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
   (a) temperature *(1981 - 1 Mark)*
   (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 3.0×10^{-4} s^{-1}, 104.4 kJ mol^{-1} and 6.0×10^{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) $3.6 \times 10^{30}\, s^{-1}$

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 $3.0 \times 10^{-5}\ sec^{-1}$. 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. 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 $= -d[N_2]/dt = -1/3\, d[H_2]/dt = 1/2\, d[NH_3]/dt$
(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 $= -d[N_2]/dt = -d[H_2]/dt = d\,[NH_3]/dt$

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, $A \rightarrow$ 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) $1.73 \times 10^{-5}\, M\, min^{-1}$

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. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$; $k_1 = 6.8 \times 10^{-3}$
$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $k_2 = 1.6 \times 10^{-3}$
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}

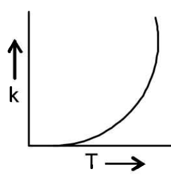
18. Consider a reaction $aG + bH \rightarrow$ Products. When concentration of both the reactants *G* and *H* is doubled, the rate increases by eight times. However, when concentration of *G* is doubled keeping the concentration of *H* fixed, the rate is doubled. The overall order of the reaction is *(2007)*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

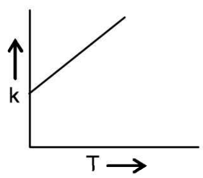
19. A positron is emitted from $^{23}_{11}Na$. The ratio of the atomic mass and atomic number of the resulting nuclide is *(2007)*
(a) 22/10 (b) 22/11
(c) 23/10 (d) 23/12

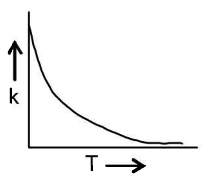
20. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio (k_1/k_0) of the rate constant for first order (k_1) and zero order (k_0) of the reaction is – *(2008)*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

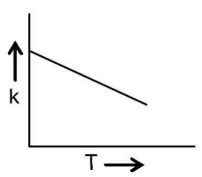
21. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (*k*) was found to follow the equation $\log k = -(2000)\frac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a, respectively, are *(2009)*
(a) $1.0 \times 10^6\ s^{-1}$ and 9.2 kJ mol^{-1}
(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}

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

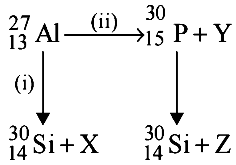
(a)


(b)


(c)


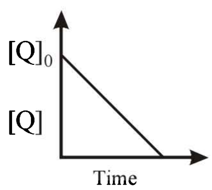
(d)


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 $M \rightarrow N$, 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 ***(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)***
$$RCl + NaOH(aq.) \rightarrow ROH + NaCl$$
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.

3. Nuclear reactions accompanied with emission of neutron(s) are : ***(1988 - 1 Mark)***
(a) $^{17}_{13}Al + ^{4}_{2}H \rightarrow ^{30}_{15}P$
(b) $^{12}_{6}C + ^{1}_{1}H \rightarrow ^{13}_{7}N$
(c) $^{30}_{15}P \rightarrow ^{30}_{14}Si + ^{0}_{1}e$
(d) $^{241}_{96}Am + ^{4}_{2}He \rightarrow ^{244}_{97}Bk + ^{0}_{1}e$

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, $X \rightarrow P$
(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

6. For the first order reaction ***(2011)***
$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$
(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 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)*

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_1H to ^1_1H 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)*

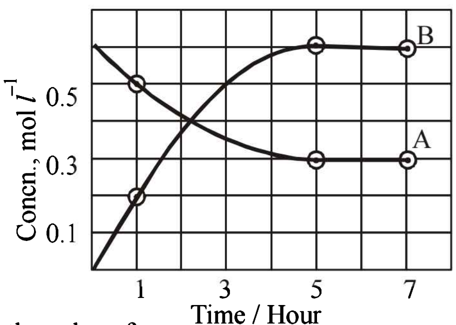
12. A first order reaction $A \rightarrow B$, requires activation energy of 70kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy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

$$\log(K) = 14.34 - \frac{1.25\times10^4 K}{T}$$ ***(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 $1.5\times10^7\ s^{-1}$ at 50°C and $4.5\times10^7\ s^{-1}$ 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 $4.5\times10^{-3}\ min^{-1}$. 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*) $_{92}Th^{234} \longrightarrow .... + 7\ _2He^4 + 6\ _{-1}\beta^0$ ***(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)***

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).

$$_7N^{14} + {_0}n^1 \longrightarrow {_6}C^{14} + {_1}H^1$$

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 :

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

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 $\rightarrow$ 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. 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) $\frac{1}{\text{time}}$ vs C_t
(c) time vs C_t (d) $\frac{1}{\text{time}}$ 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]**

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

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

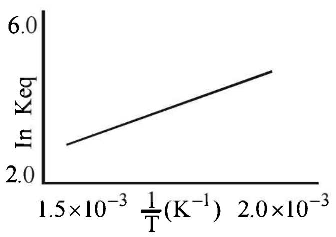
16. Hydrogen bomb is based on the principle of **[2005]**

(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 ($A_2 + B_2 \to 2AB$) 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 $\rightarrow$ 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 $\frac{1}{2}A \rightarrow 2B$, 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 :

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

The rate equation for this reaction is

rate = $k[Cl_2][H_2S]$

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

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

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

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

$Cl_2 + HS^- \rightarrow 2Cl^- + H^+ + S$ (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) $\rightarrow$ 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 $2A + B \rightarrow C + D$, 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}