1}{\text{T}} + 11$$

$$\therefore 3 = \frac{-(\text{E}_\text{a})_\text{b}}{2.303\,\text{R}}.\frac{1}{\text{T}} + 11$$

$$\frac{(\text{E}_\text{a})_\text{b}}{2.303\text{R}} = 8 \times 500 = 4000$$

$$\log \text{k}_\text{b} = -4000 \times \frac{1}{250} + 11 = -5$$

$$(\log \text{k}_\text{b}) = 5$$

6. **(– 8500)**

$$A(\text{g}) + B(\text{g}) \rightleftharpoons AB(\text{g})$$

$E_{a_b} = E_{a_f} + 2RT$ and $A_f = 4A_b$

Now,

Rate constant of forward reaction $k_f = A_f e^{-Ea_f/RT}$

Rate constant of reverse reaction $k_b = A_b e^{-E_{ab}/RT}$

Equilibrium constant

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f}{A_b} e^{-(E_{af} - E_{ab})/RT}$$

$$K_{eq} = 4e^{2RT/RT} = 4e^2$$

Now, $\Delta G° = -RT \ln K_{eq} = -2500 \ln (4e^2)$
$= -2500 (\ln 4 + \ln e^2) = -2500 (1.4 + 2)$
$= -2500 \times 3.4 = -8500$ J/mol.

7. **(100)** According to Arrhenius equation $k = Ae^{-E_a/RT}$
Let E_a of the reaction in absence of catalyst = x kJ mol^{-1}
Therefore E_a of the reaction in presence of catalyst $= x - 20$ kJ mol^{-1}
The Arrhenius equations in the two conditions can thus be written as

$$k = Ae^{-\frac{x}{R \times 500}} \quad ...(i)$$

$$k = Ae^{-\frac{x-20}{R \times 400}} \quad ...(ii)$$

Dividing equation (i) by (ii), we get

$$e^{-\frac{x}{500R}} = e^{-\frac{x-20}{400R}} \Rightarrow \frac{x}{500} = \frac{x-20}{400} \text{ or } x = 100 \text{ kJ mol}^{-1}$$

8. **(20.34)** $k_{653\text{K}} = \dfrac{0.693}{360} = 1.925 \times 10^{-3} \text{ min}^{-1}$

Calculation of $k_{723\text{ K}}$
$E_a = 200 \text{ kJ mol}^{-1} = 200 \times 10^3 \text{ J mol}^{-1}$
$T_2 = 723$ K, $T_1 = 653$ K
$k_{653\text{K}} = 1.925 \times 10^{-3} \text{min}^{-1}$

We know that, $\dfrac{k_2}{k_1} = e^{-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$

or $\dfrac{k_{723K}}{1.925 \times 10^{-3}} = e^{-\frac{200 \times 10^3}{8.314}\left[\frac{1}{723} - \frac{1}{653}\right]}$

On usual calculations, $k_{723\text{ K}} = 6.81 \times 10^{-2} \text{ min}^{-1}$
Calculation of time for 75% decomposition at 723 K
Let the initial amount of H_2O_2, $a = 1$
$\therefore$ Amount at the required time, $(a - x) = 0.25$
Substituting the values in the given relation,

$$t = \frac{2.303}{k_{723K}} \log \frac{a}{a-x} = \frac{2.303}{6.81 \times 10^{-2}} \log \frac{1}{0.25} = 20.34 \text{ min}$$

9. **(311.35)**
According to Arrhenius equation

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

We know that $k = \dfrac{0.693}{t_{½}} = \dfrac{0.693}{10 \times 60}$ ($t_{½} = 10 \times 60$ sec.)
$= 1.555 \times 10^{-3}$

Substituting the various values in the above equation, we get

$$\log 1.155 \times 10^{-3} = \log 4 \times 10^{13} - \frac{98.6}{2.303 \times 8.314 \times 10^{-3} \times T}$$

On usual calculations, $T = 311.35$ K

10. **very high temperature** ($T = \infty$) or zero activation energy.

11. **True :** The rate of a reaction increases with increase in temperature because at higher temperature more number of molecules attain the activation energy.

Note : For a reversible exothermic reaction, the rate of both forward and backward reactions will increase with increase in temperature. But according to Le Chatelier's principle, increased temperature favour the backward reaction.

12. **False :** Catalyst lowers the energy of activation and therefore influences the rate as well as rate constant of the reaction.

13. **False :** Catalyst does not make a reaction more exothermic, but decreases the activation energy and hence, increase the rate of reaction.

14. **(a, c)** On increasing temperature, concentration of product decreases.
Hence, reaction is exothermic $\Rightarrow \Delta H^\circ < 0$

$$\frac{\ln K_{T_1}}{\ln K_{T_2}} > 1 \Rightarrow \ln K_{T_1} > \ln K_{T_2} \text{ so, } K_{T_1} > K_{T_2}$$

Also, $\frac{\ln K_{T_1}}{\ln K_{T_2}} > \frac{T_2}{T_1}$

or $T_1 \ln K_{T_1} > T_2 \ln K_{T_2} \Rightarrow -RT_1 \ln K_{T_1} > -RT_2 \ln K_{T_2}$

or $\Delta G^\circ_{T_1} < \Delta G^\circ_{T_2}$ $(\because \Delta G = -RT \ln K)$

or $\Delta H^\circ - T_1 \Delta S^\circ < \Delta H^\circ - T_2 \Delta S^\circ$
(Also $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$: Gibbs Helmholtz equation)

As $T_1 < T_2$, this is possible only when $\Delta S^\circ < 0$

15. **(a, b)** : According to Arrhenius equations

$$k = Ae^{-Ea/RT}$$

where, A = Frequency factor
Taking into account orientation factor,

$$P = \frac{A}{Z} \text{ or } A = PZ$$

$$k = PZ\,e^{-Ea/RT}$$

where, P = steric factor, Z = collision frequency
The value of steric factor lies between 0 and 1 predicted by Arrhenius equation. Thus, the experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation. Thus, (b) is correct.

16. **(b, c, d)**
(a) High activation energy usually implies a **slow reaction**.
(b) Rate constant of a reaction increases with increase in temperature due to increase in number of collisions whose energy exceeds the activation energy.
(c) $k = P \times Z \times e^{-E_a/RT}$
(d) So, pre-exponential factor $(A) = P \times Z$ and it is independent of activation energy or energy of molecules.

17. **(b, c)** A catalyst provides a new path of lower activation energy. The catalyst reacts with the reactants to form an activated complex of low activation energy. The activated complex then decomposes to form the products along with regeneration of catalyst. Thus, the reaction mechanism changes completely.

18. **(a)** Assertion is correct as for every 10ºC raise in temperature, the specific rate constant, K nearly doubles. (Although, it is not correct for all reactions. For some reactions, K even gets tripled for 10ºC raise).
[The value of temperature coefficient is the ratio of rate constants at two different temperature (which differ by 10°C) generally lies between 2 and 3]
The statement is clearly true and it explains the assertion, as the rate of collision among the molecules doubles for 10° rise in temperature.

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

$$\therefore \log \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{8.314 \times 2.303}\left[\frac{373 - 323}{373 \times 323}\right]$$

$$\therefore E_a = \mathbf{2.2 \times 10^4\ J\ mol^{-1}}$$

Now $k = Ae^{-E_a/RT}$

$$\therefore 4.5 \times 10^7\ \text{J mol}^{-1} = A.e^{-\frac{2.2 \times 10^4}{8.314 \times 373}} \quad \therefore A = \mathbf{5.42 \times 10^{10}\ sec^{-1}}$$

20. (i) The Arrhenius equation is
$k = A \exp(-E_a/RT)$
Taking natural logarithm, we get
$\ln k = \ln A - E_a/RT$

Thus $\log k = \log A - \frac{Ea}{2.303 R} . \frac{1}{T}$

Comparing this expression with the given one, we get

$$\frac{E_a}{2.303R} = 1.25 \times 10^4\ \text{K}$$

Hence, $E_a = (1.25 \times 10^4\ \text{K})(2.303)(8.314\ \text{JK}^{-1}\ \text{mol}^{-1})$
$= 2.39 \times 10^5\ \text{J mol}^{-1} = \mathbf{239\ kJ\ mol^{-1}}$

(ii) The reaction is first order as the unit of rate constant is s^{-1}. For a first order reaction,

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

Hence, $k = \frac{0.693}{256 \times 60\,\text{s}} = 4.51 \times 10^{-5}\ \text{s}^{-1}$

Substituting this in the given expression, we get

$$\log\left(4.51 \times 10^{-5}\right) = 14.34 - \frac{1.25 \times 10^{-5}\ \text{K}}{T}$$

$$\text{or } -4.346 = 14.34 - \frac{1.25 \times 10^{-4}\ \text{K}}{T}$$

$$\text{or } T = \frac{1.25 \times 10^{-4}\ \text{K}}{18.686} = \mathbf{669\ K}$$

21. Let the order with respect to A is x and the order with respect to B is y
Then, Rate $= k[A]^x[B]^y$

$5.0 \times 10^{-4} = k[2.5 \times 10^{-4}]^x[3.0 \times 10^{-5}]^y$ ...(*i*)
$4.0 \times 10^{-3} = k[5.0 \times 10^{-4}]^x[6.0 \times 10^{-5}]^y$ ...(*ii*)
$1.6 \times 10^{-2} = k[1.0 \times 10^{-3}]^x[6.0 \times 10^{-5}]^y$ ...(*iii*)
From (*ii*) and (*iii*), we get $2^x = 4;\ x = 2$
From (*i*) and (*ii*), we get $2^{x+y} = 8;\ x + y = 3; y = 1$
$\therefore$ The rate equation for the reaction is
Rate $= k[A]^2[B]$

(i) Thus, **order of reaction with respect to $A = 2$ and order of reaction with respect to $B = 1$.**

(ii) Rate constant (k_1) at 300 K

$$k_1 = \frac{\text{Rate}}{[\text{A}]^2[\text{B}]}$$

$$= \frac{5.0 \times 10^{-4}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1}}{(2.5 \times 10^{-4}\ \text{mol}\,\text{L}^{-1})^2\ (3.0 \times 10^{-5}\ \text{mol}\ \text{L}^{-1})}$$

$= \mathbf{2.66 \times 10^8\ mol^{-2}\ L^2\ s^{-1}}$

(iii) Determination of energy of activation :
Rate constant (k_2) at 320 K

$$k_2 = \frac{\text{Rate}}{[A]^2[B]}$$

$$k_2 = \frac{2.0 \times 10^{-3}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1}}{(2.5 \times 10^{-4}\ \text{mol}\,\text{L}^{-1})^2\ (3.0 \times 10^{-5}\ \text{mol}\ \text{L}^{-1})}$$

$= 1.066 \times 10^9\ \text{mol}^{-2}\,\text{L}^2\,\text{s}^{-1}$

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

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

$$= 2.303 \times 8.314\left[\log \frac{1.066 \times 10^9}{2.66 \times 10^8}\right]\left[\frac{320 \times 300}{20}\right]$$

$= \mathbf{5.54 \times 10^4\ J}$

(iv) Determination of the pre-exponential factor

$$\log k = -\frac{E_a}{2.303\,R} \times \frac{1}{T} + \log A$$

$$\log 2.66 \times 10^8 = \frac{5.54 \times 10^4}{2.303 \times 8.314} \times \frac{1}{300} + \log A$$

or $8.425 + 9.645 = \log A;\ \log A = 18.07$
$\therefore \mathbf{A = 1.175 \times 10^{18}\ L^2\ mol^{-2}\ sec}$

22. According to Arrhenius equation

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Calculation of k at 25°C (298 K), i.e. k_1
Here $a = 100, a - x = 100 - 25, t = 20$ mts.

$$\text{Thus } k_1 = \frac{2.303}{20}\ \log \frac{100}{75} = 0.014386\ \text{min}^{-1}$$

Calculation of k at 40°C (313 K) i.e., k_2
Substituting various values, we get

$$\log \frac{k_2}{0.014386} = \frac{70 \times 10^3}{2.303 \times 8.314} \times \left(\frac{1}{298} - \frac{1}{313}\right)$$

$$= \frac{70 \times 10^3 \times 15}{2.303 \times 8.314 \times 298 \times 313} = 0.587$$

$\log k_2 = 0.014386 \times 0.587; k_2 = 0.05570\ \text{min}^{-1}$
Calculation of % decomposition at 40°C
Thus here $a = 100,\ a - \text{x} = 100 - x, t = 20$ min, $k_2 = 0.05570$
Substituting the values in the first order reaction equation :

$$k_2 = 0.05570 = \frac{2.303}{20} \log \frac{100}{100 - x}$$

On usual calculations, $x = 67.169 = \mathbf{67.17\%}$
Value of rate constant k does not depend on the initial concentration (20% or 30% solution).

23. $A \rightarrow$ Products ...(i)
$B \rightarrow$ Product ...(ii)
Half-life of (i) reaction at 310 K = 30 min.

$$\therefore {}_Ak_{310} = \frac{0.693}{30}\ \text{min}^{-1} \quad ...(1)$$

$$\text{Also given, } \frac{{}_Ak_{310}}{{}_Ak_{300}} = 2 \quad ...(2)$$

$$\text{Also at 310 } k,\ {}_Bk_{310} = 2\,{}_Ak_{310} \quad ...(3)$$

$$\text{Also } E_B = \frac{1}{2}\,E_A$$

According to Arrhenius equation, $k = Ae^{-E/RT}$ ...(4)

$$\text{or } \log \frac{k_2}{k_1} = \frac{E}{2.303\,R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right]$$

For reaction (*i*),

$$\log \frac{{}_Ak_{310}}{{}_Ak_{300}} = \frac{E_A}{2.303\,R}\left[\frac{10}{300 \times 310}\right] \quad ...(5)$$

For reaction (*ii*),

$$\log \frac{{}_Bk_{310}}{{}_Bk_{300}} = \frac{E_B}{2.303\,R}\left[\frac{10}{300 \times 310}\right] \quad ...(6)$$

Dividing (6) by (5),

$$\frac{\log \dfrac{{}_Bk_{310}}{{}_Bk_{300}}}{\log \dfrac{{}_Ak_{310}}{{}_Ak_{300}}} = \frac{E_B}{E_A} = \frac{1}{2} \qquad \left(\because E_B = \frac{1}{2}\,E_A\right)$$

$$\text{or } \log \frac{{}_Ak_{310}}{{}_Ak_{300}} = 2 \log \frac{{}_Bk_{310}}{{}_Bk_{300}} = \log\left(\frac{{}_Bk_{310}}{{}_Bk_{300}}\right)^2$$

$$\text{or } \frac{{}_Ak_{310}}{{}_Ak_{300}} = \left(\frac{{}_Bk_{310}}{{}_Bk_{300}}\right)^2 \quad ...(7)$$

Combining (7), (2) and (3), we get $\left(\frac{2_A k_{310}}{_B k_{300}}\right)^2 = 2$

$$2_A k_{310} = \sqrt{2} \times {_B k_{300}} \; ; \; {_B k_{300}} = \sqrt{2} \times {_A k_{310}}$$

$${_B k_{300}} = 1.414 \times \frac{0.693}{30} = \mathbf{3.267 \times 10^{-2}\ min^{-1}}$$

24. $k = \frac{0.693}{t_{1/2}}$; $\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1.T_2}\right]$

$T_1 = 300K, T_2 = 320\,K$

Substituting the value at the two given conditions

$$k_{27^\circ} = \frac{0.693}{30} = \mathbf{0.0231\ min^{-1}};\ k_{47^\circ}$$

$$= \frac{0.693}{10} = 0.0693\,\text{min}^{-1}$$

We also know that $\log\frac{k_{47}}{k_{27}} = \frac{E_a}{2.303\,R} \times \frac{T_2 - T_1}{T_1 \times T_2}$

or $E_a = \frac{2.303\,R \times T_1 \times T_2}{T_2 - T_1}\log\frac{k_{47}}{k_{27}}$

$$= \frac{2.303 \times 8.314 \times 10^{-3} \times 300 \times 320}{320 - 300} \times \log\frac{0.0693}{0.0231}$$

$$= \mathbf{43.848\ kJ\ mol^{-1}}$$

Topic-3: Nuclear Chemistry

1. (a) $_{13}Al^{27} + {_2\alpha^4} \longrightarrow {_{14}Si^{30}} + \underset{(X)}{_1p^1}$

$$_{13}Al^{27} + {_2\alpha^4} \longrightarrow {_{15}P^{30}} + \underset{(Y)}{_0n^1}$$

$$_{15}P^{30} \longrightarrow {_{14}Si^{30}} + \underset{(Z)}{_{+1}\beta^0}$$

2. (c) $^{23}_{11}Na \longrightarrow {^{23}_{10}X} + {^0_1\beta}$

3. (a) n/p ratio of ^{24}Na nuclide is 13/11 i.e. greater than unity and hence ^{24}Na is radioactive. To achieve stability, it would tend to adjust its n/p ratio to the proper value of unity. This can be done by breaking a neutron into proton and electron.

$$_0n^1 \longrightarrow {_{+1}p^1} + {_{-1}e^0} \text{ or } \beta^-$$

The proton will stay inside the nucleus whereas electron which cannot exist in the nucleus, will be emitted out as β-ray.

4. (d) The sum of mass number and atomic numbers of reactants = The sum of mass number and atomic no. of products in a nuclear reaction.

The given nuclear fission reaction is

$$^{235}_{92}U + {^1_0n} \rightarrow {^{139}_{54}Xe} + {^{94}_{38}Sr} + 3\,{^1_0n}$$

5. (b) The species $_{13}Al^{29}$ (No. of neutrons = 16) contains more neutrons than the stable isotope $_{13}Al^{27}$ (No. of neutrons = 14).

Neutron on decomposition shows β -emission.

$$_0n^1 \rightarrow {_{+1}p^1} + \underset{\beta-\text{particle}}{_{-1}e^0}$$

6. (d) $N = N_0\left(\frac{1}{2}\right)^n$

where, N = Amount of radioactive substance which is left after certain number of half-life periods (n)

N_0 = Initial amount of radioactive substance.

$$\text{No. of half-lives} = \frac{\text{total time}}{\text{half life period}} = \frac{560}{140} = 4$$

In 'n' half-lives, the element will reduce to

$$\left(\frac{1}{2}\right)^n \times \text{Initial wt.} = \left(\frac{1}{2}\right)^4 \times 1 = \frac{1}{16}\text{g}$$

7. (d) α- and β-rays, made up of positively and negatively charged particles and are deflected by a magnetic field in opposite directions; γ-rays remain undeflected. (as they do not have charge).

8. (b) $_{92}U^{238} \rightarrow {_{90}U^{234}} + \underset{(\alpha\text{-particle})}{^4_2He}$

9. (9) Number of moles in gas phase, at start $(n_i) = 1$

$$^{238}_{92}U \rightarrow {^{206}_{82}Pb} + 8\,{^4_2He} + 6\,{^0_-\beta}$$

Now number of moles in gas phase, after decomposition $(n_F) = 1 + 8 = 9$ mole

At constant temperature and pressure

$$\frac{P_F}{P_{in}} = \frac{n_F}{n_{in}} = \frac{9}{1} = 9$$

10. (8) $^{63}_{29}Cu + {^1_1H} \rightarrow 6\,{^1_0n} + {^4_2He} + 2\,{^1_1H} + {^A_ZX}$

Balancing the atomic mass and atomic number

$63 + 1 = (6 \times 1) + 4 + 2 + A \Rightarrow A = 52$

$29 + 1 = (6 \times 0) + 2 + 2 + Z \Rightarrow Z = 26$

Thus $^A_ZX = {^{52}_{26}X}$ or $^{52}_{26}Fe$

Hence, X belongs to group 8 in the periodic table.

11. (3) $_{92}U^{235} \rightarrow {_{54}Xe^{142}} + {_{38}Sr^{90}} + y\,{_0n^1}$

$235 = 142 + 90 + y \Rightarrow y = 3.$

The number of neutrons emitted are 3.

12. (8) $_{92}U^{238} \xrightarrow{-6\alpha} {_{80}X^{214}} \xrightarrow{-2\beta} {_{82}Pb^{214}}$

Hence, total number of particles emitted are 2 + 6 = 8

13. (1.20) $^{238}_{92}U \longrightarrow {^{206}_{82}Pb}$

$$\text{Initial moles of } U^{238} = \frac{68 \times 10^{-6}}{238} = x$$

Number of α-particles emitted per nuclei of

$${}^{238}_{92}\text{U} = \frac{238-206}{4} = 8$$

Moles of U^{238} decayed in three half-lives $= \frac{7}{8}\text{x}$

No. of α-particles emitted $= \left(\frac{7}{8}\text{x}\right) \times 8 \times N_A$

$$= 7 \times \frac{68 \times 10^{-6}}{238} \times 6.022 \times 10^{23} = 1.204 \times 10^{18}$$

$\therefore \quad Z = 1.20$

14. **(0.061)**

Wt. of ^{90}Sr at start, $N_0 = 1\,\mu\text{g}$, Wt. of ^{90}Sr after 20 years, $N_t = ?$, Time $t = 20$ years

Half-life of ^{90}Sr, $T_{1/2} = 28.1$ years

Calculation of decay constant,

$$\lambda = \frac{0.693}{T_{1/2}} = \frac{0.693}{28.1} = 0.0247 \text{ years}^{-1}$$

Substituting the values in the relation

$N_t = N_0 e^{-\lambda t} = 1\, e^{-0.0247 \times 20} = 0.061\ \mu\text{g}$

15. **Isotope;** (because new atom has same atomic number but different atomic mass). [Refer to Q. 1 above]

16. **8;** ${}^{14}_{6}\text{C} \to {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e}$

Due to emission of the β particle, atomic number increases by 1.

17. ${}^{A-4}_{Z}M$

When an element emits α-particle, atomic mass decreases by four and atomic number decreases by two. Loss of β-particle results in increase in atomic number by 1 and no change in atomic mass.

$${}^{A}_{Z}M \xrightarrow{-\alpha} {}^{A-4}_{Z-2}X \xrightarrow{-\beta} {}^{A-4}_{Z-1}Y \xrightarrow{-\beta} {}^{A-4}_{Z}M$$

18. **False :** In β-emission (${}_{-1}e^0$) the atomic number of the daughter nuclei increases by 1.

19. **(a, b, d)**

${}^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He};\ x_1 = \alpha$

${}^{234}_{90}\text{Th} \longrightarrow {}^{234}_{91}\text{Pa} + {}^{0}_{-1}\text{e};\ x_2 = \beta$

${}^{234}_{91}\text{Pa} \longrightarrow {}^{234}_{92}\text{Z} + {}^{0}_{-1}\text{e};\ x_3 = \beta$

${}^{234}_{92}\text{Z} \longrightarrow {}^{230}_{90}\text{Th} + {}^{4}_{2}\text{He};\ x_4 = \alpha$

20. **(b, d)** When N/P ratio is less than one, then proton changes into neutron to increase the ratio.

Position emission : ${}^{1}_{1}\text{H} \longrightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\beta$

K-electron capture : ${}^{1}_{1}\text{H} + {}^{0}_{-1}\text{e} \longrightarrow {}^{1}_{0}\text{n} + \text{X-rays}$

21. **(a, b)** The reaction can occur by following two ways.

${}^{9}_{4}\text{Be} + \gamma \to {}^{8}_{4}\text{Be} + {}^{1}_{0}\text{n}\ ;\ {}^{9}_{4}\text{Be} + {}^{1}_{1}\text{H} \to {}^{2}_{1}\text{H} + {}^{8}_{4}\text{Be}$

22. **(a,c,d)**

(a) ${}_{z}X^{A} \xrightarrow{-\alpha} {}_{z-2}Y^{A-4}$ (α - emission) ;

(b) ${}_{z}X^{A} \xrightarrow{-\beta} {}_{z+1}Z^{A}$ (β - emission);

(c) ${}_{z}X^{A} \xrightarrow{-{}_{+1}e^{0}} {}_{z-1}D^{A}$ (positron - emission);

(d) ${}_{z}X^{A} + {}_{-1}e^{0} \to {}_{z-1}D^{A}$ (electron - capture)

Atomic number increases during β-emission

23. **(a, d)**

Balance various given nuclear reactions.

(a) ${}_{13}\text{Al}^{27} + {}_{2}\text{He}^{4} \to {}_{15}\text{P}^{30} + {}_{0}\text{n}^{1}$

(d) ${}_{96}\text{Am}^{241} + {}_{2}\text{He}^{4} \to {}_{97}\text{Bk}^{244} + {}_{1}\text{e}^{0} + {}_{0}\text{n}^{1}$

24. **(c)** It is clear from the 3rd paragraph, which states that in living organisms a dynamic equilibrium is established whereby the ratio of C^{14} to C^{12} remains constant. The C^{14} which decays into N^{14} is replenished by the production of new isotopes.

25. **(b)** As the half-life of C^{14} is 5760 years, so a 6 year old fossil's age can't be determined. Further this technique cannot be used to date objects older than 30,000 years. After this length of time the radioactivity is too low to be measured.

26. **(a)** $T_1 = \frac{1}{\lambda} \ln C_1,\ T_2 = \frac{1}{\lambda} \ln C_2$

Let the concentration of C^{14} in the fossil be C. In nearby areas concentration of C^{14} in living beings will be C_1 and in far off places C_2, obviously $C_1 > C_2$.

Hence, age of fossil in nearby areas,

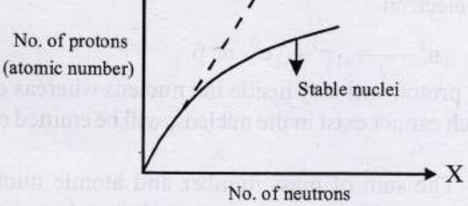
$$T_1 = \frac{1}{\lambda} \ln \frac{C_1}{C} \quad \text{....... (i)}$$

And age in far off places, $T_2 = \frac{1}{\lambda} \ln \frac{C_2}{C}$ ..... (ii)

From (i) and (ii), $T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$

Since, $C_1 > C_2$, R.H.S. is positive *i.e.*, $T_1 > T_2$.

27. **(a)**



A look at the above curve shows that for stable nuclei it shows a curvature towards x-axis from the line of 45° slope (dotted line) as the atomic number (*i.e.* number of protons) increases. So statement 1 is true.

The proton - proton repulsion would overcome the attractive force of proton and neutron. Thus, statement 2 in True. Also this statement 2 is a correct explanation for statement 1. Therefore the correct answer is option (a).

28. **(c)** Nuclides having both even number of protons and neutrons have maximum stability. So the reason is incorrect. But the assertion is correct as ${}^{40}Ca_{20}$ has even number of neutrons and protons as compared to ${}^{30}Al_{13}$, which has odd neutrons and protons.

29. (i) Sum of atomic masses of reactant = sum of atomic masses of products

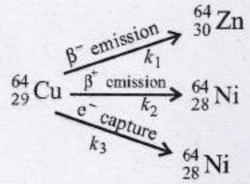
(ii) Sum of atomic numbers of reactant = sum of atomic numbers of products

(*i*) The atomic number of the final stable product $= 90 - 7 \times 2 + 1 \times 6 = 82$ and the mass number of the final stable product $= 234 - 7 \times 4 + 0 = 206$. Thus, the element should be ${}_{82}Pb^{206}$

(*ii*) ${}_{92}U^{235} + {}_{0}n^{1} \longrightarrow {}_{52}Te^{137} + {}_{40}Zr^{97} + 2{}_{0}n^{1}$

(*iii*) ${}_{34}Se^{86} \longrightarrow 2{}_{-1}e^{0} + {}_{36}Kr^{86}$

30.



Let the rate constants of the above emission processes be k_1, k_2 and k_3 respectively and the overall rate constant be k. Then,

$$k = k_1 + k_2 + k_3 = \frac{0.693}{t_{1/2}} = \frac{0.693}{12.8} h^{-1}.$$

Also, $k_1 = 0.38\,k = 0.38 \times \frac{0.693}{12.8} h^{-1}$

$$t_1 = \frac{0.693 \times 12.8}{0.38 \times 0.693} = \mathbf{33.68h}$$

Similarly,

$$t_2 = \frac{0.693}{k_2} = \frac{0.693}{0.19k} = \frac{0.693}{0.19 \times 0.693} \times 12.8 = \mathbf{67.36h},$$

$$t_3 = \frac{0.693}{k_3} = \frac{0.693}{0.43k} = \frac{12.8}{0.43} = \mathbf{29.76h}$$

where t_1, t_2 and t_3 are the partial half-lives for β^- emission, β^+ emission and electron capture processes, respectively.

31. Let the number of α-particles emitted = a and number of β-particles emitted = b

${}_{92}U^{238} \longrightarrow a\,{}_{2}\alpha^{4} + b\,{}_{-1}\beta^{0} + {}_{82}Pb^{206}$

Thus $4a + 206 = 238$; Therefore $a = 8$

Further $2a - b + 82 = 92$; Therefore $b = 6$

Composition of the ore indicates that it has 1 g of U and 0.1 gm of Pb; thus here $N_t = 1$ g

Determination of N_0

206 g Pb is obtained from 238 g of U

0.1 g Pb is obtained from $= \frac{238}{206} \times 0.1g = 0.1155g$

Therefore, initial amount of U $(N_0) = 1 + 0.1155 = 1.1155$

Now we know that

$$t = \frac{2.303}{k} \log \frac{N_0}{N_t} = \frac{2.303}{0.693/4.5 \times 10^9} \log \frac{1.1155}{1}$$

By usual calculations, $\boldsymbol{t = 7.097 \times 10^8}$ **years.**

32. ${}_{7}N^{14} + {}_{2}He^{4} \longrightarrow [{}_{9}F^{18}] \rightarrow {}_{8}O^{17} + {}_{1}H^{1}$

33. $\lambda_{Ac} = \frac{0.693}{21.8} = 3.18 \times 10^{-2}$ year^{-1}

Since, the decay involves two parallel paths

$Th^{227} \longleftarrow Ac^{227} \longrightarrow Fr^{223}$

$\lambda_{Ac} = \lambda_{Th} + \lambda_{Fr}$

Thus, Fractional yield of Th $= \frac{\lambda_{Th}}{\lambda_{Ac}}$

or $\lambda_{Th} = 3.18 \times 10^{-2} \times \frac{1.2}{100} = \mathbf{3.81 \times 10^{-4}\,yr^{-1}}$

Similarly, Fractional yield of Fr $= \frac{\lambda_{Fr}}{\lambda_{Ac}}$

$\therefore \lambda_{Fr} = 3.18 \times 10^{-2} \times \frac{98.8}{100} = \mathbf{3.14 \times 10^{-2}\,yr^{-1}}$

34. The ratio of $H^3 : H^1 :: 8 \times 10^{-18} : 1$

$\because$ No. of H atoms in 18 g $H_2O = 2N_A$

$\therefore$ No. of H^3 atoms in 18 g of H_2O

$= 2N_A \times 8 \times 10^{-18} = 2 \times 6.023 \times 10^{23} \times 8 \times 10^{-18}$ atoms

$\therefore$ No. of H^3 atoms in 10 g H_2O

$= \frac{2 \times 6.023 \times 10^{23} \times 8 \times 10^{-18} \times 10}{18}$ atoms

$= 5.354 \times 10^6$ atoms

No. of atoms left after 40 years are derived as follows using the relation

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$$

$$40 = \frac{2.303 \times 12.3}{0.693} \log \frac{5.354 \times 10^6}{N} \quad \therefore \boldsymbol{N = 5.624 \times 10^5}\ \textbf{atoms}$$

35. Minimum number of β-particles required in one minute = 346

No. of β-particles required for carrying out the experiment for 6.909×60 minutes $= 346 \times 6.909 \times 60 = 143431$

$\therefore$ Amount of β-particles required

$= \frac{143431}{6.023 \times 10^{23}} = 2.3814 \times 10^{-19}$ mol

Now we know that, $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{66.6} = 0.0104\,hr^{-1}$

Further we know that, $\lambda = \frac{2.303}{t} \log \frac{a}{a-x}$

where a = Initial concentration of β-particles

x = Consumed concentration of β-particles

$$\log \frac{a-x}{a} = -\frac{\lambda t}{2.303} = -\frac{0.0104 \times 6.909}{2.303} = -0.0312$$

$$= \bar{1}.9688$$

or $\frac{a-x}{a} = 0.931$ [Taking antilog]

or $\frac{a - 2.3814 \times 10^{-19}}{a} = 0.931$ [$\because x = 2.3814 \times 10^{-19}$]

On usual calculations, $a = \mathbf{3.451 \times 10^{-18}}$ **mol**

36. $^{234}_{90}\text{Th} \rightarrow ^{206}_{82}\text{Pb}$

For emission of one α-particle, atomic mass decreases by 4 and atomic number by 2. Further, for the emission of one β-particle, the atomic mass does not change but the atomic number increases by 1.

So, we first find the α-particles :

Decrease in atomic mass = 234 – 206 = 28

No. of α-particles emitted $= \frac{28}{4} = 7$

Hence, atomic number should have decrease to $90 - (7 \times 2) = 76$

Now, atomic number of Pb = 82, which is more by (82 – 76) = 6

This increase is due to emission of β-particles.

Therefore, β-particles emitted = 6

37. $N = N_0 \left(\frac{1}{2}\right)^n$

Half life, $t_{1/2} = 5770$ years

Let the original sample be 1 g.

∴ After every 5770 years one-half of radioactive carbon would decay or disintegrate.

Thus, 1 g sample becomes ½ g after 5770 years and $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$ left after 11,540 years.

∴ 25% of radioactive carbon remains after 11540 years.

Rate constant, k for first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770} = \mathbf{1.2 \times 10^{-4}\ year^{-1}}.$$