CHAPTER 14

Chemical Kinetics and Nuclear Chemistry

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. An element $^{A}_{Z}M$ undergoes an α-emission followed by two successive β-emissions. The element formed is .... *(1982 - 1 Mark)*
2. The rate of chemical change is directly proportional to .... *(1985 - 1 Mark)*
3. The number of neutrons in the parent nucleus which gives $^{14}_{7}N$ on beta emission is .... *(1985 - 1 Mark)*
4. The hydrolysis of ethyl acetate in .... medium is a .... order reaction. *(1986 - 1 Mark)*
5. A radioactive nucleus decays emitting one alpha and two beta particles; the daughter nucleus is .... of the parent. *(1989 - 1 Mark)*
6. 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)*
7. In the Arrhenius equation, $k = A \exp(-E_a/RT)$, A may be termed as the rate constant at .... *(1997 - 1 Mark)*

B True / False

1. For a first order reaction, the rate of the reaction doubles as the concentration of the reactant (s) doubles. *(1986 - 1 Mark)*
2. Catalyst makes a reaction more exothermic. *(1987 - 1 Mark)*
3. Catalyst does not affect the energy of activation in a chemical reaction. *(1989 - 1 Mark)*
4. In β-emission from a nucleus the atomic number of the daughter element decreases by one. *(1990 - 1 Mark)*
5. The rate of an exothermic reaction increases with increasing temperature. *(1990 - 1 Mark)*

C MCQs with One Correct Answer

1. 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. The rate constant of a reaction depends on *(1981 - 1 Mark)*
   (a) temperature
   (b) initial concentration of the reactants
   (c) time of reaction
   (d) extent of reaction
3. 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
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
5. 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
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 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 $T \to \infty$ is, *(1996 - 1 Mark)*

(a) $2.0\times10^{18}\ s^{-1}$ (b) $6.0\times10^{14}\ s^{-1}$
(c) infinity (d) $3.6\times10^{30}\ s^{-1}$

8. $^{27}_{13}Al$ is a stable isotope, $^{29}_{13}Al$ is expected to disintegrate by *(1996 - 1 Mark)*
(a) α-emission (b) β-emission
(c) positron emission (d) proton emission

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

10. The rate constant for the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, is $3.0\times10^{-5}\ sec^{-1}$. 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. 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

12. 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 $= -d[N_2]/dt = -1/3d[H_2]/dt = 1/2d[NH_3]/dt$
(b) Rate $= -d[N_2]/dt = -3d[H_2]/dt = 2d[NH_3]/dt$
(c) Rate $= d[N_2]/dt = 1/3d[H_2]/dt = 1/2d[NH_3]/dt$
(d) Rate $= -d[N_2]/dt = -d[H_2]/dt = d[NH_3]/dt$

13. 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}

14. ^{23}Na is the more stable isotope of Na. Find out the process by which $^{24}_{11}Na$ can undergo radioactive decay *(2003S)*
(a) β^- emission (b) α emission
(c) β^+ emission (d) K electron capture

15. The reaction, A → 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) 1.73×10^{-4} M min^{-1} (b) 3.47×10^{-5} M min^{-1}
(c) 3.47×10^{-4} M min^{-1} (d) 1.73×10^{-5} M min^{-1}

16. 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.

17. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+;\ k_1 = 6.8\times10^{-3}$

$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+;\ k_2 = 1.6\times10^{-3}$

then the formation constant of $[Ag(NH_3)_2]^+$ is *(2006 - 3M, –1)*
(a) 6.8×10^{-6} (b) 1.08×10^{-5}
(c) 1.08×10^{-6} (d) 6.8×10^{-5}

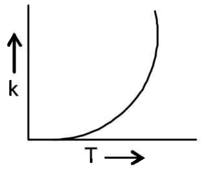
18. Consider a reaction $aG + bH \rightarrow$ Products. When concentration of both the reactants *G* and *H* is doubled, the rate increases by eight times. However, when concentration of *G* is doubled keeping the concentration of *H* fixed, the rate is doubled. The overall order of the reaction is *(2007)*
(a) 0 (b) 1
(c) 2 (d) 3

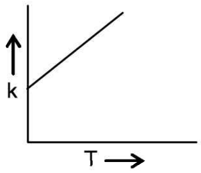
19. A positron is emitted from $^{23}_{11}Na$. The ratio of the atomic mass and atomic number of the resulting nuclide is *(2007)*
(a) 22/10 (b) 22/11
(c) 23/10 (d) 23/12

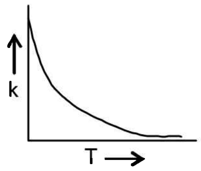
20. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio (k_1/k_0) of the rate constant for first order (k_1) and zero order (k_0) of the reaction is – *(2008)*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

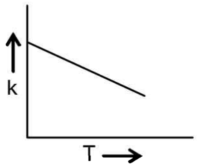
21. For a first order reaction A→P, the temperature (T) dependent rate constant (*k*) was found to follow the equation $\log k = -(2000)\frac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a, respectively, are *(2009)*
(a) $1.0\times10^6\ s^{-1}$ and 9.2 kJ mol^{-1}
(b) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(c) $1.0\times10^6\ s^{-1}$ and 16.6 kJ mol^{-1}
(d) $1.0\times10^6\ s^{-1}$ and 38.3 kJ mol^{-1}

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

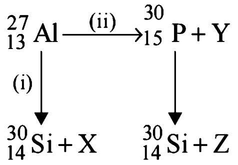
(a)


(b)


(c)


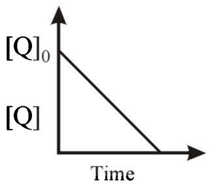
(d)


23. 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)*



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

24. 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 *(JEE Adv. 2013)*



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

25. For the elementary reaction ***M*** → ***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 *(JEE Adv. 2014)*

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

D MCQs with One or More Than One Correct

1. 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

2. The rate law for the reaction : *(1988 - 1 Mark)*

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

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.

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

(a) ${}^{17}_{13}Al + {}^{4}_{2}H \to {}^{30}_{15}P$

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

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

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

4. 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}.

5. 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, $X \to P$
(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

6. For the first order reaction *(2011)*

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

(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

7. In the nuclear transmutation *(JEE Adv. 2013)*

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

(X, Y) is(are)
(a) (γ, n) (b) (p, D)
(c) (n, D) (d) (γ, p)

8. According to the Arrhenius equation, *(JEE 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.

9. 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) *(JEE Adv. 2016)*
(a) β^-–decay (β emission)
(b) orbital or K–electron capture
(c) neutron emission
(d) β^-–decay (positron emission)

E Subjective Problems

1. 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?

2. 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)*

3. 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)*

4. $^{234}_{90}Th$ disintegrates to give $^{206}_{82}Pb$ as the final product. How many alpha and beta particles are emitted during this process? *(1986 - 2 Marks)*

5. 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)*

6. A first order reaction is 50% complete in 30 minutes at 27ºC and in 10 minutes at 47ºC. Calculate the reaction rate constant at 27ºC and the energy of activation of the reaction in kJ/mole. *(1988 - 3 Marks)*

7. 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)*

8. 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)*

9. The decomposition of N_2O_5 according to the equation : *(1991 - 6 Marks)*

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

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.

10. 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)*

11. The nucleidic ratio, $^{3}_{1}H$ to $^{1}_{1}H$ in a sample of water is $8.0 \times 10^{-18} : 1$. 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)*

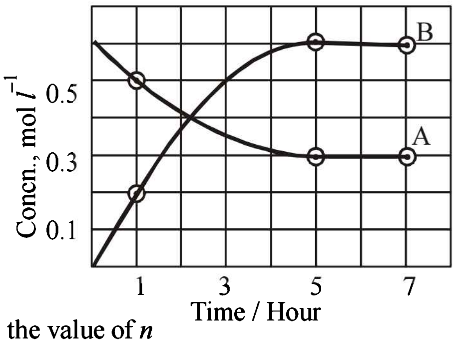
12. A first order reaction $A \rightarrow B$, requires activation energy of 70kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy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

13. 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)*

14. 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)*

15. 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

16. One of the hazards of nuclear explosion is the generation of ^{90}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 ${}^{90}Sr$ will remain in his bones after 20 years? *(1995 - 2 Marks)*

17. 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)*

18. ${}^{227}Ac$ 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)*

19. The ionisation constant of NH_4^+ in water is 5.6×10^{-10} at 25°C. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{10} L $mol^{-1} s^{-1}$. Calculate the rate constant for proton transfer from water to NH_3. *(1996 - 3 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. Write a balanced equation for the reaction of ${}^{14}N$ with α-particle. *(1997 - 1 Mark)*

22. 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)*

23. The rate constant for an isomerisation reaction, $A \to B$ 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)*

24. ${}^{238}_{92}U$ 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)*

25. 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)*

26. 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)*

27. 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)*

28. ${}^{64}Cu$ (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)*

29. For the given reactions, $A + B \to$ 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

30. Complete and balance the following reactions.

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

(*ii*) ${}_{92}U^{235} + {}_0n^1 \longrightarrow \ldots\ldots\ldots + {}_{52}Te^{137} + {}_{40}Zr^{92}$ *(2005 - 1 Mark)*

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

31. 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.

G Comprehension 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 ${}_6C^{14}$ (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).

$${}_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{14} + {}_1H^1$$

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 :

$$_6C^{14} \longrightarrow {}_7N^{14} + {}_{-1}\beta^0$$

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.

1. 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
2. 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
3. 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) $\frac{T_1}{T_2} = \frac{C_1}{C_2}$

H Assertion & Reason Type Questions

1. Read the following assertion and statement and answer as per the options given below :
   Assertion : For each ten degree rise of temperature the specific rate constant is nearly doubled.
   Statement : Energy-wise distribution of molecules in a gas is an experimental function of temperature. *(1989 - 2 Marks)*
   (a) If both assertion and statement are correct and statement is an explanation of assertion.
   (b) If assertion is correct and statement is wrong, statement is not an explanation of assertion.
   (c) If assertion is wrong and statement is correct, statement is not an explanation of assertion.
   (d) If both assertion and statement are wrong and statement is not explanation of assertion.

I Integer Value Correct Type

1. The total number of α and β particles emitted in the nuclear reaction $^{238}_{92}U \rightarrow {}^{214}_{82}Pb$ is *(2009)*
2. The concentration of R in the reaction R → 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. The number of neutrons emitted when $^{235}_{92}U$ undergoes controlled nuclear fission to $^{142}_{54}Xe$ and $^{90}_{38}Sr$ is *(2010)*
4. 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)*
5. 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)*
   $$^{63}_{29}Cu + {}^1_1H \rightarrow 6\,{}^1_0n + {}^4_2\alpha + 2\,{}^1_1H + X$$
6. A closed vessel with rigid walls contains 1 mol of $^{238}_{92}U$ and 1 mol of air at 298 K. Considering complete decay of $^{238}_{92}U$ to $^{206}_{82}Pb$, the ratio of the final pressure to the initial pressure of the system at 298 K is *(JEE Adv. 2015)*
7. 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

Section-B JEE Main / AIEEE

1. Units of rate constant of first and zero order reactions in terms of molarity M unit are respectively **[2002]**

(a) sec^{-1}, $Msec^{-1}$ (b) sec^{-1}, M
(c) $Msec^{-1}$, sec^{-1} (d) M, sec^{-1}.

2. For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A]\,[B]^2$ then the order of the reaction is **[2002]**

(a) 3 (b) 6
(c) 5 (d) 7.

3. The differential rate law for the reaction **[2002]**

$H_2 + I_2 \rightarrow 2HI$ is

(a) $-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$

(b) $\frac{d[H_2]}{dt} = \frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$

(c) $\frac{1}{2}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$

(d) $-2\frac{d[H_2]}{dt} = -2\frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$

4. If half-life of a substance is 5 yrs, then the total amount of substance left after 15 years, when initial amount is 64 grams is

(a) 16 grams (b) 2 grams **[2002]**
(c) 32 grams (d) 8 grams.

5. The integrated rate equation is **[2002]**

$Rt = \log C_0 - \log C_t.$

The straight line graph is obtained by plotting

(a) time vs $\log C_t$ (b) $\frac{1}{time}$ vs C_t

(c) time vs C_t (d) $\frac{1}{time}$ vs $\frac{1}{C_t}$

6. β-particle is emitted in rdioactivity by **[2002]**

(a) conversion of proton to neutron
(b) from outermost orbit
(c) conversion of neutron to proton
(d) β-particle is not emitted.

7. The radionucleide $^{234}_{90}Th$ undergoes two successive β-decays followed by one α-decay. The atomic number and the mass number respectively of the resulting radionucleide are **[2003]**

(a) 94 and 230 (b) 90 and 230
(c) 92 and 230 (d) 92 and 234

8. The half-life of a radioactive isotope is three hours. If the initial mass of the isotope were 256 g, the mass of it remaining undecayed after 18 hours would be **[2003]**

(a) 8.0 g (b) 12.0 g
(c) 16.0 g (d) 4.0 g

9. In respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the following statements is correct ?

(a) A is adsorption factor **[2003]**
(b) E_a is energy of activation
(c) R is Rydberg's constant
(d) k is equilibrium constant

10. The rate law for a reaction between the substances A and B is given by

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

On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as **[2003]**

(a) $(m+n)$ (b) $(n-m)$

(c) $2^{(n-m)}$ (d) $\frac{1}{2^{(m+n)}}$

11. For the reaction system : **[2003]**

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO, the rate of reaction will

(a) diminish to one-eighth of its initial value
(b) increase to eight times of its initial value
(c) increase to four times of its initial value
(d) diminish to one-fourth of its initial value

12. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M is 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is

(a) 7.5 minutes (b) 15 minutes **[2004]**
(c) 30 minutes (d) 60 minutes

13. The rate equation for the reaction $2A + B \rightarrow C$ is found to be : rate = k[A][B]. The correct statement in relation to this reaction is that the **[2004]**

(a) rate of formation of C is twice the rate of disappearance of A
(b) $t_{1/2}$ is a constant
(c) unit of k must be s^{-1}
(d) value of k is independent of the initial concentrations of A and B

14. Consider the following nuclear reactions : **[2004]**

$${}^{238}_{92}M \rightarrow {}^{x}_{y}N + 2\,{}^{4}_{2}He\ ;\ {}^{x}_{y}N \rightarrow {}^{A}_{B}L + 2\beta^{+}$$

The number of neutrons in the element L is

(a) 140 (b) 144

(c) 142 (d) 146

15. The half-life of a radioisotope is four hours. If the initial mass of the isotope was 200 g, the mass remaining after 24 hours undecayed is **[2004]**

(a) 3.125 g (b) 2.084 g

(c) 1.042 g (d) 4.167 g

16. Hydrogen bomb is based on the principle of **[2005]**

(a) artificial radioactivity

(b) nuclear fusion

(c) natural radioactivity

(d) nuclear fission

17. A reaction involving two different reactants can never be

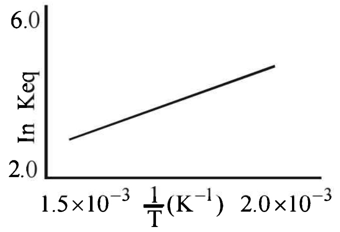
(a) bimolecular reaction **[2005]**

(b) second order reaction

(c) first order reaction

(d) unimolecular reaction

18. A schematic plot of $\ln K_{eq}$ versus inverse of temperature for a reaction is shown below **[2005]**



The reaction must be

(a) highly spontaneous at ordinary temperature

(b) one with negligible enthalpy change

(c) endothermic

(d) exothermic

19. A photon of hard gamma radiation knocks a proton out of ${}^{24}_{12}Mg$ nucleus to form **[2005]**

(a) the isobar of ${}^{23}_{11}Na$

(b) the nuclide ${}^{23}_{11}Na$

(c) the isobar of parent nucleus

(d) the isotope of parent nucleus

20. $t_{\frac{1}{4}}$ can be taken as the time taken for the concentration of a reactant to drop to $\frac{3}{4}$ of its initial value. If the rate constant for a first order reaction is K, the $t_{\frac{1}{4}}$ can be written as

(a) 0.75/K (b) 0.69/K **[2005]**

(c) 0.29/K (d) 0.10/K

21. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will **[2006]**

(a) increase by a factor of 4

(b) double

(c) remain unchanged

(d) triple

22. Rate of a reaction can be expressed by Arrhenius equation as : **[2006]**

$$k = A\,e^{-E/RT}$$

In this equation, E represents

(a) the total energy of the reacting molecules at a temperature, T

(b) the fraction of molecules with energy greater than the activation energy of the reaction

(c) the energy above which all the colliding molecules will react

(d) the energy below which all the colliding molecules will react

23. In the transformation of ${}^{238}_{92}U$ to ${}^{234}_{92}U$, if one emission is an α-particle, what should be the other emission(s)? **[2006]**

(a) one β^- and one γ (b) one β^+ and one β^-

(c) two β^- (d) two β^- and one β^+

24. The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr :

$$NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$$

$$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$$

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is **[2006]**

(a) 3 (b) 2

(c) 1 (d) 0

25. The energies of activation for forward and reverse reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction ($A_2 + B_2 \rightarrow 2AB$) in the presence of a catalyst will be (in kJ mol^{-1}) **[2007]**

(a) 20 (b) 300
(c) 120 (d) 280

26. Consider the reaction, 2A + B → products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is **[2007]**

(a) s^{-1} (b) $L\ mol^{-1}\ s^{-1}$
(c) no unit (d) $mol\ L^{-1}\ s^{-1}$.

27. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial velocity is ten times the permissible value, after how many days will it be safe to enter the room? **[2007]**

(a) 100 days (b) 1000 days
(c) 300 days (d) 10 days.

28. Which of the following nuclear reactions will generate an isotope? **[2007]**

(a) β - particle emission
(b) Neutron praticle emission
(c) Positron emission
(d) α – particle emission.

29. For a reaction $\frac{1}{2}A \to 2B,$ rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression **[2008]**

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

(c) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (d) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$

30. The half life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be ($\log 2 = 0.301$) **[2009]**

(a) 23.03 minutes (b) 46.06 minutes
(c) 460.6 minutes (d) 230.03 minutes

31. The time for half life period of a certain reaction A $\longrightarrow$ Products is 1 hour. When the initial concentration of the reactant 'A', is 2.0 mol L^{-1}, how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1} if it is a zero order reaction ? **[2010]**

(a) 4 h (b) 0.5 h
(c) 0.25 h (d) 1 h

32. Consider the reaction :

$$Cl_2(aq) + H_2S(aq) \to S(s) + 2H^+(aq) + 2Cl^-(aq)$$

The rate equation for this reaction is

$$\text{rate} = k[Cl_2][H_2S]$$

Which of these mechanisms is/are consistent with this rate equation? **[2010]**

A. $Cl_2 + H_2S \to H^+ + Cl^- + Cl^+ + HS^-$ (slow)

$Cl^+ + HS^- \to H^+ + Cl^- + S$ (fast)

B. $H_2S \rightleftharpoons H^+ + HS^-$ (fast equilibrium)

$Cl_2 + HS^- \to 2Cl^- + H^+ + S$ (Slow)

(a) B only (b) Both A and B
(c) Neither A nor B (d) A only

33. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about : **[2011]**

(a) 10 times (b) 24 times
(c) 32 times (d) 64 times

34. For a first order reaction (A) → products the concentration of A changes from 0.1 M to 0.025 M in 40 minutes.

The rate of reaction when the concentration of A is 0.01 M is : **[2012]**

(a) 1.73×10^{-5} M/min (b) 3.47×10^{-4} M/min
(c) 3.47×10^{-5} M/min (d) 1.73×10^{-4} M/min

35. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be : ($R = 8.314\ JK^{-1}\ mol^{-1}$ and $\log 2 = 0.301$) **[JEE M 2013]**

(a) 53.6 kJ mol^{-1} (b) 48.6 kJ mol^{-1}
(c) 58.5 kJ mol^{-1} (d) 60.5 kJ mol^{-1}

36. For the non - stoichimetre reaction $2A + B \to C + D,$ the following kinetic data were obtained in three separate experiments, all at 298 K. **[JEE M 2014]**

Initial Concentration (*A*)	Initial Concentration (*B*)	Initial rate of formation of *C* (mol L^{-1} s^{-1})
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is:

(a) $\frac{dc}{dt}=k[A][B]$ (b) $\frac{dc}{dt}=k[A]^2[B]$

(c) $\frac{dc}{dt}=k[A][B]^2$ (d) $\frac{dc}{dt}=k[A]$

37. Higher order (>3) reactions are rare due to : **[JEE M 2015]**

(a) shifting of equilibrium towards reactants due to elastic collisions

(b) loss of active species on collision

(c) low probability of simultaneous collision of all the reacting species

(d) increase in entropy and activation energy as more molecules are involved

38. Decomposition of H_2O_2 follows a first order reaction. In fifty minutes the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be: **[JEE M 2016]**

(a) 2.66 L min^{-1} at STP

(b) 1.34×10^{-2} mol min^{-1}

(c) 6.96×10^{-2} mol min^{-1}

(d) 6.93×10^{-4} mol min^{-1}

14

Chemical Kinetics & Nuclear Chemistry

Section-A : JEE Advanced/ IIT-JEE

A **1.** ${}^{A-4}_{Z}M$ **2.** Product of active masses of reactants at that temperature

3. 8 **4.** acidic, first (or basic, second) **5.** isotope

6. 1.765×10^{-4} kg/hr **7.** very high temperature or zero activation energy

B **1.** T **2.** F **3.** F **4.** F **5.** F

C **1.** (b) **2.** (a) **3.** (d) **4.** (c) **5.** (d) **6.** (d) **7.** (b) **8.** (b) **9.** (d) **10.** (d)

11. (b) **12.** (a) **13.** (c) **14.** (a) **15.** (c) **16.** (d) **17.** (b) **18.** (d) **19.** (c) **20.** (a)

21. (d) **22.** (a) **23.** (a) **24.** (d) **25.** (b)

D **1.** (b, c) **2.** (b, c) **3.** (a, d) **4.** (a, d) **5.** (a, b, d) **6.** (a, b, d) **7.** (a, b) **8.** (b, c, d) **9.** (b, d)

E **1.** 1, 0, 1.386 min **2.** 1.2×10^{-4} yrs^{-1}, 1/4 **3.** first order

4. 7, 6 **5.** 5.2%, 128.33 hours **6.** 0.0231 min^{-1}, 43.848 kJ mol^{-1} **7.** 3.451×10^{-18} mol

8. 311.35 K **9.** 5.2×10^{-3} min^{-1} **10.** 3.267×10^{-2} min^{-1} **11.** 5.624×10^{5} atoms

12. 67.17% **13.** 0.749 atm **14.** (i) 2, (ii) 1.2 M, (iii) 0.1 mol/*l*/hr

15. (i) 2, 1; (ii) $2.66 \times 10^{8}\ mol^{-2}\ l^{2}\ s^{-1}$; (iii) 5.54×10^{4} J; (iv) $1.175 \times 10^{18}\ l^{2} mol^{-2}$ sec **16.** 0.061 μg

17. 20.34 min **18.** 3.81×10^{-4} yr^{-1}, 3.14×10^{-2} yr^{-1} **19.** 6.07×10^{5}

20. (i) 239 kJ mol^{-1}, (ii) 669 K **22.** 5.42×10^{10} sec^{-1}, 2.2×10^{4} mol^{-1}

23. 3.4354×10^{-3} M min^{-1} **24.** 7.097×10^{8} yrs **25.** 100 kJ mol^{-1}

26. 24.14 min **27.** 1.005×10^{-4} min^{-1} **29.** (a) $R_0 = k\,[A_0]$; (b) 0.5 sec^{-1}

31. (i) 1, (ii) 6.93×10^{-3} min^{-1}, (iii) 200 min, (iv) 950 mm Hg

G **1.** (c) **2.** (b) **3.** (a)

H **1.** (a)

I **1.** 8 **2.** 5 **3.** 3 **4.** 9 **5.** 8 **6.** 9 **7.** 8

Section-B : JEE Main/ AIEEE

1. (a) **2.** (b) **3.** (d) **4.** (d) **5.** (a) **6.** (c) **7.** (b)

8. (d) **9.** (b) **10.** (c) **11.** (b) **12.** (c) **13.** (d) **14.** (b)

15. (a) **16.** (b) **17.** (d) **18.** (d) **19.** (b) **20.** (c) **21.** (a)

22. (c) **23.** (c) **24.** (b) **25.** (a) **26.** (b) **27.** (a) **28.** (b)

29. (b) **30.** (b) **31.** (c) **32.** (d) **33.** (c) **34.** (b) **35.** (a)

36. (d) **37.** (c) **38.** (d)

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **A-4**

TIPS/Formulae :

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.

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

2. **Product of active masses of reactants at that time**

3. **8;** ${}^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e$. 2 particles.

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

4. **acidic, first (or basic, second).**

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

6. **1.765 × 10^{-4} kg/hr;**

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

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

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

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

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

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

7. **very high temperature** (T=∞) or zero activation energy.

B. True/False

1. **True :** The rate of reaction of first order is directly proportional to the concentration of reacting substance.
2. **False :** Catalyst does not make a reaction more exothermic, but decreases the activation energy and hence increase the rate of reaction.
3. **False :** Catalyst lowers the energy of activation and therefore influences the rate as well as rate constant of the reaction.
4. **False :** In β-emission (${}_{-1}e^0$) the atomic number of the daughter nuclei increases by 1.
5. **True :** The rate of a reaction increases with increase in temperature because at higher temperature more number of molecules attain the activation energy.

C. MCQs with One Correct Answer

1. **(b)** $${}_{92}U^{238} \rightarrow {}_{90}U^{234} + \underset{(\alpha\text{-particle})}{{}^{4}_{2}He}$$

2. **(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.

3. **(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.

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

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

6. **(d)** **TIPS/Formulae :**

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

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. **(b)** The Arrhenius equation is : $k = A \exp(-E_a/RT)$

As $T \rightarrow \infty$, $\exp(-E_a/RT) \rightarrow 1$. Hence, $k = A$

where A, the Arrhenius parameter, is 6.0×10^{14} s^{-1}

[NOTE : 'A' is also known as frequency factor]

8. **(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.

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

9. **(d)** **TIPS/Formulae :**

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

$${}^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{139}_{54}Xe + {}^{94}_{38}Sr + 3\,{}^{1}_{0}n$$

10. (d) TIPS/Formulae :

Find the order of reaction and then use appropriate equation.

As unit of k is $\sec^{-1}$, reaction is of **first order**,

$$r = k[N_2O_5];\ \therefore\ [N_2O_5] = \frac{2.4\times10^{-5}}{3\times10^{-5}} = 0.8\ \text{mol/L}$$

11. (b) NOTE : 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.

12. (a) NOTE : 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)

13. (c) TIPS/Formulae :

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

$$\therefore\ k = \frac{2.303}{2\times10^4}\log\frac{800}{50} = 1.386\times10^{-4}\,\text{s}^{-1}$$

14. (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.

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

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

15. (c) TIPS/Formulae :

For first order reaction ,

Rate = *k* [conc. of reactant]

Since 0.1 M of ***X*** changes to 0.025 M in 40 minutes,

$t_{1/2}$ of reaction = 40/2 = 20 minutes

Rate of reaction of

$$X = k[X] = \frac{0.693}{t_{1/2}}\times[X] = \frac{0.693}{20}\times0.01$$

$$= 3.47\times10^{-4}\,\text{M min}^{-1}$$

16. (d) Order of a reaction can be fractional. Rest of all are true.

[**NOTE :** Order of a reaction can be determined experimentally]

17. (b) The required reaction is

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+;\ K = ?$$

From the given equations, we have

$$k_1 = \frac{[Ag(NH_3)]^+}{[Ag^+][NH_3]};\ k_2 = \frac{[Ag(NH_3)_2]^+}{[Ag(NH_3)]^+[NH_3]}$$

$\therefore$ The value of *K* is given by

$K = k_1 \times k_2 = 6.8\times10^{-3}\times1.6\times10^{-3} = 1.08\times10^{-5}$.

18. (d) TIPS/Formulae :

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	2*a*	2*b*	8*r*
3	2*a*	*b*	2*r*

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.

19. (c) $^{23}_{11}\text{Na} \longrightarrow {}^{23}_{10}\text{X} + {}^{0}_{1}\beta$

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

$$k_0 = \frac{A_0}{2\times t_{1/2}}$$

[where A_0 = initial concentration, and $t_{1/2}$ = half-life period]

$$\text{and}\quad k_1 = \frac{0.693}{t_{1/2}}$$

substituting various given values, we get

$$k_0 = \frac{1.386\,\text{mol litre}^{-1}}{2\times20\ \text{sec}} \quad \text{...(i)}$$

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

Dividing (ii) by (i), we get

$$\frac{k_1}{k_0} = \frac{0.693}{40}\times\frac{2\times20}{1.386}\,\text{mol}^{-1}\,\text{litre}$$

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

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

Thus the correct answer is (a).

21. (d) $$\log k = \log A - \frac{E_a}{2.303RT} \quad \text{...(1)}$$

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

On comparing equations, (1) and (2)

$\log A = 6.0 \Rightarrow A = 10^6\,s^{-1}$

and $\dfrac{E_a}{2.303\,R} = 2000$;

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

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

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

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

$${}_{15}P^{30} \longrightarrow {}_{14}Si^{30} + \underset{(Z)}{{}_1\beta^0}$$

24. **(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 $1 + 0 = 1$

25. **(b)** $M \to N$

$r = k\,[M]^x$

when $M = 2M$; $r = 8r$, thus

$8r = k[2M]^x$

$8 = (2)^x$

$x = 3$

D. MCQs with One or More Than One Correct

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

2. **(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.

3. **(a, d)** **TIPS/Formulae :**

Balance various given nuclear reactions.

(a) ${}_{13}Al^{27} + {}_2He^4 \to {}_{15}P^{30} + {}_0n^1$

(d) ${}_{96}Am^{241} + {}_2He^4 \to {}_{97}Bk^{244} + {}_1e^0 + {}_0n^1$

4. **(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.

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

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

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

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

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

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

For first order reaction

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

Hence concentration of [NO_2] decreases exponentially.

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

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

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

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

$${}^9_4Be + \gamma \to {}^8_4Be + {}^1_0n\ ;\ {}^9_4Be + {}^1_1H \to {}^2_1H + {}^8_4Be$$

8. **(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.

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

Position emission : ${}^1_1H \longrightarrow {}^1_0n + {}^0_{+1}\beta$

k-electron capture : ${}^1_1H + {}^0_{-1}e \longrightarrow {}^1_0n$ + X-rays

E. Subjective Problems

1. 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}). This shows that the rate of reaction varies directly as the first power of the concentration. 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, $A + B \to$ Products, is given by

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

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

[∵ $r=0.005$ mol/*l*/m and $[A]=0.01$ mol/*l*]

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

=1.386 minutes

2. **TIPS/Formulae :**

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

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

Let the original sample be 1 gram.

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

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

∴ 25% of radioactive carbon remains after 11540 years.

Rate constant, k for first order reaction,

$$\text{k}=\frac{0.693}{t_{1/2}}=\frac{0.693}{5770}=\mathbf{1.2\times10^{-4}\ year^{-1}.}$$

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

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

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

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.

4. $^{234}_{90}\text{Th}\rightarrow{}^{206}_{82}\text{Pb}$

NOTE : 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 $=\dfrac{28}{4}=7$

Hence, atomic number should have decrease to

$90-(7\times2)=76$

Now, atomic number of Pb = 82,

which is more by $(82-76)=6$

This increase is due to ionisation of β-particles.

Therefore, β-particles emitted = **6**

5. **TIPS/Formulae :**

For a first order reaction we know that

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

Here, $t=10\times60\times60$ sec. and let $a=1$, then substituting the values, we get

$$1.5\times10^{-6}=\frac{2.303}{10\times3600}\log\frac{1}{(1-x)}$$

$$\frac{1.5\times10^{-6}\times10\times3600}{2.303}=\log\frac{1}{(1-x)}$$

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

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

$$t_{1/2}=\frac{0.693}{k}=\frac{0.693}{1.5\times10^{-6}}=462000\ \text{second}=\mathbf{128.33\ hours}$$

6. **TIPS/Formulae :**

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

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

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

$$=\frac{2.303\times8.314\times10^{-3}\times300\times320}{320-300}\times\log\frac{0.0693}{0.0231}$$

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

7. 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 × 6.909 × 60 = 143431

∴ Amount of β-particles required

$$=\frac{143431}{6.023\times10^{23}}=2.3814\times10^{-19}\ \text{mol}$$

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

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

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

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

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

8. **TIPS/Formulae :**

According to Arrhenius equation

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

We know that $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{10 \times 60}$ $(t_{1/2} = 10 \times 60 \text{ sec.})$

$$= 1.555 \times 10^{-3}$$

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**

9. $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

2 mol of gaseous nitrogen pentoxide on complete decomposition gives 5 mol of gaseous products.

Therefore, initial pressure of $N_2O_5 = 584.5 \times \dfrac{2}{5}$

$$= 233.8 \text{ mm Hg}.$$

Let x be the amount of N_2O_5 decomposed after 30 min.

$\therefore$ After 30 min.

Pressure due to $N_2O_5 = 233.8 - x$; Pressure due to $NO_2 = 2x$

and pressure due to $O_2 = \dfrac{x}{2}$

Total pressure after 30 min

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

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

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

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

10. $A \rightarrow$ Products ...(i)
$B \rightarrow$ Product ...(ii)

Half-life of (i) reaction at 310 k = 30 min.

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

Also given, $\dfrac{{}_Ak_{310}}{{}_Ak_{300}} = 2$ ...(2)

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

Also $E_B = \dfrac{1}{2} E_A$

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

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

$$2\,{}_Ak_{310} = \sqrt{2} \times {}_Bk_{300}\,; \quad {}_Bk_{300} = \sqrt{2} \times {}_Ak_{310}$$

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

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

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

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

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

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

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

$= 5.354 \times 10^6$ atoms

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

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

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

12. **TIPS/Formulae :**

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 $a = 100,\ a - x = 100 - x, t = 20$ mts., $k_2 = 0.05570$

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, $x = 67.169 =$ **67.17%**

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

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**

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

(iii) Initial rate of conversion of *A*

= Change in conc. of *A* during 1 hour

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

15. 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

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

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

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

(iii) Determination of energy of activation :

Rate constant (k_2) at 320 K

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

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

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

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

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

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

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

(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 $8.425+9.645=\log A;\ \log A=18.07$

$\therefore\ \mathbf{A=1.175\times 10^{18}\ \ell^2\ mol^{-2}\ sec}$

16. Wt. of ^{90}Sr at start, N_0 = 1mg, 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

$N_t=N_0e^{-\lambda t}=1\ e^{-0.0247\times 20}=\mathbf{0.061\ \mu g}$

17. $$k_{653\,K}=\frac{0.693}{360}=1.925\times 10^{-3}\ \text{min}^{-1}$$

Calculation of $k_{723\text{ K}}$

$E_a=200\text{ kJ mol}^{-1}=200\times 10^3\text{ J mol}^{-1}$

$T_2=723\text{ K},\ T_1=653\text{ K}$

$k_{653\text{ K}}=1.925\times 10^{-3}\text{min}^{-1}$

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

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

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,

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

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

Since the decay involves two parallel paths

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

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

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

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

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

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

19. $NH_3+H_2O\underset{K_b}{\overset{K_f}{\rightleftharpoons}}NH_4^{\ +}+OH^-;\ K_b=3.4\times 10^{10}$

$NH_4^{\ +}+H_2O\rightleftharpoons NH_4OH+H^+;\ K_a=5.6\times 10^{-10}$

$$K_{base}=\frac{K_f}{K_b}=\frac{K_w}{K_{acid}}\text{ or }\frac{K_f}{3.4\times 10^{10}}=\frac{10^{-14}}{5.6\times 10^{-10}}$$

$\therefore\ K_f=6.07\times 10^5$

20. (i) The Arrhenius equation is

$k=\text{A}\exp(-E_a/RT)$

Taking natural logarithm, we get

$\ln k=\ln A-E_a/RT$

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

Comparing this expression with the given one, we get

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

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,

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

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

Substituting this in the given expression, we get

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

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

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

21. $${}_7\text{N}^{14} + {}_2\text{He}^4 \longrightarrow [{}_9\text{F}^{18}] \rightarrow {}_8\text{O}^{17} + {}_1\text{H}^1$$

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

$$\therefore \log\frac{4.5\times10^7}{1.5\times10^7} = \frac{E_a}{8.314\times2.303}\left[\frac{373-323}{373\times323}\right]$$

$$\therefore E_a = \mathbf{2.2\times10^4\,J\,mol^{-1}}$$

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

$$\therefore 4.5\times10^7\,\text{J mol}^{-1} = \text{A.e}^{-\frac{2.2\times10^4}{8.314\times373}} \therefore \text{A} = \mathbf{5.42 \times 10^{10}\ sec^{-1}}$$

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

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

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

$$4.5\times10^{-3} = \frac{2.303}{60}\log\frac{1}{(a-x)} \quad \therefore (a-x) = 0.7634$$

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

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

24. Let the number of α-particles emitted = a

and number of β-particles emitted = b

$${}_{92}\text{U}^{238} \longrightarrow a\,{}_2\alpha^4 + b\,{}_{-1}\beta^0 + {}_{82}\text{Pb}^{206}$$

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

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

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

Determination of N_0

206 g Pb is obtained from 238 g of U

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

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

Now we know that

$$t = \frac{2.303}{k}\log\frac{N_0}{N_t} = \frac{2.303}{0.693/4.5\times10^9}\log\frac{1.1155}{1}$$

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

25. 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

$$k = Ae^{-\frac{x}{R\times500}} \quad \ldots(i)$$

$$k = Ae^{-\frac{x-20}{R\times400}} \quad \ldots(ii)$$

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

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

26. $r_2 = k_1c_1$ and $r_2 = k_2c_2$

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

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

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

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

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

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

$$= \left(\frac{x}{12+x}\times300\right) + \left(\frac{12}{12+x}\times500\right) = \frac{6000+300x}{12+x}$$

According to Raoult's law

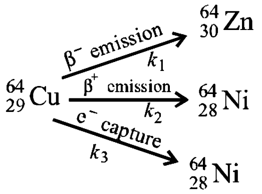
$$\frac{\left(\dfrac{6000+300x}{12+x}\right) - 400}{\dfrac{6000+300x}{12+x}} = \frac{0.525}{x+12+0.525}$$

On solving we get, $x = 9.9$

Now according to first order kinetics,

$$k = \frac{2.303}{100}\log\frac{10}{9.9} = \mathbf{1.005\times10^{-4}\ min^{-1}}$$

28.



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

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

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

$$t_1 = \frac{0.693\times12.8}{0.38\times0.693} = \mathbf{33.68h}$$

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.

29. (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 $\boldsymbol{R_0 = k\,[A_0]}$

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

30. **TIPS/Formulae :**

(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 $= 90 - 7 \times 2 + 1 \times 6 = 82$ & the mass number of the final stable product $= 234 - 7 \times 4 + 0 = 206$. Thus the element X should be ${}_{82}Pb^{206}$.

(*ii*) ${}_{92}U^{235} + {}_0n^1 \longrightarrow {}_{52}Te^{137} + {}_{40}Zr^{97} + 2\,{}_0n^1$

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

31. (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, $k = \dfrac{0.693}{t_{1/2}}$

$$= \frac{0.693}{100} = \mathbf{6.93 \times 10^{-3}\ min^{-1}}$$

(iii) Time taken for 75% completion of reaction

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

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

when the pressure of X is 700 mm of Hg then,
$800 - 2P = 700$
$2P = 100$; $P = 50$ mm of Hg
Total pressure $= 800 - 2P + 3P + 2P = 800 + 150$
$= \mathbf{950\ mm\ of\ Hg}$

G. Comprehension Based Questions

1. **(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.

2. **(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.

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

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, $T_2 = \dfrac{1}{\lambda}\ln\dfrac{C_2}{C}$ ..... (ii)

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

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

H. Assertion & Reason Type Questions

1. **(a)** Assertion is correct as for every 10°C 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 10°C raise).
[NOTE : 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.

I. Integer Value Correct Type

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

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

2. The integrated form of a zero-order reaction is
$[A_0] - [A_t] = k_0 t$; $1.0 - 0.75 = k_0 \times 0.05$, $k_0 = 5$
Again, $1.0 - 0.4 = k_0 \times 0.12$, $k_0 = 5$

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.

4. **9**

$$t_{1/8} = \frac{2.303 \log 8}{k} = \frac{2.303 \times 3 \log 2}{k}$$

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

$$\left[\frac{t_{1/8}}{t_{1/10}}\right]\times 10=\frac{\left(\dfrac{2.303\times 3\log 2}{k}\right)}{\left(\dfrac{2.303}{k}\right)}\times 10=9$$

5. **8**

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

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 ${}^{A}_{Z}X={}^{52}_{26}X$ or ${}^{52}_{26}Fe$

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

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

$${}^{238}_{92}U\rightarrow{}^{206}_{82}Pb+8\,{}^{4}_{2}He+6\,{}^{0}_{-}\beta$$

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

at constant temperature and pressure

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

7. **(8)** $8H^{+}+5[Fe(H_2O)_2(OX)_2]^{2-}+MnO_4^{-}\rightarrow Mn^{2+}+$

$+5\,[Fe(H_2O)_2(OX)_2]^{-}+4H_2O$

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

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

Section-B JEE Main/ AIEEE

1. **(a)** For a zero order reaction.

rate $=k[A]^{\circ}$ i.e. rate $=k$

hence unit of $k=M.sec^{-1}$

For a first order reaction.

rate $=k[A]$

$k=M.sec^{-1}/M=sec^{-1}$

2. **(a)** **NOTE :** Order is the sum of the power of the concentrations terms in rate law expression.

Hence the order of reaction is $=1+2=3$

3. **(d)** rate of appearance of HI $=\dfrac{1}{2}\dfrac{d[HI]}{dt}$

rate of formation of $H_2=\dfrac{-d[H_2]}{dt}$

rate of formation of $I_2=\dfrac{-d[I_2]}{dt}$

hence $\dfrac{-d[H_2]}{dt}=-\dfrac{d[I_2]}{dt}=\dfrac{1}{2}\dfrac{d[HI]}{dt}$

or $-\dfrac{2d[H_2]}{dt}=-\dfrac{2d[I_2]}{dt}=\dfrac{d[HI]}{dt}$

4. **(d)** $t_{1/2}=5$ years, $T=15$ years hence total number of half life periods $=\dfrac{15}{5}=3$.

$\therefore$ Amount left $=\dfrac{64}{(2)^3}=8g$

5. **(a)** $Rt=\log C_o-\log C_t$

It is clear from the equation that if we plot a graph between $\log C_t$ and time, a straight line with a slope equal to $-\dfrac{k}{2.303}$ and intercept equal to $\log [A_o]$ will be obtained.

6. **(c)** ${}_{0}n^{1}\rightarrow{}_{+1}p^{1}+{}_{-1}e^{0}$

7. **(b)** ${}^{234}_{90}Th\xrightarrow{-\beta}{}^{234}_{91}X\xrightarrow{-\beta}{}^{234}_{92}Th\xrightarrow{-\alpha}{}^{230}_{90}Th$

8. **(d)** $t_{1/2}=3$hrs. $T=18$ hours $\because T=n\times t_{1/2}$

$$\therefore n=\frac{18}{3}=6$$

Initial mass $(C_0)=256$ g

$$\therefore C_n=\frac{C_0}{2^n}=\frac{256}{(2)^6}=\frac{256}{64}=4g.$$

9. **(b)** In equation $K=Ae^{-E_a/RT}$; $A=$ Frequency factor

$K=$ velocity constant, $R=$ gas constant and $E_a=$ energy of activation

10 **(c)** $\text{Rate}_1=k[A]^n[B]^m$; $\text{Rate}_2=k[2A]^n[½B]^m$

$$\therefore\frac{\text{Rate}_2}{\text{Rate}_1}=\frac{k[2A]^n[½B]^m}{k[A]^n[B]^m}=[2]^n[½]^m=2^n.2^{-m}=2^{n-m}$$

11. **(b)** $r=k[O_2][NO]^2$. When the volume is reduced to 1/2, the conc. will double

$\therefore$ New rate $=k[2O_2][2\,NO]^2=8\,k[O^2][NO]^2$

The new rate increases to eight times of its initial.

12. **(c)** As the concentration of reactant decreases from 0.8 to 0.4 in 15 minutes hence the $t_{1/2}$ is 15 minutes. To fall the concentration from 0.1 to 0.025 we need two half lives i.e., 30 minutes.

13. **(d)** The velocity constant depends on temperature only. It is independent of concentration of reactants.

14. **(b)** ${}^{238}_{92}M\rightarrow{}^{230}_{88}N+2\,{}^{4}_{2}He$

${}^{230}_{88}N\rightarrow{}^{230}_{86}L+2\beta^{+}$

The number of neutrons in element $L=230-86=144$

15. (a) $N_t = N_0\left(\frac{1}{2}\right)^n$ where n is number of half life periods.

$$n=\frac{\text{Total time}}{\text{half life}}=\frac{24}{4}=6$$

$$\therefore N_t = 200\left(\frac{1}{2}\right)^6 = 3.125\text{g}.$$

16. (b) Such reaction in which two lighter nucleus are fused together to form a heavier nuclei is called nuclear fusion.

NOTE : In hydrogen bomb, a mixture of deuterium oxide (H_2O) and tritium Oxide (T_2O) is enclosed in a space surrounding an ordinary atomic bomb. The temperature produced by the atomic bomb initiates the fusion reaction between ${}_1H^3$ and ${}_1H^2$ releasing a large amount of energy.

17. (d) The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

NOTE : The reaction involving two different reactant can never be unimolecular.

18. (d) The graph show that reaction is exothermic.

$$\log k = \frac{-\Delta H}{RT} + I$$

For exothermic reaction $\Delta H < 0$

$\therefore$ log k Vs $\frac{1}{T}$ would be negative straight line with positive slope.

19. (b) ${}_{12}Mg^{24} \longrightarrow {}_{11}Na^{23} + {}_1H^1$.

20. (c) $t_{1/4} = \frac{2.303}{K}\log\frac{1}{3/4} = \frac{2.303}{K}\log\frac{4}{3}$

$$= \frac{2.303}{K}(\log 4 - \log 3) = \frac{2.303}{K}(2\log 2 - \log 3)$$

$$= \frac{2.303}{K}(2 \times 0.301 - 0.4771) = \frac{0.29}{K}$$

21. (a) Since the reaction is 2nd order w.r.t CO. Thus, rate law is given as.

$r = k[CO]^2$

Let initial concentration of CO is a i.e. $[CO] = a$

$\therefore r_1 = k(a)^2 = ka^2$

when concentration becomes doubled, i.e. $[CO] = 2a$

$\therefore r_2 = k(2a)^2 = 4ka^2$ $\therefore r_2 = 4r_1$

So, the rate of reaction becomes 4 times.

22. (c) In Arrhenius equation $K = A\,e^{-E/RT}$, E is the energy of activation, which is required by the colliding molecules to react resulting in the formation of products.

23. (c) ${}^{238}_{92}U \xrightarrow{-\alpha} {}^{234}_{90}Th \xrightarrow{-2\beta} {}^{234}_{92}U$

24. (b) (i) $NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$

(ii) $NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$

Rate law equation $= k[NOBr_2][NO]$

But $NOBr_2$ is intermediate and must not appear in the rate law equation

from Ist step $K_C = \frac{[NOBr_2]}{[NO][Br_2]}$

$\therefore [NOBr_2] = K_C[NO][Br_2]$

$\therefore$ Rate law equation $= k.K_C[NO]^2[Br_2]$

hence order of reaction is 2 w.r.t. NO.

25. (a) $\Delta H_R = E_f - E_b = 180 - 200 = -20$ kJ/mol

The nearest correct answer given in choices may be obtained by neglecting sign.

26. (b) For a first order reaction $t_{1/2} = \frac{0.693}{K}$ i.e. for a first order reaction $t_{1/2}$ does not depend up on the concentration. From the given data, we can say that order of reaction with respect to $B = 1$ because change in concentration of B does not change half life.

Order of reaction with respect to $A = 1$ because rate of reaction doubles when concentration of B is doubled keeping concentration of A constant.

$\therefore$ Order of reaction = 1 + 1 = 2 and units of second order reaction are L mol^{-1} sec^{-1}.

27. (a) Suppose activity of safe working = A

Given $A_0 = 10A$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

$$t_{½} = \frac{2.303}{\lambda}\log\frac{A_0}{A} = \frac{2.303}{0.693/30}\log\frac{10A}{A}$$

$$= \frac{2.303 \times 30}{0.693} \times \log 10 = 100 \text{ days.}$$

28. (b) **NOTE :** Isotopes are atoms of same element having same atomic number but different atomic masses. Neutron has atomic number 0 and atomic mass 1. So loss of neutron will generate isotope. e.g.,

$${}_{92}U^{238} + {}_0n^1 \to {}_{92}U^{239}$$

29. (b) The rates of reactions for the reaction

$$\frac{1}{2}A \longrightarrow 2B$$

can be written either as

$-2\frac{d}{dt}[A]$ with respect to 'A'

or $\frac{1}{2}\frac{d}{dt}[B]$ with respect to 'B'

From the above, we have

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

i.e., correct answer is (b)

30. **(b)** For first order reaction,

$$k=\frac{2.303}{t}\log\frac{100}{100-99}$$

$$\frac{0.693}{6.93}=\frac{2.303}{t}\log\frac{100}{1}$$

$$\frac{0.693}{6.93}=\frac{2.303\times 2}{t}\Rightarrow t=46.06\text{ min}$$

31. **(c)** For the reaction
A → Product; given $t_{1/2}=1$ hour
for a zero order reaction

$$t_{\text{completion}}=\frac{[A_0]}{k}=\frac{\text{initial conc.}}{\text{rate constant}}$$

$$\therefore\ t_{1/2}=\frac{[A_0]}{2k}\ \text{ or }\ k=\frac{[A_0]}{2t_{1/2}}=\frac{2}{2\times 1}=1\ \text{mol lit}^{-1}\text{hr}^{-1}$$

Further for a zero order reaction

$$k=\frac{dx}{dt}=\frac{\text{change in concentration}}{\text{time}}$$

$$1=\frac{0.50-0.25}{\text{time}}\qquad\therefore\ \text{time}=0.25\text{ hr.}$$

32. **(d)** Since the slow step is the rate determining step hence if we consider option (1) we find

Rate $=k\left[Cl_2\right]\left[H_2S\right]$

Now if we consider option (2) we find

$$\text{Rate}=k\left[Cl_2\right]\left[HS^-\right]\qquad\text{...(1)}$$

From equation (i)

$$k=\frac{\left[H^+\right]\left[HS^-\right]}{H_2S}\quad\text{or}\quad\left[HS^-\right]=\frac{k\left[H_2S\right]}{H^+}$$

Substituting this value in equation (1) we find

$$\text{Rate}=k\left[Cl_2\right]K\frac{\left[H_2S\right]}{H^+}=k'\frac{\left[Cl_2\right]\left[H_2S\right]}{\left[H^+\right]}$$

hence only, mechanism (1) is consistent with the given rate equation.

33. **(c)** Since for every 10°C rise in temperature rate doubles for 50°C rise in temp increase in reaction rate $=2^5=32$ times

34. **(b)** For a first order reaction

$$k=\frac{2.0303}{t}\log\frac{a}{a-x}=\frac{2.303}{40}\log\frac{0.1}{0.025}$$

$$=\frac{2.303}{40}\log 4=\frac{2.303\times 0.6020}{40}=3.47\times 10^{-2}$$

$R=K(A)^1=3.47\times 10^{-2}\times 0.01=3.47\times 10^{-4}$

35. **(a)** Activation energy can be calculated from the equation

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

given $\frac{k_2}{k_1}=2\quad T_2=310\text{ K}\quad T_1=300\text{ K}$

$$=\log 2=\frac{-E_a}{2.303\times 8.314}\left(\frac{1}{310}-\frac{1}{300}\right)$$

$E_a=53598.6\text{ J/mol}=53.6\text{ kJ/mol}$.

36. **(d)** Let rate of reaction $=\frac{d[C]}{t}=k[A]^x[B]^y$

Now from the given data
$1.2\times 10^{-3}=k[0.1]^x[0.1]^y$ .....(i)
$1.2\times 10^{-3}=k[0.1]^x[0.2]^y$ .....(ii)
$2.4\times 10^{-3}=k[0.2]^x[0.1]^y$ .....(iii)
Dividing equation (i) by (ii)

$$\Rightarrow\ \frac{1.2\times 10^{-3}}{1.2\times 10^{-3}}=\frac{k[0.1]^x[0.1]^y}{k[0.1]^x[0.2]^y}$$

We find, $y=0$
Now dividing equation (i) by (iii)

$$\Rightarrow\ \frac{1.2\times 10^{-3}}{2.4\times 10^{-3}}=\frac{k[0.1]^x[0.1]^y}{k[0.2]^x[0.1]^y}$$

We find, $x=1$

Hence $\frac{d[C]}{dt}=k[A]^1[B]^0$

37. **(c)** Reactions of higher order (>3) are very rare due to very less chances of many molecules to undergo effective collisions.

38. **(d)** $H_2O_2(aq)\rightarrow H_2O(aq)+\frac{1}{2}O_2(g)$

For a first order reaction

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

Given a = 0.5, (a − x) = 0.125, t = 50 min

$$\therefore\quad k=\frac{2.303}{50}\log\frac{0.5}{0.125}$$

$=2.78\times 10^{-2}\ \text{min}^{-1}$
$r=k[H_2O_2]=2.78\times 10^{-2}\times 0.05$
$=1.386\times 10^{-3}\ \text{mol min}^{-1}$

Now

$$-\frac{d\left[H_2O_2\right]}{dt}=\frac{d\left[H_2O\right]}{dt}=\frac{2d\left[O_2\right]}{dt}$$

$$\therefore\ \frac{2d\left[O_2\right]}{dt}=-\frac{d\left[H_2O_2\right]}{dt}$$

$$\therefore\ \frac{d\left[O_2\right]}{dt}=\frac{1}{2}\times\frac{d\left[H_2O_2\right]}{dt}$$

$$=\frac{1.386\times 10^{-3}}{2}=6.93\times 10^{-4}\ \text{mol min}^{-1}$$