Exercise-1

✍ **Marked questions are recommended for Revision.**

PART - I : SUBJECTIVE QUESTIONS

CHEMICAL KINETICS-I

Section (A) : Rate of chemical reaction and Dependence of Rate : Basic

A-1. The oxidation of iodide ion by peroxy disulphate ion is described by the equation :

$$3I^- (aq) + S_2O_8^{2-} (aq) \longrightarrow I_3^- (aq) + 2SO_4^{2-} (aq)$$

(a) If $-\dfrac{\Delta[S_2O_8^{2-}]}{\Delta t} = 1.5 \times 10^{-3}\ Ms^{-1}$ for a particular time interval, what is the value of $-\dfrac{\Delta[I^-]}{\Delta t}$ for the same time interval ?

(b) What is the average rate of formation of SO_4^{2-} during that time interval ?

A-2.✍ In the following reaction $2H_2O_2\,(aq) \longrightarrow 2H_2O(\ell) + O_2\,(g)$ rate of formation of O_2 is 36 g min^{-1},

(a) What is rate of formation of H_2O? (b) What is rate of disappearance of H_2O_2?

A-3. Hydrogenation of vegetable ghee at 25ºC reduces the pressure of H_2 from 2 atm to 1.2 atm in 50 minute. Calculate the rate of reaction in terms of change :

(a) In pressure per minute. (b) In molarity per second.

A-4. The stoichiometric equation for the oxidation of bromide ions by hydrogen peroxide in acid solution is

$$2Br^- (aq) + H_2O_2\,(aq) + 2H^+ (aq) \longrightarrow Br_2\,(\ell) + 2H_2O\,(\ell)$$

Since the reaction does not occur in one stage, the rate equation does not correspond to this stoichiometric equation but is rate = $k[H_2O_2]\,[H^+]\,[Br^-]$.

(a) If the concentration of H_2O_2 is increased by a factor of 3, by what factor is the rate of consumption of Br^- ions increased.

(b) If, under certain conditions, the rate of consumption of Br^- ions is 7.2×10^{-3} mole $dm^{-3}\,s^{-1}$, what is the rate of consumption of hydrogen peroxide. What is the rate of production of bromine.

(c) What is the effect on the rate constant k of increasing the concentration of bromide ions.

(d) If by the addition of water to the reaction mixture the total volume were doubled, what would be the effect on the rate of change of the concentration of Br^-. What would be the effect on the rate constant k.

Section (B) : Integrated rate law : Zero and First Order Reaction

B-1. For the zero order reaction $A \longrightarrow 2B$, the rate constant is 2×10^{-6} M min^{-1}. The reaction is started with 10 M of A.

(i) What will be the concentration of A after 2 days? (ii) What is the initial half-life of the reaction ?

(iii) In what time, the reaction will complete?

B-2.✍ Substance A reacts according to a first order rate law with $k = 5 \times 10^{-5}\ s^{-1}$.

(a) If the initial concentration of A is 1.0 M, what is initial rate.

(b) What is the rate after 1.0 hour. (Given $e^{-0.18} = 0.84$)

B-3.✍ A and B are two different chemical species undergoing 1st order decomposition with half lives equal to 5 sec. and 7.5 sec. respectively. If the initial concentration of A and B are in the ratio 3 : 2. Calculate $\dfrac{C_{A_t}}{C_{B_t}}$ after three half lives of A. Report your answer after multiplying it with 100.

B-4.✍ In the biological processes, the time taken by certain virus or bacteria to double its population, is called generation time. In milk, at 37ºC, lactobacillus acidophilus has a generation time of about 75 min. Calculate the population relative to the initial value at 60 min.

Section (C) : Integrated Rate law : Second Order & Pseudo first order reaction

C-1. The rate constant for a certain second order reaction is 8×10^{-5} M^{-1} min^{-1} . How long will it take a 1 M solution to be reduced to 0.5 M in reactant ? How long will it take from that point until the solution is 0.25 M in reactant.

C-2. Compound A and B react to form C and D in a reaction that was found to be second-order over all and second-order in A . The rate constant –at 30ºC is 0.622 L mol^{-1} min^{-1}. What is the half-life of A when 4.10×10^{-2} M of A is mixed with excess B ?

C-3. The reaction $CH_3–CH_2–NO_2 + OH^- \longrightarrow CH_3–\overset{\ominus}{C}H–NO_2 + H_2O$ obeys the rate law for pseudo first order kinetics in the presence of a large excess of hydroxide ion. If 1% of nitro ethane undergoes reaction in half a minute when the reactant concentration is 0.002 M. What is the pseudo first order rate constant ? (log 99 = 1.996)

Section (D) : Experimental method to calculate order and rate law of reaction and methods to monitor the progress of reaction

D-1.✍ The following data are for the reaction A + B $\rightarrow$ products :

conc. A (M)	**conc. B (M)**	**Initial Rate (mol L^{-1} s^{-1})**
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	2.0×10^{-3}
0.5	0.5	1.0×10^{-2}

(i) What is the order with respect to A and B for the reaction?
(ii) Calculate the rate constant.
(iii) Determine the reaction rate when the concentrations of A and B are 0.20 M and 0.35 M, respectively.

D-2. **(a)** The half life period and initial concentration for a reaction are as follows. What is order of reaction?

Initial concentration	350	540	158
$t_{1/2}$	425	275	941

(b) The half-life period for the thermal decomposition of PH_3 at three different pressures are given below

Initial pressure (mm Hg)	707	79	37.5
Half--life (seconds)	84	84	83

What is the order of the reaction ?

D-3.✍ For the reaction A $\longrightarrow$ products, the following data is given for a particular run.

time (min.) :	0	5	15	35
$\frac{1}{[A]}$ (M^{-1}) :	1	2	4	8

Determine the order of the reaction.

Section (E) : Method to monitor the progress of Reactions (Titration Method and Optical Activity Method)

E-1. The kinetic of hydrolysis of methyl acetate in excess dilute HCl at 25°C were followed by withdrawing 2 mL of the reaction mixture at intervals of (t), adding 50 mL water and titrating with baryta water. Determine the velocity constant of hydrolysis.

t (in minute)	0	75	119	259	∞
Titre value (in mL)	19.24	24.20	26.60	32.23	42.03

$[\ln \frac{22.79}{17.83} = 0.2454, \ln \frac{22.79}{15.43} = 0.39, \ln \frac{22.79}{9.8} = 0.8439]$

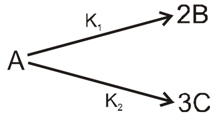
E-2. The decomposition of hydrogen peroxide in an aqueous solution is a first order reaction. It can be studied by titrating quickly 10 mL portions of reactions mixture at various times from the t = 0 of reaction against a standard solution of $KMnO_4$. Volume of $KMnO_4$ solution used in each case is proportional to the remaining concentration of H_2O_2.
From the following data calculate the rate constant of the reaction,

Time (seconds)	0	600	1200
$KMnO_4$ solution used (mL)	22.8	13.8	8.2

E-3. For a first order reaction $A \longrightarrow 2B + C$. It was found that at the end of 10 minutes from the start, the total optical rotation of the system was 60° and when the reaction is complete, it was 180°. The B and C are only optically active and intially only A was taken.
(i) What is the rate constant of the above reaction (in $hour^{-1}$) ?
(ii) At what time (in minute) from the start, total optical rotation will be 90º.
(Take log2 = 0.3, log3 = 0.48, log7 = 0.85, ln10 = 2.3)

Section (F) : Complication in 1st Order Reaction

F-1.✍ For a first order reaction



Percentage of B in the product is 30%.Calculate the value of k_1 and k_2. ($(t_{1/2})_{\text{over all}}$ = 100 hr))

F-2. An organic compound dissociates into n parallel first order reactions simultaneously and produces n different products P_1, P_2, P_3, ..., P_n having rate constants k, 2k, 3k, ..., nk and activation energies E, 2E, 3E ...., nE respectively. Calculate the overall energy of activation of the compound P.

CHEMICAL KINETICS-II

Section (G) : Temperature dependence of rate

G-1. From the following data for the reaction between A and B.

	[A] (mole dm^{-3})	[B] (mole dm^{-3})	Initial rate (mole dm^{-3} min^{-1})	
			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 the following
(i) The order w.r.t. A and w.r.t. B
(ii) The rate constant at 300 K
(iii) The energy of activation
(iv) The pre-exponential factor
[$e^{-22.18} = 2.3283 \times 10^{-10}$, ln2 = 0.693]

G-2.✍ Find out the percentage of the reactant molecules crossing over the activation energy barrier at 325 K, given that ΔH_{325} = 0.12 kcal, $E_{a(b)}$ = + 0.02 kcal.

G-3. Consider the following figure for the reaction :

$$A + B \longrightarrow M + N$$

Answer the following :

(A) Energy level of (A + B)

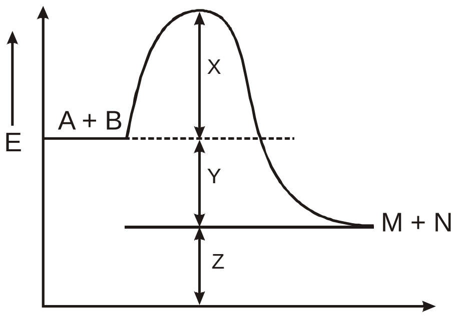
(B) Energy lelvel of (M + N)

(C) Threshold energy level for the reaction

(D) Energy of activation for the forward reaction.

(E) Energy of activation for the backward reaction.

(F) ΔH or heat of reaction.



→ Energy of activation diagram

Section (H) : Catalyst dependence of rate and type of Reaction and Determination of rate law and order with the help of given mechanism

H-1.✍ On introducing a catalyst at 500 K, the rate of a first order increase to 1.718 times. The activation energy in the presence of a catalyst is 6.05 KJ/mole. The slope of the plot of lnk (sec^{-1}) against 1/T in the absence of catalyst is.

H-2. The thermal decomposition of N_2O_5 occurs in the following steps.

Step - I $N_2O_5 \xrightarrow{slow} NO_2 + NO_3$

Step - II $N_2O_5 + NO_3 \xrightarrow{fast} 3NO_2 + O_2$

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

suggest the rate expression.

H-3. The reaction $2NO\ (g) + Br_2\ (g) \longrightarrow 2NOBr\ (g)$, obeys the following mechanism.

(i) $NO\ (g) + Br_2\ (g) \xrightleftharpoons{Fast} NOBr_2\ (g)$

(ii) $NOBr_2\ (g) + NO\ (g) \xrightarrow{Slow} 2NOBr\ (g)$

Suggest the rate expression.

H-4. Given the following steps in the mechanism for a chemical reaction :

$A + B \longrightarrow C$ (fast)

$B + C \longrightarrow D + E$ (slow)

$D + F \longrightarrow A + E$ (fast)

At any time [C] is directly proportional to [A].

(a) What is the stoichiometric equation for the reaction ?

(b) Which species, if any, are catalysts in this reaction ?

(c) Which species, if any, are intermediates in this reaction?

(d) Write the rate law for the rate-determining step.

(e) Write the rate law for this reaction.

(f) What is overall order of the reaction ?

Section (I) : Radio Activity

I-1.✍ The activity of a radio-isotope falls to 12.5% in 90 days. Compute the half life and decay constant of the radio-isotope.

I-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.

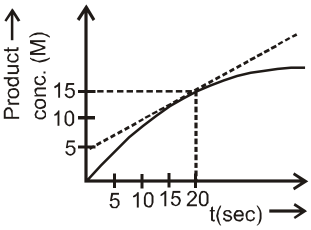
I-3. 1 gram of $_{79}Au^{198}$ ($t_{1/2}$ = 65 hrs) decays by beta emission and produces stable mercury. How much mercury will be present after 260 hours.

I-4. A sample of U^{238} (half life = 4.5×10^9 year) ore is found to contain 23.8 g of U^{238} and 20.6 g of Pb^{206}. Calculate the age of the ore.

PART - II : ONLY ONE OPTION CORRECT TYPE

CHEMICAL KINETICS-I

Section (A) : Rate of chemical reaction and Dependence of Rate : Basic

A-1. 

Rate of formation of product at t = 20 seconds is

(A) 0.5 MS^{-1} (B) 1 M S^{-1} (C) 1.5 M S^{-1} (D) 2MS^{-1}

A-2. In the following reaction : $xA \longrightarrow yB$

$$\log\left[-\frac{d[A]}{dt}\right] = \log\left[\frac{d[B]}{dt}\right] + 0.3$$

where –ve sign indicates rate of disappearance of the reactant. Thus, x : y is :

(A) 1 : 2 (B) 2 : 1 (C) 3 : 1 (D) 3 : 10

A-3. Rate of formation of SO_3 in the following reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is 100 g min^{-1}. Hence rate of disappearance of O_2 is :

(A) 50 g min^{-1} (B) 40 g min^{-1} (C) 200 g min^{-1} (D) 20 g min^{-1}

A-4. $aA + bB \longrightarrow$ Product, $dx/dt = k\,[A]^a\,[B]^b$. If concentration of A is doubled, rate is four times. If concentration of B is made four times, rate is doubled. What is relation between rate of disappearance of A and that of B ?

(A) $-\{d\,[A] / dt\} = -\{d\,[B] / dt\}$
(B) $-\{d\,[A] / dt\} = -\{4\,d\,[B] / dt\}$
(C) $-\{4\,d\,[A] / dt\} = -\{d\,[B]/ dt\}$
(D) None of these

A-5. For the reaction, $2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$ the rate expression can be written in the following ways:

$\{d\,[N_2] / dt\} = k_1\,[NO][H_2]$; $\{d[H_2O] / dt\} = k[NO][H_2]$; $\{-\,d[NO] / dt\} = k'_1\,[NO]\,[H_2]$; $\{-d[H_2] / dt\} = k''_1\,[NO][H_2]$

The relationship between k, k_1 , k'_1 and k''_1. is :

(A) $k = k_1 = k'_1 = k''_1$ (B) $k = 2k_1 = k'_1 = k''_1$ (C) $k = 2k'_1 = k_1 = k''_1$ (D) $k = k_1 = k'_1 = 2\,k''_1$

A-6. For a reaction $pA + qB \rightarrow$ products, the rate law expression is $r = k[A]^1\,[B]^m$, then :

(A) (p+1) < (1+ m)
(B) (p + q) > (1 + m)
(C) (p + q) may or may not be equal to (1+ m)
(D) (p + q) = (1 + m)

A-7. For the irreversible process, $A + B \longrightarrow$ products, the rate is first–order w.r.t. A and second–order w.r.t. B. If 1.0 mol each of A and B introduced into a 1.0 L vessel, and the initial rate was 1.0×10^{-2} mol L^{-1} s^{-1} , rate when half reactants have been turned into products is :

(A) 1.25×10^{-3} mol L^{-1} s^{-1}
(B) 1.0×10^{-2} mol L^{-1} s^{-1}
(C) 2.50×10^{-3} mol L^{-1} s^{-1}
(D) 2.0×10^{-2} mol L^{-1} s^{-1}

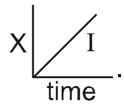
A-8. If rate constant is numerically the same for the three reactions of first, second and third order respectively. Assume all the reactions of the kind $A \rightarrow$ products. Which of the following is correct :

(A) if [A] = 1 then $r_1 = r_2 = r_3$
(B) if [A] < 1 then $r_1 > r_2 > r_3$
(C) if [A] > 1 then $r_3 > r_2 > r_1$
(D) All

Section (B) : Integrated rate law : Zero and First Order Reaction

B-1. The rate constant of the reaction A → 2B is 1.0×10^{-3} mol lit^{-1} min^{-1}, if the initial concentration of A is 1.0 mole lit^{-1} what would be the concentration of B after 100 minutes.
(A) 0.1 mol lit^{-1} (B) 0.2 mol lit^{-1} (C) 0.9 mol lit^{-1} (D) 1.8 mol lit^{-1}

B-2. A drop of solution (volume 0.05 mL) contains 3.0×10^{-6} moles of H^+. If the rate constant of disappearance of H^+ is 1.0×10^{7} mole $litre^{-1}$ sec^{-1}. How long would it take for H^+ in drop to disappear :
(A) 6×10^{-8} sec (B) 6×10^{-7} sec (C) 6×10^{-9} sec (D) 6×10^{-10} sec

B-3. Graph between concentration of the product and time of the reaction A → B is of the type 

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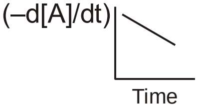
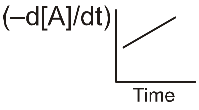
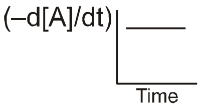
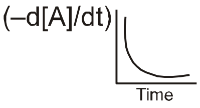
Hence graph between – d[A]/dt and time will be of the type :

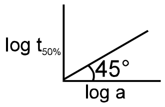
(A) 

(B) 

(C) 

(D) 

B-4. What will be the order of reaction and rate constant for a chemical change having log $t_{50\%}$ vs log concentration of (A) curves as :

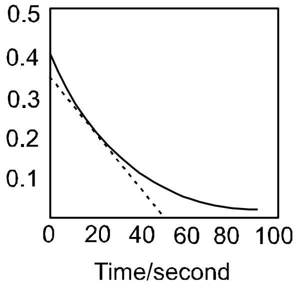


(A) 0, 1/2 (B) 1, 1 (C) 2, 2 (D) 3, 1

B-5. For a reaction 2A + B → product, rate law is $-\frac{d[A]}{dt} = k[A]$. At a time when $t = \frac{1}{k}$, concentration of the reactant is : (C_0 = initial concentration)
(A) $\frac{C_0}{e}$ (B) C_0e (C) $\frac{C_0}{e^2}$ (D) $\frac{1}{C_0}$

B-6. Two substances A ($t_{1/2}$ = 5 min) and B ($t_{1/2}$ = 15 min) are taken in such a way that initially [A] = 4[B]. The time after which both the concentration will be equal is : (Assume that reaction is first order)
(A) 5 min (B) 15 min
(C) 20 min (D) concentration can never be equal

B-7. A reaction follows the given concentration (M)–time graph. The rate for this reaction at 20 seconds will be :



(A) 4×10^{-3} M s^{-1} (B) 8×10^{-2} M s^{-1} (C) 2×10^{-2} M s^{-1} (D) 7×10^{-3} M s^{-1}

B-8. In a first order reaction the reacting substance has half-life period of ten minutes. What fraction of the substance will be left after an hour the reaction has occurred ?
(A) 1/6 of initial concentration (B) 1/64 of initial concentration
(C) 1/12 of initial concentration (D) 1/32 of initial concentration

B-9. A certain zero order reaction has k = 0.025 M s^{-1} for the disappearance of A. What will be the concentration of A after 15 seconds if the initial concentration is 0.50 M ?
(A) 0.50 M (B) 0.375 M (C) 0.125 M (D) 0.060 M

Section (C) : Integrated Rate law : Second Order & Pseudo first order reaction

C-1. A reaction, which is second order, has a rate constant of 0.002 L mol^{-1} s^{-1}. If the initial conc. of the reactant is 0.2 M. how long will it take for the concentration to become 0.0400 M ?

(A) 1000 sec (B) 400 sec (C) 200 sec (D) 10, 000 sec

C-2.✍ Which is not true for a second order reaction ?

(A) It can have rate constant 1×10^{-2} L mol^{-1} s^{-1}

(B) Its half-life is inversely proportional to its initial concentration

(C) Time to complete 75% reaction is twice of half-life

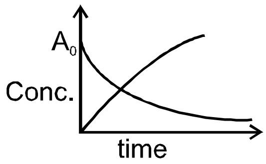
(D) $T_{50} = \frac{1}{K \times \text{Initial conc.}}$

C-3. For the reaction $2NO_2 \longrightarrow N_2O_2 + O_2$, rate expression is as follows :

$-\frac{d[NO_2]}{dt} = k\,[NO_2]^n$, where $k = 3 \times 10^{-3}$ mol^{-1} L sec^{-1}. If the rate of formation of oxygen is 1.5×10^{-4} mol L^{-1} sec^{-1}, then the molar concentration of NO_2 in mole L^{-1} is

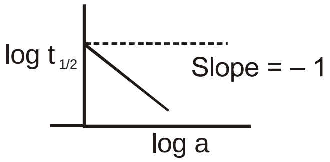
(A) 1.5×10^{-4} (B) 0.0151 (C) 0.214 (D) 0.316

C-4.✍ At the point of intersection of the two curves shown, the conc. of B is given by.......for, A → nB :



(A) $\frac{nA_0}{2}$ (B) $\frac{A_0}{n-1}$ (C) $\frac{nA_0}{n+1}$ (D) $\left(\frac{n-1}{n+1}\right)A_0$

C-5. A graph between log $t_{1/2}$ and log a (abscissa) a being the initial concentration of A in the reaction For reaction A → Product, the rate law is



(A) $\frac{-d[A]}{dt} = k$ (B) $\frac{-d[A]}{dt} = k\,[A]$ (C) $\frac{-d[A]}{dt} = k\,[A]^2$ (D) $\frac{-d[A]}{dt} = k\,[A]^3$

Section (D) : Experimental Method to calculate order and rate law of reaction and Methods to Monitor the progress of Reaction

D-1. The data for the reaction A + B → C is

Exp.	$[A]_0$	$[B]_0$	initial rate
1	0.012	0.035	0.10
2	0.024	0.035	0.80
3	0.012	0.070	0.10
4	0.024	0.070	0.80

The rate law is

(A) $r = k\,[B]^3$ (B) $r = k\,[A]^3$ (C) $r = k\,[A]\,[B]^4$ (D) $r = k\,[A]^2\,[B]^2$.

D-2. The kinetic data for the given reaction A(g) + 2B(g) $\longrightarrow$ C(g) is provided in the following table for three experiments at 300 K.

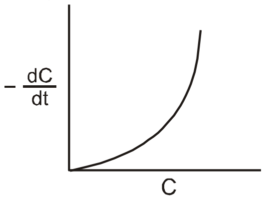
Ex. No.	**[A/M]**	**[B/M]**	**[Initial rate (M sec^{-1})]**
1	0.01	0.01	6.930×10^{-6}
2	0.02	0.01	1.386×10^{-5}
3	0.02	0.02	1.386×10^{-5}

In another experiment starting with intitial concentration of 0.5 and 1 M respectively for A and B at 300 K. Find the rate of reaction after 50 minutes from start of experiment (in m/sec) ?

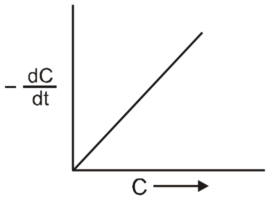
(A) 6.93×10^{-4} (B) 0.25×10^{-7} (C) 4.33×10^{-5} (D) 3.46×10^{-9}

D-3.✍ In three different reactions, involving a single reactant in each case, a plot of rate of the reaction on the y–axis, versus concentration of the reactant on the x–axis, yields three different curves shown below.

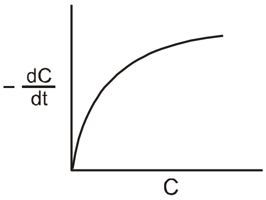
(i)



(ii)



(iii)



What are the possible orders of the reactions (i), (ii), (iii).

(A) 1, 2, 3 (B) 2, 1, 1/2 (C) 0, 1, 2 (D) 0, 1, ½

D-4. At 373 K, a gaseous reaction A → 2B + C is found to be of first order. Starting with pure A, the total pressure at the end of 10 min was 176 mm of Hg and after a long time when A was completely dissociated, it was 270 mm of Hg. The pressure of A at the end of 10 minutes was :

(A) 94 mm of Hg (B) 47 mm of Hg (C) 43 mm of Hg (D) 90 mm of Hg

D-5. The reaction A(s) → 2 B(g) + C(g) is first order. The pressure after 20 min and after very long time are 150 mm Hg and 225 mm Hg. The value of rate constant and pressure after 40 min are :

(A) 0.05 In 1.5 min^{-1} ,200 mm (B) 0.5 ln 2 min^{-1} ,300 mm
(C) 0.05 In 3 min^{-1}, 300 mm (D) 0.05 In 3 min^{-1} , 200 mm

D-6. Which integrated equation is correct for the following Ist order reaction started with only A(g) in a closed rigid vessel.

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

P_i = initial pressure ; P_t = total pressure at time t

(A) $K = \frac{2.303}{t}\log_{10}\left[\frac{P_i}{P_t}\right]$ (B) $K = \frac{2.303}{t}\log_{10}\left[\frac{P_t}{P_i}\right]$

(C) $K = \frac{2.303}{t}\log_{10}\left[\frac{2P_i}{3P_i - P_t}\right]$ (D) $K = \frac{2.303}{t}\log_{10}\left[\frac{3P_i}{2P_i - 3P_t}\right]$

D-7. The decompostion NH_3 gas on a heated tungsten surface gave the following results :

Initial pressure (mm of Hg)	65	105	y	185
Half-life (sec)	290	x	670	820

Calculate approximately the values of x and y.

(A) x = 410 sec, y = 115 mm of Hg (B) x = 467 sec , y = 150 mm of Hg
(C) x = 490 sec, y = 120 mm of Hg (D) x = 430 sec, y = 105 mm of Hg

D-8.✍ In the reaction NH_4NO_2 (aq.) → N_2 (g) + 2 H_2O (l) the volume of N_2 after 20 min and after a long time is 40 ml and 70 ml respectively. The value of rate constant is :

(A) (1/20) log (7/4) min^{-1} (B) (2.303 /1200) log (7/3) sec^{-1}
(C) (1/20) log (7/3) min^{-1} (D) (2.303 / 20) log (11/7) min^{-1}

D-9.^ If no catalyst (H^+) is present in acid hydrolysis of ester then rate constant k is : (Where V_0, V_t and V_∞ are volumes of NaOH used to titrate reaction mixture at t = 0, t = t and t = ∞)

(A) $\frac{2.303}{t}\log\frac{V_0}{(V_t - V_\infty)}$ (B) $\frac{2.303}{t}\log\frac{V_\infty}{(V_\infty - V_t)}$

(C) $\frac{2.303}{t}\log\frac{V_0}{V_t}$ (D) $\frac{2.303}{t}\log\frac{V_\infty}{(V_t - V_\infty)}$

Section (E) : Method to monitor the progress of Reactions (Titration Method and Optical Activity Method)

E-1. For a reaction A $\longrightarrow$ B + C, it was found that at the end of 10 minutes from the start the total optical rotation of the system was 50° and when the reaction is complete, it was 100°. Assuming that only B and C are optically active and dextrorotatory. Calculate the rate constant of this first order reaction.

(A) 0.693 min^{-1} (B) 0.0693 sec^{-1} (C) 0.0693 min^{-1} (D) 0.00693 sec^{-1}

E-2. The following data were obtained in an experiment on inversion of cane sugar (a first order kinetics)

Time (min)	0	10	After a long time
Total angle of rotation (degree)	+40	+15	– 10

The rate constant (in $second^{-1}$) is [ln 2 = 0.693]

(A) 0.0693 (B) 1.15×10^{-3} (C) 0.693 (D) 1.15×10^{-2}

E-3. Half life of reaction : $H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$ is independent of initial concentration of H_2O_2 volume of O_2 gas after 20 minute is 5L at 1 atm and 27°C and after completion of reaction 50L. The rate constant is

(A) $\frac{1}{20}\log 10\,min^{-1}$ (B) $\frac{2.303}{20}\log 10\,min^{-1}$

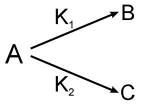
(C) $\frac{2.303}{20}\log\frac{50}{45}min^{-1}$ (D) $\frac{2.303}{20}\log\frac{45}{50}min^{-1}$

E-4. The decomposition of N_2O_5 in chloroform was followed by measuring the volume of O_2 gas evolved : $2N_2O_5(CCl_4) \rightarrow 2N_2O_4(CCl_4) + O_2(g)$. The maximum volume of O_2 gas obtained was 100 cm^3. In 500 minutes, 90 cm^3 of O_2 were evolved. The first order rate constant (in min^{-1}) for the disappearance of N_2O_5 is :

(A) $\frac{2.303}{500}$ (B) $\frac{2.303}{500}\log\frac{100}{90}$ (C) $\frac{2.303}{500}\log\frac{90}{100}$ (D) $\frac{100}{10\times 500}$

Section (F) : Complication in 1st Order Reaction

F-1. The substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as :



$K_1 = 1.26 \times 10^{-4}\ sec^{-1}$ and $K_2 = 3.8 \times 10^{-5}\ sec^{-1}$

The percentage distribution of B and C

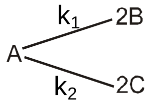
(A) 80% B and 20% C (B) 76.83% B and 23.17%C

(C) 90% B and 10% C (D) 60% B and 40% C

F-2. The rate constant for two parallel reactions were found to be $1.0 \times 10^{-2} dm^3\ mol^{-1}\ s^{-1}$ and $3.0 \times 10^{-2}\ dm^3 mol^{-1} s^{-1}$. If the corresponding energies of activation of the parallel reactions are 60.0 kJ mol^{-1} and 70.0 kJ mol^{-1} respectively, what is the apparent overall energy of activation ?

(A) 130.0 kJ mol^{-1} (B) 67.5 kJ mol^{-1} (C) 100.0 kJ mol^{-1} (D) 65.0 kJ mol^{-1}

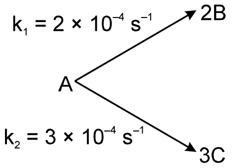
F-3. For a hypothetical elementary reaction.



where $\frac{k_1}{k_2} = \frac{1}{2}$

Initially only 2 moles of A are present. The total number of moles of A, B and C at the end of 75% of reaction are :

(A) 2 (B) 3 (C) 4 (D) 3.5

F-4. For the follwing parallel chain reaction  if the sum of the concentration of B and C at any time is 2M then what will be $[B]_t$ and $[C]_t$ respectively ?

(A) $\frac{11}{12}$M , $\frac{13}{12}$M (B) $\frac{3}{4}$M,$\frac{5}{4}$M (C) $\frac{4}{5}$M,$\frac{6}{5}$M (D) $\frac{8}{13}$M,$\frac{18}{13}$M

CHEMICAL KINETICS-II

Section (G) : Temperature dependence of rate

G-1. The rate constant, the activation energy and the frequency factor 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 :

(A) $2.0 \times 10^{18}\ s^{-1}$ (B) $6.0 \times 10^{14}\ s^{-1}$ (C) infinite (D) $3.6 \times 10^{30}\ s^{-1}$

G-2. The rate constant K_1 of a reaction is found to be double that of rate constant K_2 of another reaction. The relationship between corresponding activation energies of the two reactions at same temperature (E_1 and E_2) can be represented as :

(A) $E_1 > E_2$ (B) $E_1 < E_2$ (C) $E_1 = E_2$ (D) None of these

G-3. When a graph between log K and 1/T is drawn a straight line is obtained. The point at which line cuts y-axis and x -axis respectively correspond to the temp :

(A) 0, E_a / 2.303 R log A (B) ∞, Ea / (R ln A)

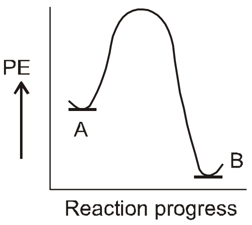
(C) 0, log A (D) None of these.

G-4. How much faster would a reaction proceed at 25°C than at 0°C if the activation energy is 65 kJ?

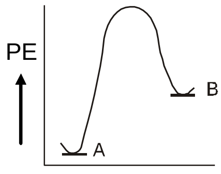
(A) 2 times (B) 5 times (C) 11 times (D) 16 times

G-5. For a reaction $A \to B$, E_a = 10 kJ mol^{-1} , ΔH = 5 kJ mol^{-1} . Thus, potential energy profile for this reaction is :

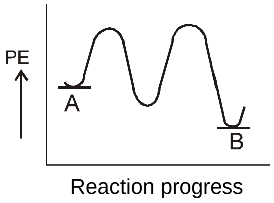
(A)



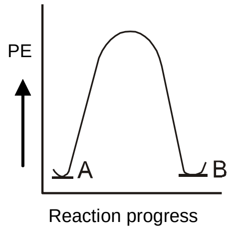
(B)



(C)



(D)

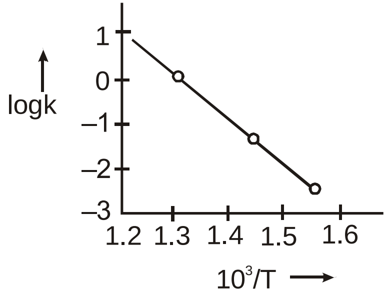


Section (H) : Catalyst dependence of rate and type of Reaction and Determination of rate law and order with the help of given mechanism

H-1.✍ The E_a of a reaction in presence of a catalyst is 4.15 kJ mol^{-1} and in absence of a catalyst is 8.3 kJ mol^{-1}. What is slope of the plot of ln k vs $\frac{1}{T}$ in the absence of catalyst

(A) + 1 (B) –1 (C) + 1000 (D) –1000

H-2. For the decomposition of HI the following logarithmic plot is shown : [R = 1.98 cal/mol-K]



The activation energy of the reaction is about

(A) 45600 cal (B) 13500 cal (C) 24600 cal (D) 32300 cal

H-3. For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ the experiment data suggested that $r = k[H_2][Br_2]^{1/2}$
The molecularity and order of the reaction are respectively :

(A) 2, 3/ 2 (B) 3/2 , 3/2 (C) Not defined, 3/2 (D) 1,1/2

H-4. The reaction of NO_2 (g) and O_3 (g) is first-order in NO_2 (g) and O_3 (g)

$$2\,NO_2(g) + O_3(g) \longrightarrow N_2O_5(g) + O_2(g)$$

The reaction can take place by mechanism :

I : $NO_2 + O_3 \xrightarrow{\text{slow}} NO_3 + O_2$

$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$

II : $O_3 \underset{k_b}{\overset{k_a\ \text{fast}}{\rightleftharpoons}} O_2 + [O]$

$NO_2 + O \xrightarrow{\text{slow}} NO_3$

$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$

Select correct mechanism.

(A) I only (B) II only (C) both I and II (D) None of I and II

H-5. A hypothetical reaction $X_2 + Y_2 \longrightarrow 2XY$ follows the mechanism given below.

$X_2 \rightleftharpoons X + X$ [Fast]

$X + Y_2 \longrightarrow XY + Y$ [Slow]

$X + Y \longrightarrow XY$ [Fast]

The order of overall reaction is

(A) 2 (B) 1 (C) 1.5 (D) Zero

H-6. The reaction of hydrogen, and iodine monochloride is represented by the equation :

$$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$$

This reaction is first–order in H_2(g) and also first–order in ICl(g). Which of these proposed mechanism can be consistent with the given information about this reaction ?

Mechanism I : $H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$

Mechanism II : $H_2(g) + ICl(g) \xrightarrow{\text{Slow}} HCl(g) + HI(g)$

$HI(g) + ICl(g) \xrightarrow{\text{fast}} HCl(g) + I_2(g)$

(A) I only (B) II only (C) both I and II (D) neither I nor II

H-7. Reaction A + B $\longrightarrow$ D + E take place as

$A + B \xrightarrow{K_1} 2C$

$C + B \xrightarrow{K_2} 2D$

$C + A \xrightarrow{K_3} 2E$

The rate of disapperance of C is given by

(A) $-\frac{d[C]}{dt} = K_2[B][C] + K_3[A][C] - 2K_1[A][B]$ (B) $-\frac{d[C]}{dt} = K_2[B][C] + K_3[E] - K_1[C]$

(C) $-\frac{d[C]}{dt} = K_2[D]O + K_3[E] - K_1[C]$ (D) $-\frac{d}{dt}[C] = 2K_1[A][B] - K_2[B][C] - K_3[A][C]$

RADIO ACTIVITY

Section (I) : Radio Activity

I-1. Radioactivity is affected by :
(A) temperature (B) Pressure
(C) electric and magnetic field (D) none of these

I-2.✍ Half life period of 10 gm radioactive element is 20 days. Then half life period of 100 gm of this element is :
(A) 20 days (B) 200 days (C) 100 days (D) 10 days

I-3. Determine the average life of U^{238} having $t_{0.5}$ = 138.5 day.
(A) 138.5 day (B) 199.86 day (C) 238 day (D) None of these

I-4. A radioactive element has a half life of one day. After three days the amount of the element left will be :
(A) 1/2 of the original amount (B) 1/4 of the original amount
(C) 1/8 of the original amount (D) 1/16 of the original amount

I-5.✍ The activity per mL of a solution of radioactive substance is x. How much water be added to 200 mL of this solution so that the acitivity falls to x/20 per mL after 4 half-lives ?
(A) 100 mL (B) 150 mL (C) 80 mL (D) 50 mL

I-6. A sample of rock from moon contains equal number of atoms of uranium and lead ($t_{1/2}$ for U = 4.5×10^9 years). The age of the rock would be :
(A) 9.0×10^9 years (B) 4.5×10^9 years (C) 13.5×10^9 years (D) 2.25×10^9 years

I-7. The half-life of ^{99}Tc is 6.0 h. The total residual activity in a patient after receiving an injection containing ^{99}Tc must not be more than 0.01 μCi , after 36.0 hours. What is the maximum activity (in μCi) that the sample injected can have ?
(A) 0.06 (B) 0.16 (C) 0.32 (D) 0.64

I-8. The radioactive decay is first order reaction. Its rate, on increasing 10ºC temperature
(A) increases 2-3 times (B) decreases 2-3 times
(C) does not change (D) increases 10 times

I-9.✍ The half – life of a radioactive isotope is 3 hours . If the initial mass of the isotope were 256 gm , the mass of it remaining undecayed after 18 hours would be :
(A) 4 gm (B) 8 gm (C) 12 gm (D) 16 gm

I-10. A radioactive isotope X with half - life of 6.93×10^9 years decay to Y which is stable. A sample of rock from the moon was found to contain both the element X and Y in the mole ratio 1 : 7.What is the age of the rock?
(A) 2.079×10^{10} years (B) 1.94×10^{10} years (C) 1.33×10^9 years (D) 10^{10} years

PART - III : MATCH THE COLUMN

1.✍ Match the following :

	Column-I		**Column -II**
	(Graph)		**(Slope)**
(A)	c vs t (abscissa) for zero order	(p)	unity
(B)	log c vs t (abscissa) for first order	(q)	zero
(C)	$\left(\frac{-dc}{dt}\right)$ vs c for zero order	(r)	$-k$
(D)	$\ln\left(\frac{-dc}{dt}\right)$ vs ln c for first order	(s)	$-\frac{k}{2.303}$

2. Match the following :

	Column–I		**Column–II**
(A)	$A + B \longrightarrow C + D$ $r = k_1 [A] [B]$	(p)	Unit of rate constant possess concentration unit
(B)	$A + B \longrightarrow C + D$ $r = k_2 [A] [B]^o$	(q)	Rate constant for the reaction of both the reactants are equal
(C)	$A + B \longrightarrow C + D$ $r = k_3 [A]^o [B]^o$	(r)	Rate of consumption of at least one of the reactants is equal to rate of production of at least one of the products
(D)	$2A + B \longrightarrow 2C + 3D$ (s) $r = k_3 [A]^o [B]^o$	(s)	If both reactants are taken in stoichiometric ratio, half life for both reactants are equal.

3. **Match the following :**

	Column-I		**Column-II**
(A)	If the activation energy is 65 kJ then how much time faster a reaction proceed at 25ºC than at 0ºC	(p)	2
(B)	Rate constant of a first-order reaction is 0.0693 min^{-1}. If we start with 20 mol L^{-1}, it is reduced to 2.5 mol L^{-1} in how many minutes.	(q)	Zero
(C)	Half-lives of first-order and zero order reactions are same. Ratio of rates at the start of reaction is how many times of 0.693. Assume initial concentration to be same for the both.	(r)	11
(D)	The half-life periods are given , $[A]_0$ (M) 0.0677 0.136 0.272 $t_{1/2}$ (sec) 240 480 960 order of the reaction is	(s)	30

Exercise-2

✍ **Marked questions are recommended for Revision.**

PART - I : ONLY ONE OPTION CORRECT TYPE

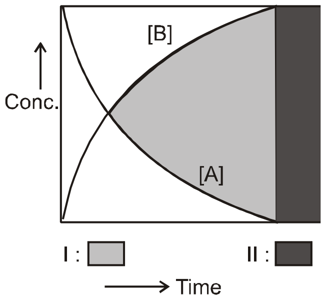
1. For a chemical reaction A → products, the rate of disappearance of A is given by :

$\frac{-dC_A}{dt} = \frac{K_1C_A}{1+K_2C_A}$ At low C_A the reaction is of the ..... order with rate constant.....(Assume K_1, K_2 are lesser than 1)

(A) I, $\frac{K_1}{K_2}$ (B) I, K_1 (C) II, K_1/K_2 (D) II, $\frac{K_1}{K_1+K_2}$

2. In the following graphical representation for the reaction

$A \longrightarrow B$ there are two types of regions :



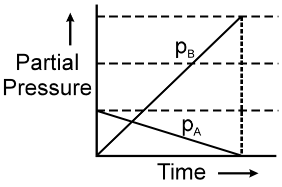
(A) I and II both represent kinetic region at different interval

(B) I and II both represent equilibrium regions at different time interval

(C) I represents kinetic while II represents equilibrium region

(D) I represents equilibrium while II represents kinetic region

3. If for a reaction in which A(g) converts to B(g) the reaction carried out at const. V & T results into the following graph.



(A) then the reaction must be $A(g) \rightarrow 3B(g)$ and is a first order reaction.
(B) then the reaction must be $A(g) \rightarrow 3B(g)$ and is a second order reaction.
(C) then the reaction must be $A(g) \rightarrow 3B(g)$ and is a zero order reaction.
(D) then the reaction must be $A(g) \leftrightarrow 3B(g)$ and is a first order reaction.

4.✍ Concentration of the reactant in first-order is reduced to $\frac{1}{e^2}$ of initial concentration after :

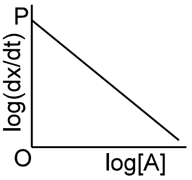
(Natural life = $\frac{1}{K}$)

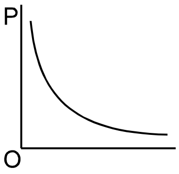
(A) one natural life-time	(B) two-natural life-time
(C) three natural life-time	(D) four natural life-time

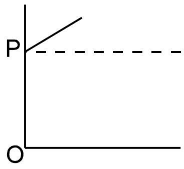
5. In a reaction involving one single reactant, the fraction of the reactant consumed may be defined as f = $\left(1-\frac{C}{C_0}\right)$ where C_0 and C are the concentrations of the reactant at the start and after time, t. For a first order reaction

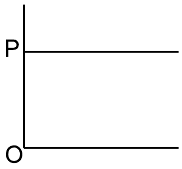
(A) $\frac{df}{dt} = k(1-f)$ (B) $-\frac{df}{dt} = kf$ (C) $-\frac{df}{dt} = k(1-f)$ (D) $\frac{df}{dt} = kf$

6.✍ $A \rightarrow$ Product and $\left(\frac{dx}{dt}\right) = k[A]^2$. If log $\left(\frac{dx}{dt}\right)$ is plotted against log [A], then graph is of the type :

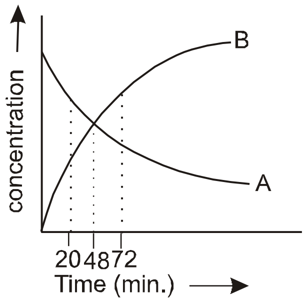
(A)


(B)


(C)


(D)


7. For a first order reaction, $nA \longrightarrow B$ whose concentration vs time curve is as shown in the figure. If half life for the reaction is 24 minutes . Find out the value of n.



(A) 1

(B) 2

(C) 3

(D) 4

8.✍ The inversion of cane sugar proceeds with half life of 50 minute at pH = 5 for any concentration of sugar. However if pH = 6, the half life changes to 500 minute of any concentration of sugar. The rate law expression for the inversion of cane sugar is written as : $r = K [sugar]^1 [H^+]^y$. Determine the value of y.
(A) $r = K [sugar]^1 [H^+]^{-1}$ (B) $r = K [sugar]^1 [H^+]^2$ (C) $r = K [sugar]^1 [H^+]^1$ (D) $r = K [sugar]^1 [H^+]^0$.

9.✍ The following data is for the decomposition of ammonium nitrite in aqeous solution.

Volume of N_2 in cc.	Time (minutes)
6.25	10
9	15
11.4	20
13.65	25
35.05	infinity

The order of the reaction is

(A) zero (B) one (C) – one (D) – two

10. For the first-order reaction T_{av} (average life), T_{50} and T_{75} in the increasing order are :

(A) $T_{50} < T_{av} < T_{75}$ (B) $T_{50} < T_{75} < T_{av}$ (C) $T_{av} < T_{50} < T_{75}$ (D) $T_{av} = T_{50} < T_{75}$

11. Formation of NO_2F from NO_2 and F_2 as per the reaction $2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$ is a second order reaction, first order with respect to NO_2 and first order with respect to F_2. If NO_2 and F_2 are present in a closed vessel in ratio 2 :1 maintained at a constant temperature with an initial total pressure of 3 atm, what will be the total pressure in the vessel after the reaction is complete?

(A) 1atm (B) 2 atm (C) 2.5 atm (D) 3 atm

12. In a hypothetical reaction, $A(aq) \rightleftharpoons 2B(aq) + C(aq)$ (1st order decomposition)

'A' is optically active (dextro-rototory) while 'B' and 'C' are optically inactive but 'B' takes part in a titration reaction (fast reaction) with H_2O_2. Hence, the progress of reaction can be monitored by measuring rotation of plane polarised light or by measuring volume of H_2O_2 consumed in titration.

In an experiment the optical rotation was found to be $\theta = 40°$ at t = 20 min and $\theta = 10°$ at t = 50 min. from start of the reaction. If the progress would have been monitored by titration method, volume of H_2O_2 consumed at t = 15 min. (from start) is 40 ml then volume of H_2O_2 consumed at t = 60 min will be:

(A) 60 ml (B) 75 ml (C) 52.5 ml (D) 90 ml

13.✍ Inversion of sucrose ($C_{12}H_{22}O_{11}$) is first-order reaction and is studied by measuring angle of rotation at different instant of time

$$\underset{\substack{\text{Sucrose}\\ \text{d}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{\text{Glucose}\\ \text{d}}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ l}}{C_6H_{12}O_6}$$

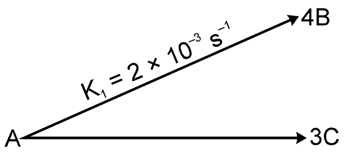
If $(r_\infty - r_0) = a$ and $(r_\infty - r_t) = (a - x)$ (where r_0, r_t and r_∞ are the angle of rotation at the start, at the time t and at the end of the reaction respectively, then there is 50% inversion when :

(A) $r_0 = 2r_t - r_\infty$ (B) $r_0 = r_t - r_\infty$ (C) $r_0 = r_t - 2r_\infty$ (D) $r_0 = r_t + r_\infty$

14.✍ A.G.M. counter is used to study the radioactive process of first-order. In absence of radioactive substance A, it counts 3 disintegration per second (dps). When A is placed in the G.M. counter, it records 23 dps at the start and 13 dps after 10 minutes. It records x dps after next 10 minutes and A has half-life period y minutes. x and y are :

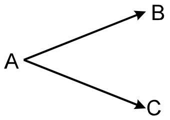
(A) 8 dps, 10 min (B) 5 dps, 10 min (C) 5 dps, 20 min (D) 5 dps, 5 min

15. For the following parallel chain reaction what will be that value of overall half-life of A in minutes? $\left[\text{Given that } \frac{[B]_t}{[C]_t} = \frac{16}{9}\right]$



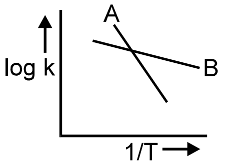
(A) 3.3 (B) 6.3

(C) 3.6 (D) None of these

16. For the follwing parallel chain reaction  the overall half life of A is 12 hours If rate of formation of C is 60% of a rate of decomposition of A then what will be half life of A while it is converting into B ?

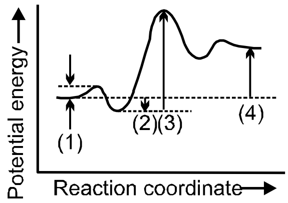
(A) 40 hours (B) 60 hours (C) 50 hours (D) 30 hours

17. The Arrhenius relationship of two different reactions is shown below. Which reaction is faster at a lower temperature and which is more sensitive to changes of temperature ?



(A) B faster, A more sensitive
(B) B in both cases
(C) A in both cases
(D) A faster, B more sensitive

18.✍ For the same mechanism as Problem refer to the given Fig. and choose the correct set of identifications.



$E + S \rightleftharpoons ES$
(enzyme) (reactant) (intermediate-1)

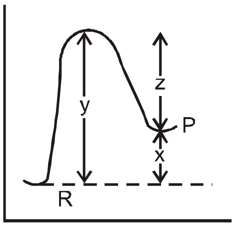
$ES \rightleftharpoons EP$
(intermediate-1) (intermediate-2)

$EP \rightleftharpoons E + P$
(intermediate-2) (enzyme) (product)

	(1)	(2)	(3)	(4)
(A)	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{overall}$ for $S \rightarrow P$	E_a for $EP \rightarrow E + P$
(B)	E_a for $E + S \rightarrow ES$	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{overall}$ for $S \rightarrow P$
(C)	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{overall}$ for $S \rightarrow P$	ΔE for $EP \rightarrow E + P$
(D)	E_a for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{overall}$ for $S \rightarrow P$
(E)	ΔE for $E + S \rightarrow ES$	$\Delta E_{overall}$ for $S \rightarrow P$	ΔE for $EP \rightarrow E + P$	E_a for $EP \rightarrow E + P$

19. The potential energy diagram for a reaction $R \longrightarrow P$ is given below :

ΔH^o of the reaction corresponds to the energy –



(A) x
(B) y
(C) z
(D) (x + y)

20.✍ In gaseous reactions important for the understanding of the upper atmosphere H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and E_a is 77 kJ mol^{-1}, then E_a for the bimolecular recombination of two OH radicals to form H_2O and O is :

(A) 3 kJ mol^{-1}
(B) 4 kJ mol^{-1}
(C) 5 kJ mol^{-1}
(D) 7 kJ mol^{-1}

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1.✍ In a catalyst experiment involving the Haber process $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of reaction was measured.

$$\text{Rate} = \frac{\Delta[NH_3]}{\Delta t} = 2.0 \times 10^{-4} \text{ mol L}^{-1} \text{ S}^{-1}.$$

The rate of reaction of N_2 is $p \times 10^{-4}$. Then find the value of p.

2. The acid catalysed hydrolysis of an organic compound A at 30ºC has a time for half change of 100 minutes, when carried out in a buffer solution at pH 5 and of 10 minutes, when carried out at pH 4. Both times of half change are independent of the initial concentration of A. If the rate of reaction is given by $\frac{-d[A]}{dt} = k[A]^a[H^+]^b$, what are the values of (a + b) ?

3.✍ For a first order reaction, time required for 99.0% completion is x times for the time required for the completion of 90% of the reaction x is :

4. The rate of decomposition of a substance increases by a factor 2.25 for 1.5 times increase in concentration of substance at same temperature. Find out order of reaction.

5. Half-life period for decomposition of NH_3 over tungsten wire are given below :

Initial Pressure in min	50	100	200
$T_{1/2}$	3.52	1.82	0.93

Calculate order of reaction.

6.✍ A substance A is mixed with equal quantities of the substance B and C. At the end of 1000 second, half of the amount of A has reacted. What fraction of A will be left unreacted at the end of 2000 second. If the reaction is zero order with respect to A ?

7.✍ At 80% of a radioactive element undergoing decay is left over after a certain period of time t from pure start, how many such periods should elapse from the start for just over 50% of the element to be left over.

8. The rate constant for the II order neutralization of 2-nitropropane by aqueous alkali obeys the equation

$$\log_{10} K = \frac{3163}{T} + 12 \qquad \text{T is temperature in Kelvin.}$$

Time and concentration were in minute and mol litre^{-1} respectively. If half life at 43.3°C and for an initial concentration of 0.001 mol litre^{-1} for each of the reactant is. Expresed as 10^{-x}, then x is :

9.✍ In a II order reaction, when the concentration of both the reactants are equal, the reaction is completed 20% in 500 sec. How long it would take for the reaction to go to 60% completion ? (Report your answer terms of minutes).

10. A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 54.0 min for A and 18.0 min for B. If the concentrations of A and B are equal initially, how long (in minute) will it take for the concentration of A to be four times that of B ?

11. The ratio of activities of two radio nuclides X and Y in a mixture at time t = 0 was found to be 4 : 1. After two hours, the ratio of activities become 1 : 1. If the $t_{1/2}$ of radio nuclide X is 20 min then $t_{1/2}$ [in minutes] of radio nuclide Y is :

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Which of the following are true about rate of a reaction?
(A) Rate of a reaction cannot be negative
(B) Rate of a reaction of a reactant is change in concentration of the reactant per unit time.
(C) Average rate and instantaneous rate can never be equal.
(D) Rate depends upon surface area of the reactants.

2. Which of the following statement is/are correct?
(A) A second order reaction must be a bimolecular elementary reaction
(B) A bimolecular elementary reaction must be a second order reaction
(C) Order of reaction can't be predicted by stoichiometry of reaction.
(D) First order reaction may be complex or elementary reaction

3.✍ For the reaction $2A + B \longrightarrow C$ with the rate law $\frac{d[C]}{dt} = k\,[A]^1\,[B]^{-1}$ and started with A and B in stoichiometric proportion. Which is/are true?
(A) unit of k is Ms^{-1}
(B) [A], [B] and [C] all will be linear functions of time
(C) [C] = 2kt
(D) [C] = kt

4.✍ Decomposition of $3\,A(g) \longrightarrow 2\,B(g) + 2C(g)$ follows first order kinetics. Initially only A is present in the container. Pressure developed after 20 min. and infinite time are 3.5 and 4 atm respectively. Which of the following is true.
(A) $t_{50\%}$ = 20 min
(B) $t_{75\%}$ = 40 min
(C) $t_{99\%}$ = 64/3 min
(D) $t_{87.5\%}$ = 60 min

5. For a second order reaction plots are made for $\frac{1}{[A]}$ vs time for the reaction, $2A \longrightarrow$ Product. Pick up the correct sentences. [K = Rate constant of A]

(A) the graph will show straight line with slope K

(B) the graph will show straight line with intercept $[A]_0$

(C) the graph will show straight line with slope $[A]_0$

(D) the graph will show straight line with intercept $\frac{1}{[A]_0}$

6. Taking the reaction, $A + 2B \longrightarrow$ Products, to be of second order, which of the following is/are the correct rate law expression(s) ?

(A) $\frac{dx}{dt} = k[A]^2$ (B) $\frac{dx}{dt} = k[A][B]^2$ (C) $\frac{dx}{dt} = k[A][B]$ (D) $\frac{dx}{dt} = k_1[A] + k_2[B]^2$

7. In the following gaseous phase first order reaction, $A(g) \longrightarrow 2B(g) + C(g)$ initial pressure was found to be 400 mm and it changed to 1000 mm after 20 min. Then :

(A) Half life for A is 10 min (B) Rate constant is 0.0693 min^{-1}

(C) Partial pressure of C at 30 min is 350 mm (D) Total pressure after 30 min is 1100 mm

8. For the reaction $CH_4 + Br_2 \longrightarrow CH_3Br + HBr$ the experimental data require the following rate equation :

$$\frac{d}{dt}[CH_3Br] = \frac{k_1[CH_4][Br_2]}{1 + k_2[HBr]/[Br_2]}$$

Which of the following is/are true regarding this ?

(A) The reaction is a single step reaction

(B) The reaction is 2nd order in the initial stages $\{[HBr] \approx 0\}$

(C) The reaction is 2nd order in the final stages $\{[Br_2] \approx 0\}$

(D) The molecularity of the reaction is two

9. A large increase in the rate of a reaction for a rise in temperature is due to

(A) increase in the number of collisions (B) the increase in the number of activated molecules

(C) The shortening of mean free path (D) the lowering of activation energy

10. Which of the following statements about the arrhenius equation are correct ?

(A) The pre exponential factor become equal to the rate constant of the reaction at temperature $T \to \infty$

(B) When the activation energy of the reaction → zero, the rate becomes independent of temperature.

(C) The term $e^{-E_a/Rt}$ represents the fractions of the molecules having energy is excess of the threshold value.

(D) On raising temperature , rate constant of the reaction of greater activation energy increases less rapidly than that of the reaction of smaller activation energy.

11. Rate constant k varies with temperature by equation , $\log k(min^{-1}) = 5 - \frac{2000}{T(K)}$. We can conclude :

(A) pre-exponential factor A is 5 (B) E_a is 2000 k cal

(C) pre-exponential factor A is 10^5 (D) E_a is 9.212 k cal

12. Activation energy of a chemical reaction can be determined by :

(A) evaluating rate constant at standard temperature

(B) evaluating velocities of reaction at two different temperatures

(C) evaluating rate constant at two different temperatures

(D) changing concentration of reactants

13.✍ Select the correct statements :

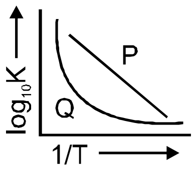
(A) the molecularity of an elementary reaction indicates how many reactant molecules take part in the step.

(B) the rate law of an elementary reaction can be predicted by simply seeing the stoichiometry of reaction.

(C) the slowest elementary step in sequence of the reactions governs the overall rate of formation of product.

(D) a rate law is often derived from a proposed mechanism by imposing the steady state approximation or assuming that there is a pre-equilibrium.

14. Which of the following statement are true regarding the log K vs. 1/T plot shown in the given diagram ?



$K = Ae^{-E_a/RT}$

(A) Plot P shows that the energy of activation is independent of temperature.

(B) Plot Q describes the behaviour of temperature dependence of energy of activation.

(C) Arrhenius behaviour is described by P.

(D) The slope of curve P gives the value $-\frac{E_a}{R}$.

15. If the rate of reaction, $2SO_2(g) + O_2(g) \xrightarrow{Pt} 2SO_3(g)$ is given by :

$$\text{Rate} = K\frac{[SO_2]}{[SO_3]^{1/2}}$$

which statements are correct :

(A) The overall order of reaction is –1/2

(B) The overall order of reaction is +1/2

(C) The reaction slows down as the product SO_3 is build up

(D) The rate of reaction does not depend upon concentration of SO_3 formed

16.✍ Rate of radioactive disintegration (–dN/dt) is also known as :

(A) Activity (B) Radioactivity (C) Half-life period (D) Average life period

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

$A(g) \longrightarrow 2B(g) + C(g)$

Initially at t = 0 gas A was present along with some amount of gas C. At t = 0 mole fraction of gas C is 1/3. After some time $t = t_1$, total pressure is half of the final total pressure at $t = t_x$ (a very long time). Assume this decomposition is a first order, at a constant temperature. It is also given at $t = t_x$, final total pressure is 35 bar.

1.✍ At $t = t_1$ pressure of gas B is :

(A) 2.5 bar (B) 1.25 bar (C) 5.0 bar (D) data is insufficient

2.✍ Rate constant (k) = (log 64 – log 49) s^{-1}. Value of t_1 in seconds is :

(A) 2.15 s (B) 1.5 s (C) 2.3 s (D) 1.15 s

3. Ratio of rate constant at $t = 0$ to $t = t_1$ to $t = t_x$ is :
(A) 2 : 3 : 4 (B) 1 : 1 : 1 (C) 1 : 3 : 5 (D) 1 : 3 : 5

Comprehension # 2

Set-I (Without catalyst)			
Reaction	**Temperature**	**E (activation)**	**k**
$A \rightarrow B$	T_1K	Ea_1	k_1
$A \rightarrow B$	T_2K	Ea_2	k_2

Set-II (With catalyst) **(Consider catalyst being positive only)**			
Reaction	**Temperature**	**E (activation)**	**k**
$A \rightarrow B$	T_1K	Ea_3	k_3
$A \rightarrow B$	T_2K	Ea_4	k_4

4. For the (Set-1) :
(A) if $T_1 > T_2$, $k_1 > k_2$ always
(B) if $T_1 > T_2$, $k_1 > k_2$ (for exothermic reaction)
(C) if $T_1 > T_2$, $k_1 < k_2$ (for endothermic reaction)
(D) $Ea_1 \neq Ea_2$

5. For the (Set-1) :
(A) $Ea_1 > Ea_2$ if $T_1 > T_2$
(B) $Ea_1 < Ea_2$ if $T_1 > T_2$
(C) $Ea_1 = Ea_2$
(D) $Ea_1 = 0.5\ Ea_2$

6. Comparing set-I and II :
(A) $k_4 > k_3$ & $k_2 > k_1$, if $T_2 > T_1$ (endothermic)
(B) $k_4 < k_3$ & $k_2 > k_1$, if $T_2 < T_1$ (endothermic)
(C) $k_4 > k_3$ & $k_2 > k_1$, if $T_2 < T_1$ (exothermic)
(D) $k_4 < k_3$ & $k_2 < k_1$, if $T_2 > T_1$ (exothermic)

Comprehension # 3

Competing first-order reactions :

Frequently a species can react in different ways to give a variety of products. For example, toluene can be nitrated at the ortho, meta, or para positions, We shall consider the simplest case, that of two competing irreversible first-order reactions :

$$A \xrightarrow{k_1} C \text{ and } A \xrightarrow{k_2} D$$

where the stoichiometric coefficients are taken as unity for simplicity. The rate law is

$$\left(\frac{d[A]}{dt}\right) = -k_1[A] - k_2[A] = -(k_1 + k_2)[A] \qquad \Rightarrow \qquad [A] = [A]_0\, e^{-(k_1+k_2)t}.$$

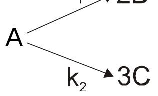
For C, we have $\left(\frac{d[C]}{dt}\right) = k_1[A] = k_1[A]_0\, e^{-(k_1+k_2)t}$. Multiplication by dt and integration from time 0 (where $[C]_0 = 0$) to an arbitary time t gives $[C] = \frac{k_1[A]_0}{k_1+k_2}(1 - e^{-(k_1+k_2)t})$

Similarly, integration of $\left(\frac{d[D]}{dt}\right)$ gives $[D]\ \frac{k_2[A]_0}{k_1+k_2} = (1 - e^{-(k_1+k_2)t})$

The sum of the rate constants $k_1 + k_2$ appears in the exponentials for both [C] and [D].

At any time we also have $\frac{[C]}{[D]} = \frac{k_1}{k_2}$

7.



starting initially with only A Which of the following is correct at time t
(A) $[A]_0 = [A]_t + [B]_t + [C]_t$
(B) $[A]_0 = [A]_t + 2[B]_t + 3[C]_t$
(C) $[A]_0 = [A]_t + \frac{[B]_t}{2} + \frac{[C]_t}{3}$
(D) $[A]_0 = \frac{2}{3}[A]_t + [B]_t + [C]_t$

8. $X \begin{array}{l} \xrightarrow{k_1} Y \\ \xrightarrow{k_2} Z \end{array}$ starting with only 'X', ratio $\frac{[X]_t}{[Y]_t + [Z]_t}$

(A) Independent of time (B) $\frac{1}{(e^{kt} - 1)}$

(C) Depends upon initial concentration of X (D) $[A]_0\ (e^{kt} - 1)$

9. At high temperature acetic acid decomposes into CO_2 & CH_4 and simultaneously into CH_2CO (ketene) and H_2O

(i) $CH_3COOH \xrightarrow{k_1=3s^{-1}} CH_4 + CO_2$

(ii) $CH_3COOH \xrightarrow{k_2=4s^{-1}} CH_2CO + H_2O$

What is the fraction of acetic acid reacting as per reaction (i) ?

(A) $\frac{3}{4}$ (B) $\frac{3}{7}$ (C) $\frac{4}{7}$ (D) none of these

10. For $A \begin{array}{l} \xrightarrow{k_1} 3B \\ \xrightarrow{k_2} 4C \end{array}$ starting with pure A ratio of rate of production of B to C is

(A) Independent of time (B) Independent of temperature

(C) Depends upon initial concentration of A (D) Independent of mechanism of reaction

Comprehension # 4

Answer Q.11, Q.12 and Q.13 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2 and 3 contain the Order of the reaction, value of K and half-life respectively.		
Column-1	**Column-2**	**Column-3**
(I) First order reaction	(i) $k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$	(P) Half life $\propto \frac{1}{a^2}$
(II) Second order reaction	(ii) $k = \frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right]$	(Q) Half life $\propto \frac{1}{a}$
(III) Third order reaction	(iii) $k = \frac{x}{t}$	(R) Half life is doubled on doubling the initial concentration
(IV) Zero order reaction	(iv) $k = \frac{1}{t}\log_e\left(\frac{a}{a-x}\right)$	(S) 50% reaction takes same time even if concentration is halved or doubled.

11. The correct combination for reaction $A \xrightarrow{2\times10^{-3}\,min^{-1}} B$ is :

(A) (II) (ii) (Q) (B) (IV) (iv) (S) (C) (I) (iv) (S) (D) (I) (iii) (R)

12. The incorrect combination among the following is :

(A) (I) (iii) (S) (B) (II) (ii) (Q) (C) (III) (i) (P) (D) (IV) (iii) (R)

13. For an elementary reaction $2A \longrightarrow B$, correct combination is :

(A) (I) (iv) (Q) (B) (I) (iv) (S) (C) (II) (ii) (Q) (D) (II) (ii) (R)

Exercise-3

*** Marked Questions may have more than one correct option.**

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1.✍ The rate constant for the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$, is 3×10^{-5} s^{-1}. If the rate is 2.4×10^{-5} mol L^{-1} s^{-1}, then the concentration of N_2O_5 (in mol L^{-1}) is : **[JEE-2000(S), 1/35]**

(A) 1.4 (B) 1.2 (C) 0.04 (D) 0.8

2. ${}^{238}_{92}U$ 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 : 0.9 the half life period of ${}^{238}_{92}U$ is 4.5×10^9 years. Calculate the age of the ore. **[JEE-2000(M)]**

3.✍ A hydrogenation reaction is carried out at 500 K. If the 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}. **[JEE-2000(M), 3/100]**

4. If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photochemical process, $AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to **[JEE-2001(S), 1/35]**

(A) C (B) I (C) I^2 (D) C.I

5. The rate of a first order reaction is 0.04 mole $litre^{-1}$ 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. **[JEE-2001(M), 5/100]**

6. Consider the chemical reaction,

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

The rate of this reaction can be expressed in terms of time derivatives of conc. of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst rate expressions : **[JEE-2002(S), 3/90]**

(A) Rate = $-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

(B) Rate = $\frac{d[N_2]}{dt} = -3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$

(C) Rate = $\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

(D) Rate = $-\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = \frac{d[NH_3]}{dt}$

7. ${}^{64}Cu$ (half life = 12.8 hours) 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. **[JEE-2002(M), 5/60]**

8. In the biologically-catalysed oxidation of ethanol, the concentration of ethanol decreases in a first order reaction from 800 mol dm^{-3} to 50 mol dm^{-3} in 2×10^4 s. The rate constant (s^{-1}) of the reaction is : **[JEE-2003(S), 3/84]**

(A) 3.45×10^{-5} (B) 1.38×10^{-4} (C) 1.00×10^{-4} (D) 5.00×10^{-5}

9.✍ Given X $\longrightarrow$ product (Taking 1st order reaction)

Given	X	product
conc (mol/lit)	0.01	0.0025
time (min)	0	40

Initial rate of reaction is in mol /□/min. **[JEE-2004(S), 3/84]**

(A) 3.43×10^{-4} (B) 1.73×10^{-4} (C) 3.43×10^{-5} (D) 1.73×10^{-5}

10. Initial rates, r_0, of the A + B → P at different initial concentrations of A and B ($[A]_0$ and $[B]_0$) are given below:

$[A]_0$ (mol L^{-1})	$[B]_0$ (mol L^{-1})	r_0 (mol L^{-1} s^{-1})
0.1	0.1	0.05
0.2	0.1	0.10
0.1	0.2	0.05

(a) Write the rate equation. (b) Calculate the rate constant of the reaction. **[JEE-2004(M), 2/60]**

11.✍ For a reaction $2X(g) \longrightarrow 3Y(g) + 2Z(g)$ the following data is obtained.

Time (min)	Px (mm of Hg) (Partial pressure of X)
0	800
100	400
200	200

Find order with respect to X, rate constant of the reaction, time taken for 75% completion and find the total pressure when partial pressure of X, Px = 700 mm of Hg. **[JEE-2005(M), 2/60]**

Comprehension #

Carbon–14 is used to determine the age of organic material. The procedure is based on the formation of ^{14}C by neutron capture in the upper atmosphere.

$$^{14}_{7}N + {}_0n^1 \longrightarrow {}^{14}_{6}C + {}_1p^1$$

^{14}C is absorbed by living organisms during photosynthesis. The ^{14}C content is constant in living organism, once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ^{14}C in the dead being, falls due to the decay which C^{14} undergoes

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + \beta^-$$

The half life period of ^{14}C is 5770 years. The decay constant (λ) can be calculated by using the following formula $\lambda = \frac{0.693}{t_{1/2}}$

The comparison of the β^- activity of the dead matter with that of the carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 years. The proportion of ^{14}C to ^{12}C in living matter is 1 : 10^{12}.

12. Which of the following option is correct? **[JEE-2006, 5/184]**

(A) Rate of exchange of carbon between atmosphere and living is slower than decay of ^{14}C.

(B) Carbon dating can be used to find out the age of earth crust and rocks

(C) Rate of exchange of ^{14}C between atmosphere and living organism is so fast that an equilibrium is set up between the intake of ^{14}C by organism and its exponential decay.

(D) Carbon dating can not be used to determine concentration of ^{14}C in dead beings.

13. What should be the age of fossil for meaningful determination of its age? **[JEE-2006, 5/184]**

(A) 6 years (B) 6000 years

(C) 60,000 years (D) It can be used to calculate any age

14. A nuclear explosion has taken place leading to increase in concentration of ^{14}C in nearby areas. ^{14}C 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 places respectively then **[JEE-2006, 5/184]**

(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) $\frac{T_1}{T_2} = \frac{C_1}{C_2}$

15. 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 : **[JEE-2007, 3/162]**
(A) 0 (B) 1 (C) 2 (D) 3

16.✍ 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 $\left(\frac{k_1}{k_0}\right)$ of the rate constant for first order (k_1) and zero order (k_0) of the reaction is. **[JEE-2008, 3/162]**
(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

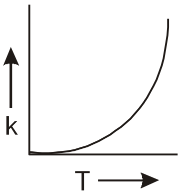
17. For a first order reaction A $\rightarrow$ P, the temperature (T) dependent rate constant (k) was found to follow the equation log k = – (2000) $\frac{1}{T}$ + 6.0. The pre-exponential factor A and the activation energy E_a, respectively, are : **[JEE-2009, 3/160]**
(A) $1.0 \times 10^6\ s^{-1}$ 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}

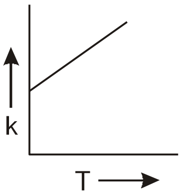
18.✍ The concentration of R in the reaction R $\rightarrow$ P was measured as a function of time and the following data is obtained :

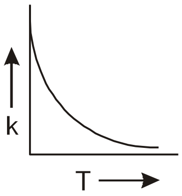
[R] (molar)	1.0	0.75	0.40	0.10
t(min.)	0.0	0.05	0.12	0.18

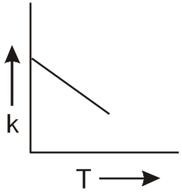
The order of the reaction is : **[JEE-2010, 3/163]**

19.✍ Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is : **[JEE-2010, 3/163]**

(A) 

(B) 

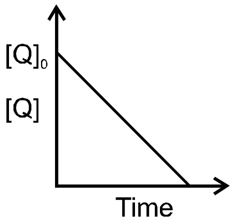
(C) 

(D) 

20.* For the first order reaction
$2N_2O_5\,(g) \rightarrow 4NO_2(g) + O_2\,(g)$ **[JEE-2011, 4/160]**
(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

21.✍ 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 $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$?
($\log_{10}2 = 0.3$) **[JEE-2012, 4/136]**

22. 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(Advanced) 2013, 2/120]
(A) 2 (B) 3
(C) 0 (D) 1



23.✍ The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The K_a of HA is : **[JEE(Advanced)-2013, 4/120]**

(A) 1×10^{-4} (B) 1×10^{-5} (C) 1×10^{-6} (D) 1×10^{-3}

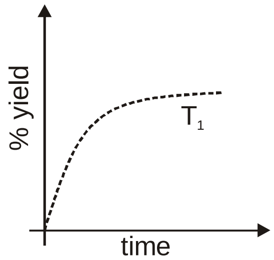
24.✍ For the elementary reaction **M** → **N**, the rate of disappearance of **M** increases by a factor of 8 upon doubling the concentration of **M**. The order of the reaction with respect to **M** is : **[JEE(Advanced) 2014, 3/120]**

(A) 4 (B) 3 (C) 2 (D) 1

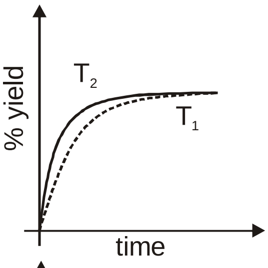
25.✍ The % yield of ammonia as a function of time in the reaction :

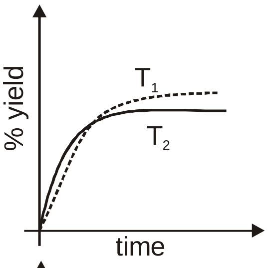
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \ \Delta H < 0$$

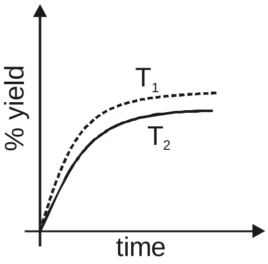
at (P, T_1) is given below.

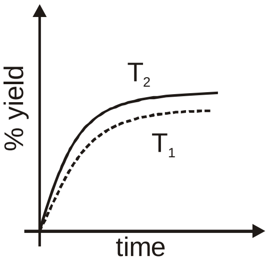


If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by : **[JEE(Advanced) 2015, 3/168]**

(A)


(B)


(C)


(D)


26. In dilute aqueous H_2SO_4, the complex diaquodioxalatoferrate(II) is oxidized by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is :**[JEE(Advanced)-2015, 4/168]**

27. According to the Arrhenius equation, **[JEE(Advanced)-2016, 4/124]**

(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.

28. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. the correct option(s) among the following is(are) **[JEE(Advanced)-2017, 4/122]**

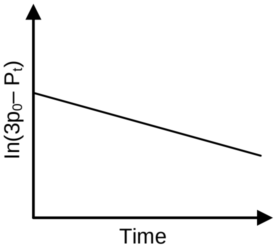
(A) The activation energy of the reaction is unaffected by the value of the steric factor.

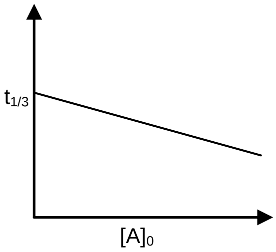
(B) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation.

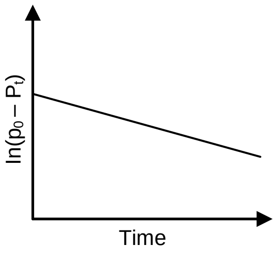
(C) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally.

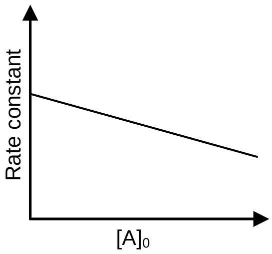
(D) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used.

29.* For a first order reaction A(g) □ 2B(g) + C(g) at constant volume and 300 K, the total pressure at the beginning (t = 0) and at time t are P_0 and P_t, respectively. Initially, only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach 1/3rd of its initial value. The correct option(s) is (are)
(Assume that all these gases behave as ideal gases) **[JEE(Advanced)-2018, 4/120]**

(A)


(B)


(C)


(D)


30. Consider the following reversible reaction,

$$A(g) + B(g) \rightleftharpoons AB(g)$$

The activation energy of the backward reaction exceeds that of the forward reaction by 2 RT (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG^{θ} (in J mole^{-1}) for the reaction at 300 K is _____.
(Given : ln(2) = 0.7, RT = 2500 J mol^{-1} at 300 K and G is the Gibbs energy)
[JEE(Advanced)-2018, 3/120]

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. Units of rate constant of first and zero order reactions in terms of molarity M unit are respectively **[AIEEE-2002, 3/225]**

(1) sec^{-1}, M sec^{-1} (2) sec^{-1}, M (3) M.sec^{-1}, sec^{-1} (4) M, sec^{-1}

2. For the reaction A + 2B → C, rate is given by R = $[A][B]^2$ then the order of the reaction is : **[AIEEE-2002, 3/225]**

(1) 3 (2) 6 (3) 5 (4) 7

3. The differential rate law for the reaction $H_2 + I_2 \rightarrow 2HI$ is : **[AIEEE-2002, 3/225]**

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

(3) $\frac{1}{2}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$ (4) $-2\frac{d[H_2]}{dt} = -2\frac{d[I_2]}{dt} = +\frac{d[HI]}{dt}$

4. 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 **[AIEEE-2003, 3/225]**

(1) $\frac{1}{2^{m+n}}$ (2) (m + n) (3) (n – m) (4) $2^{(n-m)}$.

5. For the reaction system: $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$, 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 : **[AIEEE-2003, 3/225]**

(1) diminish to one-fourth of its initial value
(2) diminish to one-eighth of its initial value
(3) increase to eight times of its initial value
(4) increase to four times of its initial value.

6.✍ In the respect of the equation $k = Ae^{-Ea/RT}$ in chemical kinetics, which one of the following statements is correct : **[AIEEE-2003, 3/225]**

(1) k is equilibrium constant (2) A is adsorption factor
(3) E_a is energy of activation (4) R is Rydberg constant.

7. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is : **[AIEEE-2004, 3/225]**

(1) 30 minutes (2) 15 minutes (3) 7.5 minutes (4) 60 minutes

8. The rate equation for the reaction $2A + B \longrightarrow C$ is found to be : rate = k[A] [B]. The correct statement in relation to this reaction is that the : **[AIEEE-2004, 3/225]**

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

9.✍ 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 : **[AIEEE-2004, 3/225]**

(1) 1.042 g (2) 2.084 g (3) 3.125 g (4) 4.167 g.

10. Consider an endothermic reaction $X \longrightarrow Y$ with the activation energies E_b and E_f for the backward and forward reaction, respectively. In general **[AIEEE-2005, 3/225]**

(1) $E_b < E_f$ (2) $\Delta H = \Delta U$ (3) $\Delta H < \Delta U$ (4) $\Delta H > \Delta U$

11. A reaction involving two different reactants can never be : **[AIEEE-2005, 3/225]**

(1) unimolecular reaction (2) first order reaction
(3) second order reaction (4) bimolecular reaction

12.✍ 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 be : **[AIEEE-2006, 3/165]**

(1) remain unchanged (2) tripled
(3) increased by a factor of 4 (4) doubled

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

$$NO\,(g) + Br_2\,(g) \rightleftharpoons NOBr_2\,(g)\ ;\ NOBr_2\,(g) + NO\,(g) \longrightarrow 2NOBr\,(g)\quad \text{(slow step)}$$

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is **[AIEEE- 2007, 3/120]**

(1) 1 (2) 0 (3) 3 (4) 2

14.✍ 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 catalyst will be (in kJ mol^{-1}). **[AIEEE- 2007, 3/120]**

(1) 280 (2) 20 (3) 300 (4) 120

15. A radioactive element gets spilled over the floor of a room. Its half-life period is 30days. If the initial activity is ten times the permissible value, after how many days will it be safe to enter the room : **[AIEEE- 2007, 3/120]**

(1) 10 days (2) 100 days (3) 1000 days (4) 300 days

16.✍ For a reaction $\frac{1}{2}A \longrightarrow 2B$, rate of disappearance of 'A' related to the rate of appearance of 'B' by the expression. **[AIEEE- 2008, 3/105]**

(1) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$ (2) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (3) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$ (4) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

17.✍ The half life period of a first order chemical reaction is 6.93 minutes. Time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301) : **[AIEEE - 2009, 8/144]**

(1) 23.03 minutes (2) 46.06 minutes (3) 460.6 minutes (4) 230.3 minutes

18. 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 ? **[AIEEE - 2010, 8/144]**

(1) 4 h (2) 0.5 h (3) 0.25 h (4) 1 h

19. Consider the reaction, $Cl_2(aq) + H_2S(aq) \longrightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$

The rate equation for this reaction is

rate = k $[Cl_2][H_2S]$

Which of these mechanisms is/are consistent with this rate equation? **[AIEEE - 2010, 4/144]**

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

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

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

$Cl_2 + HS^- \longrightarrow 2Cl^- + H^+ + S$ (slow)

(1) B only (2) Both A and B (3) Neither A nor B (4) A only

20.✍ The rate of a chemical reaction doubles for every 10ºC rise of temperature. If the temperature is raised by 50ºC, the rate of the reaction increases by about : **[AIEEE - 2011, 4/120]**

(1) 10 times (2) 24 times (3) 32 times (4) 64 times

21. A reactant (A) forms two products :

$A \xrightarrow{k_1} B$, Activation Energy Ea_1

$A \xrightarrow{k_2} C$, Activation Energy Ea_2

If $Ea_2 = 2\,Ea_1$, then k_1 and k_2 are related as : **[AIEEE - 2011, 4/120]**

(1) $k_2 = k_1 e^{Ea_1/RT}$ (2) $k_2 = k_1 e^{Ea_2/RT}$ (3) $k_1 = Ak_2 e^{Ea_1/RT}$ (4) $k_1 = 2k_2 e^{Ea_2/RT}$

22. 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 : **[AIEEE - 2012, 4/120]**

(1) 1.73×10^{-5} M/min (2) 3.47×10^{-4} M/min (3) 3.47×10^{-5} M/min (4) 1.73×10^{-4} M/min

23.✍ 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(Main) - 2013, 4/120]**

(1) 53.6 kJ mol^{-1} (2) 48.6 kJ mol^{-1} (3) 58.5 kJ mol^{-1} (4) 60.5 kJ mol^{-1}

24. For the non-stoichiometre reaction $2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial concentration (A)	Initial concentration (B)	Initial rate of formation of C (mol L^{-} S^{-})
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 : **[JEE(Main) - 2014, 4/120]**

(1) $\frac{dc}{dt}$ = k[A] [B] (2) $\frac{dc}{dt}$ = $k[A]^2[B]$ (3) $\frac{dc}{dt}$ = $k[A][B]^2$ (4) $\frac{dc}{dt}$ = k[A]

25. Higher order (>3) reactions are rare due to : **[JEE(Main)-2015, 4/120]**

(1) low probability of simultaneous collision of all the reacting species
(2) increase in entropy and activation energy as more molecules are involved
(3) shifting of equilibrium towards reactants due to elastic collisions
(4) loss of active species on collision

26. 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(Main)-2016, 4/120]**

(1) 6.93×10^{-4} mol min^{-1} (2) 2.66 L min^{-1} at STP
(3) 1.34×10^{-2} mol min^{-1} (4) 6.93×10^{-2} mol min^{-1}

27. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10kJ mol^{-1}. If k_1 and k_2 are rate constants for reactions R_1 and R_2 respectively at 300 K, then $\ln(k_2/k_1)$ is equal to : (R = 8.314 J mol^{-1} K^{-1}) **[JEE(Main)-2017, 4/120]**

(1) 12 (2) 6 (3) 4 (4) 8

28. At 518° C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 Torr s^{-1} when 5% had reacted and 0.5 Torr s^{-1} when 33% had reacted. The order of the reaction is : **[JEE(Main)-2018, 4/120]**

(1) 1 (2) 0 (3) 2 (4) 3

JEE(MAIN) ONLINE PROBLEMS

1. The half-life period of a first order reaction is 15 minutes. The amount of substance left after one hour will be : **[JEE(Main) 2014 Online (09-04-14), 4/120]**

(1) 1/4 of the original amount (2) 1/8 of the original amount
(3) 1/16 of the original amount (4) 1/32 of the original amount

2. In the reaction of formation of sulphur trioxide by contact process $2SO_2 + O_2 \rightleftharpoons 2SO_3$ the rate of reaction was measured as $\frac{d[O_2]}{dt} = -2.5 \times 10^{-4}$ mol L^{-1} s^{-1}. The rate of reaction in terms of [SO_2] in mol L^{-1} s^{-1} will be : **[JEE(Main) 2014 Online (11-04-14), 4/120]**

(1) -1.25×10^{-4} (2) -2.50×10^{-4} (3) -3.75×10^{-4} (4) -5.00×10^{-4}

3. For the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$, the rate equation can be expressed in two ways $-\frac{d\ [N_2O_5]}{dt} = k[N_2O_5]$ and $+\frac{d\ [NO_2]}{dt} = k'[N_2O_5]$ k and k' related as P: **[JEE(Main) 2014 Online (11-04-14), 4/120]**

(1) k = k' (2) 2k = k' (3) k = 2k' (4) k = 4k'

4. The rate coefficient (k) for a particular reactions is 1.3×10^{-4} M^{-1}s^{-1} at 100°C, and 1.3×10^{-3} M^{-1}s^{-1} at 150°C. What is the energy of activation (E_A) (in kJ) for this reaction ?
(R = molar gas constant = 8.314 JK^{-1} mol^{-1}) **[JEE(Main) 2014 Online (12-04-14), 4/120]**

(1) 16 (2) 60 (3) 99 (4) 132

5. For the reaction, 3A + 2B → C + D, the differential rate law can be written as : **[JEE(Main) 2014 Online (19-04-14), 4/120]**

(1) $\frac{1}{3}\frac{d[A]}{dt} = \frac{d[C]}{dt} = k[A]^n[B]^m$ (2) $-\frac{d[A]}{dt} = \frac{d[C]}{dt} = k[A]^n[B]^m$
(3) $+\frac{1}{3}\frac{d[A]}{dt} = \frac{d[C]}{dt} = k[A]^n[B]^m$ (4) $-\frac{1}{3}\frac{d[A]}{dt} = \frac{d[C]}{dt} = k[A]^n[B]^m$

6. The reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ follows first order kinetics. The pressure of a vessel containing only N_2O_5 was found to increase from 50 mmHg to 87.5 mm Hg in 30 min. The pressure exerted by the gases after 60 min. wil be (Assume temperature remains constant) : **[JEE(Main) 2015 Online (10-04-15), 4/120]**

(1) 125 mm Hg (2) 106.25 mm Hg (3) 116.25 mm Hg (4) 150 mm Hg

7. A + 2B → C, the rate equation for this reaction is given as
Rate = K[A][B]
If the concentration of A is kept the same but that of B is doubled what will happen to the rate itself ? **[JEE(Main) 2015 Online (11-04-15), 4/120]**

(1) halved (2) the same (3) doubled (4) quadrupled

8. For the equilibrium, A(g) $\rightleftharpoons$ B(g), ΔH is –40 kJ/mol. If the ratio of the activation energies of the forward (E_f) and reverse (E_b) reactions is $\frac{2}{3}$ then : **[JEE(Main) 2015 Online (11-04-15), 4/120]**

(1) E_f = 80 kJ/mol; E_b = 120 kJ/mol
(2) E_f = 60 kJ/mol; E_b = 100 kJ/mol
(3) E_f = 30 kJ/mol; E_b = 70 kJ/mol
(4) E_f = 70 kJ/mol; E_b = 30 kJ/mol

9. $A + 2B \rightarrow C$, the rate equation for this reaction is given as

Rate = K[A][B].

If the concentration of A is kept the same but that of B is doubled what will happen to the rate itself ? **[JEE(Main) 2015 Online (11-04-15), 4/120]**

(1) halved (2) the same (3) doubled (4) quadrupled

10. The reaction of ozone with oxygen atoms in the presence of chlorine atoms can occur by a two step process show below:

$O_3(g) + Cl^{\bullet}(g) \rightarrow O_2(g) + ClO^{\bullet}(g)$ ...(i)
$k_i = 5.2 \times 10^9$ L mol^{-1} s^{-1}

$ClO^{\bullet}(g) + O^{\bullet}(g) \rightarrow O_2(g) + Cl^{\bullet}(g)$ ...(ii)
$k_{ii} = 2.6 \times 10^{10}$ L mol^{-1} s^{-1}

The closest rate constant for the overall reaction $O_3(g) + O^{\bullet}(g) \rightarrow 2O_2(g)$ is: **[JEE(Main) 2016 Online (09-04-16), 4/120]**

(1) 1.4×10^{20} L mol^{-1} s^{-1} (2) 5.2×10^{9} L mol^{-1} s^{-1}
(3) 3.1×10^{10} L mol^{-1} s^{-1} (4) 2.6×10^{10} L mol^{-1} s^{-1}

11. The rate law for the reaction below is given by the expression k [A][B]

A + B → Product

If the concentration of B is increased from 0.1 to 0.3 mole, keeping the value of A at 0.1 mole, the rate constant will be : **[JEE(Main) 2016 Online (10-04-16), 4/120]**

(1) 9 k (2) 3 k (3) k/3 (4) k

12. The rate of a reaction A doubles on increasing the temperature from 300 to 310 K. By how much, the temperature of reaction B should be increased from 300 K so that rate doubles if activation energy of the reaction B is twice to that of reaction A. **[JEE(Main) 2017 Online (08-04-17), 4/120]**

(1) 9.84 K (2) 19.67 K (3) 2.45 K (4) 4.92 K

13. The rate of a reaction quadruples when the temperature changes from 300 to 310 K. The activation energy of this reaction is :

(Assume activation energy and pre-exponential factor are independent of temperature; ln2 = 0.693; R = 8.314 J mol^{-1} K^{-1}) **[JEE(Main) 2017 Online (09-04-17), 4/120]**

(1) 53.6 kJ mol^{-1} (2) 26.8 kJ mol^{-1} (3) 107.2 kJ mol^{-1} (4) 214.4 kJ mol^{-1}

14. N_2O_5 decomposes to NO_2 and O_2 and follows first order kinetics. After 50 minutes, the pressure inside the vessel increases from 50 mm Hg to 87.5 mm Hg. The pressure of the gaseous mixture after 100 minute at constant temperature will be : **[JEE(Main) 2018 Online (15-04-18), 4/120]**

(1) 136.25 mm Hg (2) 106.25 mm Hg (3) 175.0 mm Hg (4) 116.25 mm Hg

15. For a first order reaction, A → P, $t_{1/2}$ (half-life) is 10 days. The time required for $\frac{1}{4}$ th conversion of A (in days) is : (In 2 = 0.693, ln 3 = 1.1) **[JEE(Main) 2018 Online (15-04-18), 4/120]**

(1) 5 (2) 3.2 (3) 4.1 (4) 2.5

16. If 50 % of a reaction occurs in 100 second and 75 % of the reaction occurs in 200 second, the order of this reaction is : **[JEE(Main) 2018 Online (16-04-18), 4/120]**

(1) 2 (2) 3 (3) Zero (4) 1

17. The following results were obtained during kinetic studies of the reaction;

2A + B □ Products

Experiment	**[A]** **(in mol L^{-1})**	**[B]** **(in mol L^{-1})**	**Initial Rate of reaction** **(in mol L^{-1} min^{-1})**
I	0.10	0.20	6.93×10^{-3}
II	0.10	0.25	6.93×10^{-3}
III	0.20	0.30	1.386×10^{-2}

Time time (in minutes) required to consume half of A is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**

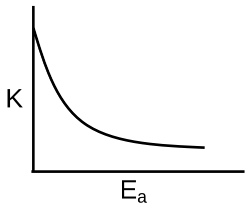
(1) 1 (2) 5 (3) 10 (4) 100

18. For the reaction, 2A + B $\rightarrow$ products, when the concentration of A and B both were doubled, the rate of the reaction increased from 0.3 mol $L^{-1}s^{-1}$ to 2.4 mol $L^{-1}s^{-1}$. When the concentration of A alone is doubled, the rate increased from 0.3 mol $L^{-1}s^{-1}$ to 0.6 mol $L^{-1}s^{-1}$.

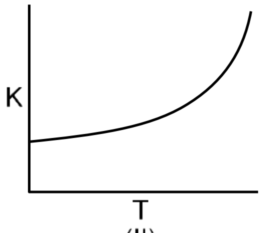
Which one of the following statements is correct? **[JEE(Main) 2019 Online (09-01-19), 4/120]**

(1) Order of the reaction with respect to B is 1
(2) Order of the reaction with respect to B is 2
(3) Total order of the reaction is 4
(4) Order of the reaction with respect to A is 2

19. Consider the given plots for a reaction obeying Arrhenius equation (0°C < T < 300°C) : (k and E_a are rate constant and activation energy, respectively)



(I)



(II)

Choose the correct option : **[JEE(Main) 2019 Online (10-01-19), 4/120]**

(1) I is right but II is wrong (2) Both I and II are wrong
(3) I is wrong but II is right (4) Both I and II are correct

20. For an elementary chemical reaction,

$A_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2A$ the expression for $\frac{d[A]}{dt}$ **[JEE(Main) 2019 Online (10-01-19), 4/120]**

(1) $2k_1[A_2]-k_{-1}[A]^2$ (2) $k_1[A_2]+k_{-1}[A]^2$
(3) $k_1[A_2]-k_{-1}[A]^2$ (4) $2k_1[A_2]-2k_{-1}[A]^2$

21. If a reaction follows the Arrhenius equation the plot lnk vs 1/(RT) gives straight line with a gradient (–y) unit . The energy required to activate the reactant is : **[JEE(Main) 2019 Online (11-01-19), 4/120]**

(1) –y unit (2) y unit (3) y/R unit (4) yR unit

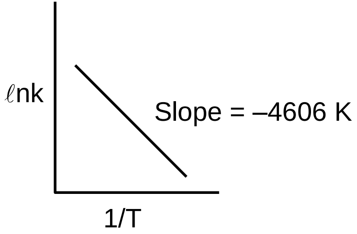
22. The reaction 2X $\rightarrow$ B is a zeroth order reaction. If the intial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be : **[JEE(Main) 2019 Online (11-01-19), 4/120]**

(1) 18.0 h (2) 12.0 h (3) 7.2 h (4) 9.0 h

23. Decomposition of X exhibits a rate constant of 0.05 μg/year. How many years are required for the decomposition of 5 μg of X into 2.5 μg ? **[JEE(Main) 2019 Online (12-01-19), 4/120]**

(1) 40 (2) 25 (3) 20 (4) 50

24. For a reaction, consider the plot of ln k versus 1/T given in the figure. If the rate constant of this reaction at 400 K is $10^{-5}\ s^{-1}$, then the rate constant at 500 K is: **[JEE(Main) 2019 Online (12-01-19), 4/120]**



(1) $10^{-4}\ s^{-1}$ (2) $4 \times 10^{-4}\ s^{-1}$ (3) $2 \times 10^{-4}\ s^{-1}$ (4) $10^{-6}\ s^{-1}$

Answers

EXERCISE - 1

PART – I

A-1. (a) 4.5×10^{-3} M sec^{-1} (b) 3.0×10^{-3} M sec^{-1}

A-2. (a) 40.5 g min^{-1} (b) 76.5 g min^{-1}

A-3. (a) 1.6×10^{-2} atm min^{-1} (b) 1.09×10^{-5} mol liter^{-1} sec^{-1}

A-4. (a) 3; (b) Both rates are 3.6×10^{-3} mole dm^{-3}s^{-1}; (c) No effect; (d) Decreased by a factor of 8; No effect

B-1. (i) 9.994 M (ii) $\dfrac{10}{2 \times (2 \times 10^{-6})}$ (iii) 5×10^{6} min

B-2. (a) 5 x 10^{-5} M/s (b) 4.2 x 10^{-5} M/s **B-3.** 0075.

B-4. 1.73 time **C-1.** 1.25×10^{4} min ; 2.5×10^{4} min

C-2. 39.2 minutes **C-3.** 1.84×10^{-2} min^{-1}

D-1. (i) rate = [A] [B] (ii) k = 4 x 10^{-2}M^{-1}s^{-1} (iii) rate = 2.8 x 10^{-3}M·s^{-1}

D-2. **(a)** n = 2, **(b)** First Order **D-3.** 2

E-1. 3.27×10^{-3} min^{-1}

E-2. Here a = 22.8, a – x = Vol. of $KMnO_4$ used at various times t.

At time 600 seconds : $K = \dfrac{2.303}{600} \log \dfrac{22.8}{13.8} = 0.000837$

At time 1200 seconds : $K = \dfrac{2.303}{1200} \log \dfrac{22.8}{8.2} = 0.000852$

Average value of K = $\dfrac{0.000837 + 0.000852}{2} = 0.000844 \times 10^{-4}$ sec^{-1}

E-3. (i) 2.484 hr^{-1} (ii) $\dfrac{50}{3}$ min. **F-1.** $k_1 = \dfrac{9 \ln 2}{2300}$; $k_2 = \dfrac{14}{2300} \ln 2$

F-2. $E_{overall} = E/3(2n+1)$

G-1. (i) 2, 1 (ii) 2.67×10^{8} mol^{-2} litre^{2} sec^{-1} (iii) 55.13 kJ mol^{-1} (iv) 1.147×10^{18} mol^{-2} litre^{2} sec^{-1}

G-2. 80.65%.

G-3. (A) y + z (B) z (C) x + y + z (D) x (E) x + y (F) – y

H-1. – 1000 **H-2.** k $[N_2O_5]$ **H-3.** Rate = k $[NO]^2$ $[Br_2]$

H-4. (a) 2 B+F $\rightarrow$ 2E; (b) A; (c) C,D; (d) rate = k [B][C]; (e) rate = k'[A][B] (f) 2.

I-1. (30 days, 0.0231 per day) **I-2.** (12.01×10^{-5} years $^{-1}$, 1/4)

I-3. 0.9375 gram. **I-4.** t = 4.5×10^{9} year.

PART – II

A-1.	(A)	**A-2.**	(B)	**A-3.**	(D)	**A-4.**	(B)	**A-5.**	(B)
A-6.	(C)	**A-7.**	(A)	**A-8.**	(D)	**B-1.**	(B)	**B-2.**	(C)
B-3.	(C)	**B-4.**	(A)	**B-5.**	(A)	**B-6.**	(B)	**B-7.**	(D)
B-8.	(B)	**B-9.**	(C)	**C-1.**	(D)	**C-2.**	(C)	**C-3.**	(D)
C-4.	(C)	**C-5.**	(C)	**D-1.**	(B)	**D-2.**	(C)	**D-3.**	(B)
D-4.	(B)	**D-5.**	(D)	**D-6.**	(C)	**D-7.**	(B)	**D-8.**	(B)
D-9.	(B)	**E-1.**	(C)	**E-2.**	(B)	**E-3.**	(C)	**E-4.**	(A)
F-1.	(B)	**F-2.**	(B)	**F-3.**	(D)	**F-4.**	(D)	**G-1.**	(B)
G-2.	(D)	**G-3.**	(B)	**G-4.**	(C)	**G-5.**	(B)	**H-1.**	(D)
H-2.	(A)	**H-3.**	(C)	**H-4.**	(C)	**H-5.**	(C)	**H-6.**	(B)
H-7.	(A)	**I-1.**	(D)	**I-2.**	(A)	**I-3.**	(B)	**I-4.**	(C)
I-5.	(D)	**I-6.**	(B)	**I-7.**	(D)	**I-8.**	(C)	**I-9.**	(A)
I-10.	(A)								

PART – III

1. (A $\rightarrow$ r) ; (B $\rightarrow$ s) ; (C $\rightarrow$ q) ; (D $\rightarrow$ p) **2.** (A) p, q, r, s ; (B) q, r, s ; (C) p, q, r, s ; (D) p, r, s

3. (A – r ; B – s ; C – p ; D – q)

EXERCISE – 2

PART – I

1.	(B)	**2.**	(C)	**3.**	(C)	**4.**	(B)	**5.**	(A)
6.	(C)	**7.**	(C)	**8.**	(C)	**9.**	(B)	**10.**	(A)
11.	(B)	**12.**	(B)	**13.**	(A)	**14.**	(A)	**15.**	(A)
16.	(D)	**17.**	(A)	**18.**	(B)	**19.**	(A)	**20.**	(C)

PART – II

1.	1	**2.**	2	**3.**	2	**4.**	2	**5.**	2
6.	Zero	**7.**	3	**8.**	10^{-19} minute	**9.**	50	**10.**	54
11.	30								

PART – III

1.	(ABD)	**2.**	(BCD)	**3.**	(ABC)	**4.**	(ABD)	**5.**	(AD)
6.	(AC)	**7.**	(ABCD)	**8.**	(BC)	**9.**	(AB)	**10.**	(ABC)
11.	(CD)	**12.**	(BC)	**13.**	(ABCD)	**14.**	(ABC)	**15.**	(BC)
16.	(AB)								

PART – IV

1.	(A)	**2.**	(D)	**3.**	(B)	**4.**	(A)	**5.**	(C)
6.	(A)	**7.**	(C)	**8.**	(B)	**9.**	(B)	**10.**	(A)
11.	(C)	**12.**	(A)	**13.**	(C)				

EXERCISE – 3

PART – I

1. (D) **2.** $t = 4.62 \times 10^9$ years. **3.** $E_A = 100$ KJ/mol

4. (B) **5.** $t_{1/2} = 24$ min. **6.** (A)

7. $(t_{1/2})_1 = 36.1\ hr^{-1}$, $(t_{1/2})_2 = 72.2\ hr^{-1}$, $(t_{1/2})_3 = 27.44\ hr^{-1}$. **8.** (B)

9. (A) **10.** (a) $R_0 = k[A_0]$, (b) 0.5 sec^{-1}.

11.

$$\begin{array}{lllll} & 2X(g) \longrightarrow & 3Y(g) & + \ 2Z(g) & \\ t = 0 & 800 & - & - & \\ t & 800 - 2x & 3x & 2x & = (800 + 3x) \end{array}$$

from given data in time 100 min the partial pressure of X decreases from 800 to 400 so $t_{1/2}$ 100 min. Also in next 100 min Px decreases from 400 to 200 to again $t_{1/2}$ = 100 min. Since half left is independent of initial concentration so reaction must Ist order with respect to X.

Rate constant $K = \dfrac{\ell n2}{t_{1/2}} = 6.93 \times 10^{-3}\ min^{-1}$.

Time taken for 75% completion = $2 \times t_{1/2}$ = 200 min.

Now when Px = 700 = 800 – 2x so x = 50 mm of Hg

so total pressure = 800 + 3x = 950 mm of Hg

12.	(C)	**13.**	(B)	**14.**	(A)	**15.**	(D)	**16.**	(A)
17.	(D)	**18.**	0	**19.**	(A)	**20.**	(ABD)	**21.**	9
22.	(D)	**23.**	(A)	**24.**	(B)	**25.**	(B)	**26.**	8
27.	(BCD)	**28.**	(AB)	**29.**	(AD)	**30.**	8500 J/mole		

PART – II

JEE(MAIN) OFFLINE PROBLEMS

1.	(1)	**2.**	(1)	**3.**	(4)	**4.**	(4)	**5.**	(3)
6.	(3)	**7.**	(1)	**8.**	(4)	**9.**	(3)	**10.**	(1)
11.	(1)	**12.**	(3)	**13.**	(4)	**14.**	(2)	**15.**	(2)
16.	(1)	**17.**	(2)	**18.**	(3)	**19.**	(4)	**20.**	(3)
21.	(3)	**22.**	(2)	**23.**	(1)	**24.**	(4)	**25.**	(1)
26.	(1)	**27.**	(3)	**28.**	(3)				

JEE(MAIN) ONLINE PROBLEMS

1.	(3)	**2.**	(4)	**3.**	(2)	**4.**	(2)	**5.**	(4)
6.	(2)	**7.**	(3)	**8.**	(1)	**9.**	(3)	**10.**	(2)
11.	(4)	**12.**	(4)	**13.**	(3)	**14.**	(2)	**15.**	(3)
16.	(4)	**17.**	(2)	**18.**	(2)	**19.**	(4)	**20.**	(4)
21.	(2)	**22.**	(1)	**23.**	(4)	**24.**	(1)		