Additional Problems for Self Practice (APSP)

✍ Marked Questions may have for Revision Questions.

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Marks: 100 **Max. Time : 1 Hour**

Important Instructions:

A. General :

1. The test paper is of **1** hour duration.
2. The Test Paper consists of **25** questions and each questions carries **4** Marks. Test Paper consists of **Two** Sections.

B. Test Paper Format and its Marking Scheme:

1. Section-1 contains **20** multiple choice questions. Each question has four choices (1), (2), (3) and (4) out of which **ONE** is correct. For each question in Section-1, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. In all other cases, minus one **(–1)** mark will be awarded.
2. Section-2 contains **5** questions. The answer to each of the question is a **Numerical Value**. For each question in Section-2, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. No negative marks will be answered for incorrect answer in this section. In this section answer to each question is **NUMERICAL VALUE** with two digit integer and decimal upto two digit. If the numerical value has more than two decimal places **truncate/round-off** the value to **TWO** decimal placed.

SECTION-1

This section contains **20** multiple choice questions. Each questions has four choices (1), (2), (3) and (4) out of which Only **ONE** option is correct.

1. The reaction $A(g) + 2B(g) \rightarrow C(g)$ is an elementary reaction. In an experiment involving this reaction, the initial partial pressures of A and B are $P_A = 0.40$ atm and $P_B = 1.0$ atm respectively. When pressure of C becomes 0.3 atm in the reaction the rate of the reaction relative to the initial rate is :

(1) $\frac{1}{12}$ (2) $\frac{1}{50}$ (3) $\frac{1}{25}$ (4) none of these

2. The rate law for the dimerisation of NO_2 is

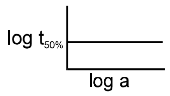
$$-\frac{d[NO_2]}{dt} = k\,[NO_2]^2$$

which of the following changes will change the value of the specific rate constant , k :

(1) Doubling the total pressure on the system (2) Doubling the temperature

(3) Both of (1) and (2) (4) None of the above

3.✍ A graph plotted between log $t_{50\%}$ vs. log concentration is a straight line. What conclusion can you draw from this graph.



(1) $n = 1$; $t_{1/2} \propto a$ (2) $n = 2$, $t_{1/2} \propto 1/a$

(3) $n = 1$; $t_{1/2} = (0.693/k)$ (4) None of these

4.✍ The forward rate constant for the elementary reversible gaseous reaction

$C_2H_6 \rightleftharpoons 2CH_3$ is 1.57×10^{-3} s^{-1} at 100 K

What is the rate constant for the backward reaction at this temperature if 10^{-4} mole of CH_3 and 10 moles of C_2H_6 are present in a 10 litre vessel at equilibrium.

(1) 1.57×10^{9} L mol^{-1} s^{-1} (2) 1.57×10^{10} L mol^{-1} s^{-1}

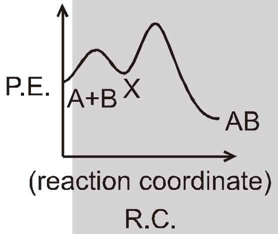
(3) 1.57×10^{11} L mol^{-1} s^{-1} (4) 1.57×10^{7} L mol^{-1} s^{-1}

5.✍ Rate constant k is 2.303 min^{-1} for a particular reaction. The initial concentration of the reaction is 1 mole/litre then rate of reaction after 1 minutes is :
(1) 2.303 M min^{-1} (2) 0.2303 M min^{-1} (3) 0.1 M min^{-1} (4) none of these

6. For an elementary reaction $2A + B \longrightarrow A_2B$ if the volume of vessel is quickly reduced to half of it's original volume then rate of reaction will -
(1) unchange (2) increase four times
(3) increase eight times (4) decrease eight time

7.✍ For a first order reaction $A \rightarrow B + 2C + 3D$ (A is optically inactive and B, C and D are dextrorotatory), the optical rotation at time t and ∞ are r_t and r_∞ respectively, the expression for rate constant is
(1) $K = \frac{1}{t} \ln \frac{r_t}{r_\infty - r_t}$ (2) $k = \frac{1}{t} \ln \frac{r_\infty}{r_\infty - r_t}$ (3) $k = \frac{1}{t} \ln \frac{r_\infty - r_t}{r_t}$ (4) none of these

8. For an exothermic chemical process occurring in two steps as follows
(i) $A + B \longrightarrow X$ (slow) (ii) $X \longrightarrow AB$ (fast)
the process of reaction can be best describe by :

(1)


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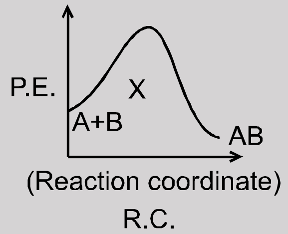
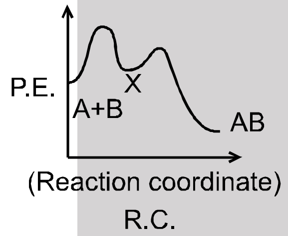
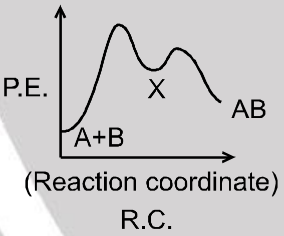


(3)


(4)


9. The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A and B are $P_A = 0.60$ and $P_B = 0.80$ atm. When $P_C = 0.2$ atm, the rate of reaction relative to the initial rate is :
(1) 1/48 (2) 1/24 (3) 9/16 (4) 1/6

10.✍ In the following reaction, how is the rate of appearance of the underlined product related to rate of disappearance of the underlined reactant :

$$BrO_3^-(aq) + 5\underline{Br}^-(aq) + 6H^+(aq) \longrightarrow 3\underline{Br_2}\,(\ell) + 3H_2O(\ell)$$

(1) $\frac{d[Br_2]}{dt} = -\frac{5}{3}\frac{d[Br^-]}{dt}$ (2) $\frac{d[Br_2]}{dt} = \frac{d[Br^-]}{dt}$ (3) $\frac{d[Br_2]}{dt} = -\frac{d[Br^-]}{dt}$ (4) $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

11. $3A \longrightarrow B + C$
It would be a zero order reaction when :
(1) the rate of reaction is proportional to square of concentration of A
(2) the rate of reaction remains same at any concentration of A
(3) the rate remains unchanged at any concentration of B and C
(4) the rate of reaction doubles if concentration of B is increased to double

12. At room temperature, the reaction between NO and O_2 to give NO_2 is fast, while that between CO and O_2 is slow. It is due to :
(1) CO is smaller in size that of NO
(2) CO is poisonous
(3) The activation energy for the reaction, $2NO + O_2 \rightarrow 2NO_2$ is less then $2CO + O_2 \rightarrow 2CO_2$.
(4) None of the above

13. The time of decay for a nuclear reaction is given by $t = 4t_{1/2}$. The relation between the mean life (T) and time of decay (t) is given by :

(1) 2 T ln 2 (2) 4 T ln 2 (3) $2T^4$ ln 2 (4) $\frac{1}{T^2}$ ln 2

14. The mechanism of the reaction, $2NO + O_2 \longrightarrow 2NO_2$ is

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \text{ (fast) ;}$$

$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2 \text{ (slow) ;}$$

The rate constant of the reaction is :

(1) k_2 (2) $k_2k_1(k_{-1})$ (3) k_2k_1 (4) $k_2\left(\frac{k_1}{k_{-1}}\right)$

15. $t_{1/2}$ = constant confirms the first order of the reaction as one $a^2\ t_{1/2}$ = constant confirms that the reaction is of :

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

16. The half-life period of a second order reaction is :

(1) Proportional to the initial concentration of reactants

(2) Independent of the initial concentration of reactants

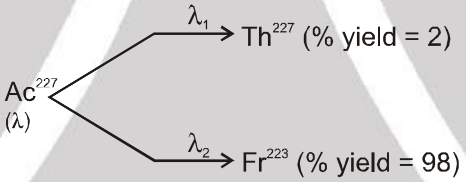
(3) Inversely proportional to the initial concentration of reactants

(4) Inversely proportional to the square of initial concentration of reactants

17. If the initial concentration of reactants in certain reaction is double, the half-life period of the reaction doubles, the order of a reaction is :

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

18. Ac^{227} has a half-life of 22 years. The decays folows two parallel paths



What are the decay constants (λ) for Th and Fr respectively ?

(1) 0.03087, 0.00063 (2) 0.00063, 0.03087 (3) 0.02, 0.98 (4) None of these

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

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

20. ${}_{84}Po^{218}$ ($t_{1/2}$ = 183 sec) decay to ${}_{82}Pb^{214}$($t_{1/2}$ = 161 sec) by α-emission, while Pb^{214} is a β-emitter. In an experiment starting with 1 mole of pure Po^{218}, how much time would be required for the number of nuclei of ${}_{82}Pb^{214}$ to reach maximum ?

(1) 147.5 (2) 247.5 (3) 182 (4) 304

SECTION-2

This section contains **5** questions. Each question, when worked out will result in **Numerical Value**.

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21. How many of the following statements are correct?

(1) unit of rate of disapperarance is Ms^{-1} (2) Unit of rate of reaction is Ms^{-1}

(3) Unit of rate constant k is depend on order (4) Unit of k for first order reaction is Ms^{-1}

22. How many of the following statements are correct?

(1) A second order reaction must be a biomolecular elementary reaction

(2) A bimolecular elementary reaction must be a second order reaction

(3) Zero order reaction must be a complex reaction

(4) First order reaction may be complex or elementary reaction

23. $A_2 + B_2 \longrightarrow 2AB$; Rate of reaction = $k[A]^a [B]^b$

Initial $[A_2]$	Initial $[Br_2]$	Rate of reaction (r) Ms^{-1}
0.2	0.2	0.04
0.1	0.4	0.04
0.2	0.4	0.08

Order of reaction with respect to A_2 and B_2 are a and b respectively. Find a + b

24. For a reaction A(s) + B(s) → C(s) is rate = $k[A]^{1/2} [B]^2$. What changes in rate if intial concentration of A and B increase by factor 4 and 2 respectively.

25. In the presence of acid, the initial concentration, of cane-sugar was reduced from 0.2 M to 0.1 M in 5 hr and to 0.05 M in 10 hr. What will be the order of reaction

Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ans.										
Que.	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Ans.										
Que.	**21**	**22**	**23**	**24**	**25**					
Ans.										

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

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 $k = Ae^{-E_a/RT}$ 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- 2006, 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 about how many days will it be just 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 → 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]**

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

(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

PART - III : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. One microcurie of radiation is the quantity of radioactive substance which produces : **[NSEC-2000]**
(A) 3.7×10^{10} disintegrations per second. (B) 6.022×10^{10} disintegrations per second
(C) 3.7×10^{4} disintegrations per second. (D) 3.7×10^{7} disintegrations per second.

2. The inversion of cane sugar using excess water in the presence of acid catalyst is a reaction of : **[NSEC-2000]**
(A) third order (B) second order
(C) first order with respect to cane sugar (D) zero order with respect to cane sugar

3. The reaction, 2A → B + C follows zero order kinetics. Its rate equation is represented by: **[NSEC-2000]**
(A) $dx/dt = k.[A]^{-}$ (B) $dx/dt = k.[A]$ (C) $dx/dt = k.[A]^{o}$ (D) $dx/dt = k.[2A]$

4. The radioactive decay of $^{226}_{88}Ra$ is a reaction belonging to : **[NSEC-2000]**
(A) fraction order kinetics (B) first order kinetics
(C) zero order kinetics (D) second order kinetics

5. A radioactive element has a half life of 4 minutes. After 20 minutes, 1 gram of the element will reduce to **[NSEC-2000]**
(A) 0.0625 g (B) 0.125 g (C) 0.25 g (D) 0.03125 g

6. Decomposition of H_2O is a first order reaction. A 16 volume solution of H_2O_2 of half-life period 30 minutes is present at start. When will the solution become one volume ? **[NSEC-2001]**
(A) after 120 minutes (B) after 90 minutes (C) after 60 minutes (D) after 150 minutes

7. According to Arrhenius equation, the rate of constant k and energy of activation (E) of a reaction are related by : **[NSEC-2001]**
(A) $A = k.e^{-E/RT}$ (B) $k = A.e^{E/RT}$ (C) $k = A.e^{-E/RT}$ (D) $k = -A.e^{E/RT}$

8. For a gaseous reaction, the following data was recorded. **[NSEC-2001]**

Concentration in mol. dm^{-3}	0.1	0.05	0.025	0.0125
Half time in s	30	29.9	30.1	30

The order of reaction is
(A) second (B) first (C) zero (D) fractional order

9. The cell potential (E) and the free energy change (ΔG) accompanying an electrochemical reaction are related by : **[NSEC-2001]**
(A) $\Delta G = nF \log E$ (B) $\Delta G = nFE$ (C) $-\Delta G = nFE$ (D) $-\Delta G = nF \log E$

10. The half time of a second order reaction is : **[NSEC-2001]**
(A) inversely proportional to the square of the initial concentration of the reactants
(B) inversely proportional to the initital concentration of the reactants
(C) proportional to the initial concentration of reactants
(D) independent of the initial concentration of reactants

11. For a third order reaction, the time for half reaction is related to the initial concentration of the reactants (a) by **[NSEC-2002]**
(A) $t_{1/2}$ is proportional to 1/a (B) $t_{1/2}$ is proportional to a
(C) $t_{1/2}$ is proportional to $1/a^2$ (D) $t_{1/2}$ is proportional to $1/a^3$.

12. The half-life of a radionuclide is 2.0×10^5 s. Its decay constant will be : **[NSEC-2002]**
(A) $3.465 \times 10^{-6}\ s^{-1}$ (B) $2.89 \times 10^5\ s^{-1}$ (C) $5.0 \times 10^{-6}\ s^{-1}$ (D) $3.465\ s^{-1}$

13. 75% of a radioactive element disintegrate 2 hours. Its half life period is : **[NSEC-2002]**
(A) half hour (B) one hour (C) two hour (D) three hour.

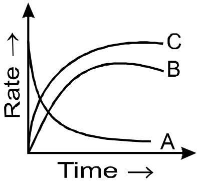
14. In an experiment, lead from drinking water is adsorbed onto activated carbon. This adsorption is a first order process with rate constant $1.8 \times 10^{-5}\ s^{-1}$. If the initial concentration of lead in water is 0.3 M, the time required to remove 90% of the initial lead is : **[NSEC-2003]**
(A) 1.3×10^5s (B) 2.4×10^4s (C) 1.8×10^7s (D) 2.7×10^6s.

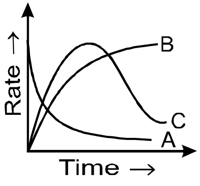
15. An isotope of a radioactive element is produced with the emission of **[NSEC-2003]**
(A) one α- and one β-particle (B) one α- and two β-particles
(C) two α- and one β-particle (C) two α- and two β-particles

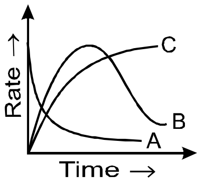
16. Gadolinium (^{153} Gd), which has a half- life of 242 days, is used to detect osteoporosis. The percentage of ^{153} Gd left in a patient`s system after 2 years will be **[NSEC-2003]**
(A) 33.0 (B) 25.0 (C) 12.5 (D) 6.25

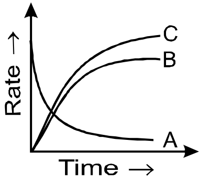
17. For a third order reaction 2A + B $\rightarrow$ 3C with rate constant k (in proper units), the correct rate law is : **[NSEC-2003]**
(A) $-\frac{d[A]}{dt} = k[A]^2[B]$ (B) $-\frac{d[B]}{dt} = k[A]^2[B]$ (C) $-\frac{d[C]}{dt} = k[A]^2[B]$ (D) $-\frac{d[A]}{dt} = k\,2[A].[B]$

18. The correct representation of the plot of rate vs time for the reaction A $\rightarrow$ B $\rightarrow$ C is : **[NSEC-2004]**

(A) 

(B) 

(C) 

(D) 

19. A container with a radioactive isotope of half-life 3 days was sent to a laboratory. The activity of the same on 12th day was found to be 3 micro curies. (μC_1) Hence, the initial activity (μC_2) of the isotope when packed was: **[NSEC-2004]**
(A) 12 (B) 24 (C) 36 (D) 48.

20. The rate constant for a chemical reaction is related to temperature by the relation log k = $10 - \frac{10^4 \times 5}{T}$.
If the reaction temperature is raised from 227ºC to 327ºC, the rate of this reaction would increase by a factor of about : **[NSEC-2004]**
(A) 20 (B) 46 (C) $e^{50/3}$ (D) 3.4×10^6.

21. The unit of the rate constant of a second order reaction with reactants having equal concentration is : **[NSEC-2004]**
(A) mol dm^{-3} s^{-1} (B) mol^2 dm^{-6} s^{-1} (C) dm^3 mol^{-1} s^{-1} (D) s^{-1}

22. The units of rate and rate constant are identical in : **[NSEC-2005]**
(A) fractional order reactions (B) first order reactions
(C) second order reactions (D) zero order reactions.

23. The main function of the catalytic converter in automobiles is **[NSEC-2005]**
(A) to control the air pollutants produced by the automobile
(B) to decrease the rate of combustion of fuel
(C) to increase the rate of combustion of fuel
(D) to decrease the sound pollution.

24. Consider a decay scheme, A → B → C where A and B are radioisotopes with half lives 10 s and 20 s respectively. In an experiment, initially (t=0) there are 10,000 atoms of A and no atoms of B and C. Identify the correct statement regarding the number of atoms of A, B and C, viz. N_A, N_B and N_C at t = 30 s. **[NSEC-2005]**
(A) N_A = 2500 and N_B more than 7500 (B) N_A = 2500 and N_C less than 1000
(C) N_A = 1250 and N_C more than 7500 (D) N_A = 1250 and N_C more than 2500.

25. In 1911 Rutherford and Boltwood studied the rate of formation of helium from radium $^{226}_{88}Ra$. The first few steps in this transformation are given as Ra > 1500 year Rn 3.83 days RaA 3.05 min RaB. The species RaA and RaB are, in a modern notation respectively **[NSEC-2005]**
(A) $^{222}_{84}Po$ and $^{218}_{82}Pb$ (B) $^{210}_{85}At$ and $^{209}_{83}Bi$ (C) $^{218}_{84}Po$ and $^{214}_{82}Pb$ (D) $^{218}_{84}Po$ and $^{218}_{85}At$.

26. The units of the rate constant of a first order reaction when time is measured in seconds is: **[NSEC-2005]**
(A) s (B) s^{-1} (C) mol L^{-1} s^{-1} (D) L mol^{-1} s^{-1}.

27. In a multi - step reaction, rate of the overall reaction is governed by the **[NSEC-2006]**
(A) rate of the fastest step (B) rate of the slowest step
(C) average rate of all the steps (D) sum of the rates of all the steps.

28. A first-order reaction has a rate constant of 0.003 s^{-1}. The time required for completion of 75% reaction is **[NSEC-2007]**
(A) 231 s (B) 201 s (C) 41.7 s (D) 462 s

29. The activation energy of a reaction is given by **[NSEC-2007]**
(A) R/(slope of a plot of ln k vs. 1/T) (B) (slope of a plot of ln k vs. 1/T)/R
(C) (slope of a plot of ln k vs. 1/T) × R (D) + (slope of a plot of ln vs. 1/T) × R

30. Viscosity is a measure of resistance of a liquid to flow and viscosity- **[NSEC-2007]**
(A) decreases with increasing temperature
(B) increases with increasing temperature
(C) remains constant with temperature
(D) shows linear relation (with positive) with temperature.

31. By observing the reaction between gases A and B, the following data was obtained :

[A] mol L^1	[B] mol L^1	Initial rate mol $L^1 s^1$
2.16×10^{-5}	1×10^{-5}	1×10^{-8}
2.14×10^{-5}	2.01×10^{-6}	2×10^{-9}
2.18×10^{-5}	3.2×10^{-5}	3.25×10^{-8}
4.31×10^{-5}	1.1×10^{-6}	4.3×10^{-9}
8.60×10^{-5}	2.1×10^{-5}	3.3×10^{-8}

The reaction orders with respect to A and B respectively are : **[NSEC-2007]**

(A) 1 and 2 (B) 0 and 2 (C) 2 and 1 (D) both are 1

32. For a reaction of the nth order, the time required for half reaction is inversely proportional to : **[NSEC-2007]**

(A) an (B) $a^{(n+1)}$ (C) $a^{(n+1)}$ (D) a

33. If the energy of a reaction is twice RT, its rate constant k is related to frequency factor A by the relation : **[NSEC-2008]**

(A) k = 0.135 A (B) k = 1.35 A (C) k = 0.0135A (D) k = 2.303A

34. For the reaction P + Q → R the following data was obtained **[NSEC-2008]**

Set	**[P]**	**[Q]**	**Rate**
I	0.125M	0.250M	0.01
II	0.250M	0.250M	0.04
III	0.250M	1.00M	0.08

The order of reaction is

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

35. For a chemical reaction, A + B → C + D, the following data was recorded :

Set No.	Initial Concentration of 'A' (mol.dm^{-3})	Initial Concentration of 'B' (mol.dm^{-3})	Rate of reaction (mol.dm^{-3}s^{-1})
1	4.00	3.00	0.10
2	12.00	3.00	0.90
3	12.00	6.00	0.90

The correct rate expression for the reaction is : **[NSEC-2009]**

(A) rate = k[A][B] (B) rate = $k[A]^2[B]^2$ (C) rate = $k[A]^2$ (D) rate = $k[A][B]^2$

36. A radioactive element has half life of 14 hours. The fraction of the radioactive isotope which will disintegrate in 56 hours is : **[NSEC-2009]**

(A) 0.75 (B) 0.875 (C) 0.9375 (D) 0.60

37. For a zero order reaction, the unit of rate constant is : **[NSEC-2009]**

(A) s^{-1} (B) mol.dm^{-3}s^{-1} (C) dm^{3}mol^{-1}s^{-1} (D) mol^2.dm^{-6}s^{-1}

38. Thorium-232 loses a total of 6α particles and 4β particles in a decay process. The isotope produced at the end is **[NSEC-2010]**

(A) ${}^{208}_{78}Pt$ (B) ${}^{208}_{82}Pb$ (C) ${}^{202}_{78}Pt$ (D) ${}^{208}_{83}Bi$

39. For a first order reaction, the half-life $t_{(1/2)}$ is related to the rate constant (k) by the relation. **[NSEC-2010]**

(A) $t_{(1/2)} = \frac{2.303}{k}\log 2$ (B) $t_{(1/2)} = \frac{1}{k}$ (C) $t_{(1/2)} = \frac{k}{2.303}\log 2$ (D) $t_{(1/2)} = \frac{2.303}{k}$

40. The rate constants k_1 and k_2 of two reactions are in the ratio 2 : 1. The corresponding energies of activation of the two reactions will be related by : **[NSEC-2010]**

(A) $E_1 > E_2$ (B) $E_1 < E_2$ (C) $E_1 = E_2$ (D) $E_1 = 2E_2$

41. The correct statement about order of reaction is : **[NSEC-2010]**

(A) it can be predicted from the stoichiometric coefficients of the reactants.
(B) it has always positive integral values.
(C) it has always positive integral or fractional values.
(D) it has to be determined experimentally.

42. The initial activity of a radionuclide is 9750 counts per min and 975 counts after 5 min. The decay constant of the radionuclide in min^{-1} is about **[NSEC-2011]**
(A) 0.23 (B) 0.46 (C) 0.69 (D) 0.99

43. The number of α-particles emitted per second by a radioactive element reduces to 6.25% of the original value in 48 days. The half-life period of the element in days is **[NSEC-2011]**
(A) 3 (B) 8 (C) 12 (D) 16

44. The half time for a second order reaction with equal concentrations of the reactants is 35 seconds. 99% reaction will be completed in : **[NSEC-2011]**
(A) 69s (B) 138s (C) 1733s (D) 3465s

45. Iodide ion is oxidized by acidified dichromate ions as shown in this equation, $Cr_2O_7^{2-}(aq) + 9I^-(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3I_3^-(aq) + 7H_2O(\ell)$. These data were obtained when the reaction was studied at a constant pH. The order of the reaction with respect to $Cr_2O_7^{2-}(aq)$ are **[NSEC-2011]**

Exeriment	$[Cr_2O_7^{2-}]$, M	$[I^-]$, M	Rate, $M.s^{-1}$
1	0.0050	0.0125	0.00050
2	0.010	0.0125	0.0010
3	0.0150	0.0250	0.0060

(A) first order with respect to both $Cr_2O_7^{2-}$ and I^-
(B) second order with respect to both $Cr_2O_7^{2-}$ and I^-
(C) second order with respect to $Cr_2O_7^{2-}$ and first order with respect to I^-
(D) first order with respect to $Cr_2O_7^{2-}$ and second order with respect to I^-

46. A first order reaction is 20% complete in 600 s. The time required to complete 75% of the same reaction will be : **[NSEC-2012]**
(A) 3120 s (B) 3720 s (C) 4320 s (D) 4920 s

47. For the reaction $NH_4^+ + NO_2^- \longrightarrow N_2 + 2H_2O$ the following data was recorded. **[NSEC-2012]**

Set	**NH_4^+ / M**	**NO_2^-**	**Rate / MS^{-1}**
1	0.010	0.020	0.020
2	0.015	0.020	0.030
3	0.010	0.010	0.005

(A) rate = K $[NH_4^+]$ $[NO_2^-]$ (B) rate = K $[NH_4^+]^2$ $[NO_2^-]$
(C) rate = K$[NH_4^+]$ $[NO_2^-]^2$ (D) rate = K$[NH_4^+]^2$ $[NO_2]^2$

48. The rate constant of a reaction increases by 5% when the temperature is increased from 27°C to 28°C. Therefore, the energy of activation of the reaction is **:** **[NSEC-2012]**
(A) 36.6 kJ mol^{-1} (B) 46.6 kJ mol^{-1} (C) 16.6 kJ mol^{-1} (D) 26.6 kJ mol^{-1}

49. How old is a fossil bone whose ^{14}C content is 15.0% of that living bone ? **[NSEC-2013]**
Half life of ^{14}C isotope is 5.73×10^3yr.
(A) 25488 yr (B) 15688 yr (C) 388 yr (D) 6818 yr

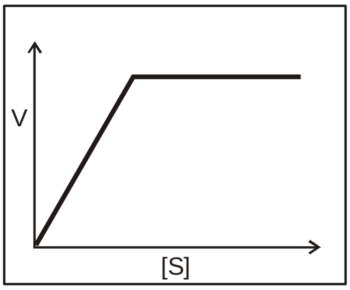
50. A plot of $1/[NO_2]$ verses time for decomposition of NO_2 was found to be linear. This means that the reaction **[NSEC-2013]**
(A) Is zero order with respect to $[NO_2]$ (B) Is first order with respect to $[NO_2]$
(C) Is second order with respect to $[NO_2]$
(D) Order cannot be determined from the information given

51. The following data was recorded for the reaction : **[NSEC-2013]**
$X + Y \longrightarrow P$

Set No.	**[A]**	**[B]**	**Rate of the reaction**
I	0.1 M	0.2 M	0.001
II	0.2 M	0.2 M	0.004
III	0.2 M	0.8 M	0.008

The order of the reaction is
(A) 1 (B) 2 (C) 2.5 (D) 3

52. The kinetics of an enzyme-catalyzed hydrolysis reaction is represented by the following graph, where [S] is the substrate concentration, and v is the rate of reaction :



The kinetic course of the reaction can be described as : **[NSEC-2013]**

(A) First order, zero order (B) Zero order, first order
(C) First order, second order (D) Second order, first order

53. As part of a diagnostic procedure for a thyroid disorder, a patient is given certain amount of iodine-131. The half life of this radioactive iodine-131 is 8.0 days. The percent fraction of iodine-131 that will remain in the body after 32 days, if there is no elimination of iodine through the body is **[NSEC-2014]**

(A) 6.25 (B) 0.0625 (C) 2.77 (D) 25

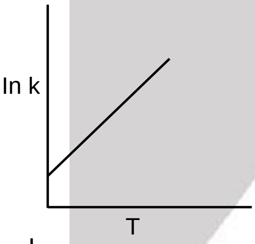
54. The experimental observations for the following reaction are given below: P + Q $\rightarrow$ Product.

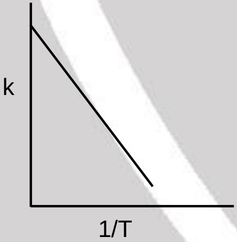
[P]/M	**[Q]/M**	**Initial Rate /mol s^{-1}**
0.2	0.5	8×10^{-3}
0.4	0.5	3.2×10^{-2}
0.2	0.25	4×10^{-3}

The order of this reaction is : **[NSEC-2014]**

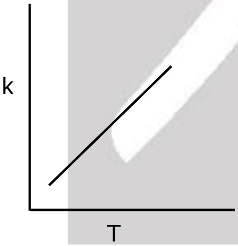
(A) Zero (B) One (C) Two (D) Three

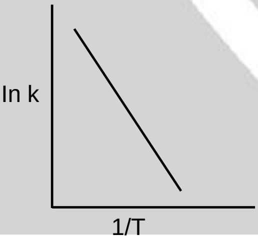
55. If k is the rate constant of the reaction and T is the absolute temperature, the correct plot is

(A)


(B)


[NSEC-2015]

(C)


(D)


56. For a gaseous reaction, A + B $\rightarrow$ products, the energy of activation was found to be 2.27 kJ mol^{-1} at 273 K. The ratio of the rate constant (k) to the frequency factor (A) at 273 K is **[NSEC-2016]**

(A) 0.368 (B) 3.68 (C) 4.34 (D) 0.434

57. The kinetic data recorded at 278 K for the reaction NH_4^+ (aq) + NO_2^- (aq) $\rightarrow$ N_2 (g) + $2H_2O$ (*l*) is

Set No.	**[NH_4^+]/M**	**[NO_2^-]/M**	**Rate of reaction/ Ms^{-1}**
1.	0.24	0.10	7.2×10^{-6}
2.	0.12	0.10	3.6×10^{-6}
3.	0.12	0.15	5.4×10^{-6}

The kinetic rate expression and the unit of rate constant (k) of the above reaction are respectively

(A) k [NH_4^+] [NO_2^-] and M s^{-1} (B) k [NH_4^+] and s^{-1} **[NSEC-2016]**
(C) k [NH_4^+] [NO_2^-] and M^{-1} s^{-1} (D) k [NO_2^-] and s^{-1}

58. For an elementary rearrangement reaction A $\rightleftharpoons$ P, the following data were recorded at 303 K, when $[P]_0 = 0$. **[NSEC-2016]**

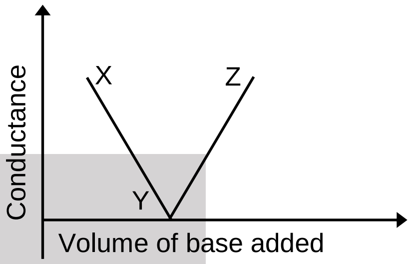
Set No.	$[A]_0$/mol L^{-1}	Rate of conversation of A/mol L^{-1} min^{-1}
1	0.340	0.100
2	0.170	0.050
3	0.085	0.025

If the equilibrium constant of the reaction is 1.12 at 303 K, the rate constant for the reaction P→ A is :

(A) 0.263 min^{-1} (B) 0.294 min^{-1} (C) 0.526 min^{-1} (D) 0.588 min^{-1}

59. NaOH solution is added dropwise to HCl solution and the conductance of the mixture is measured after addition of each drop. The variation of conductance with volume of NaOH added is as shown below.

The statement that is not true for the above is **[NSEC-2016]**



(A) decrease in conductance from X → Y is due to decrease in $[H^+]$

(B) point Y represents the equivalence point of titration.

(C) Na^+ has the higher equivalence conductance than H_3O^+

(D) segment YZ represents the conductance due to ions from NaCl and NaOH in solution.

60. For the reaction $N_2 + 3H_2 \rightarrow$ the rate expression is $-d[NH_3]/dt = k[H_2][N_2]$. The correct statement is

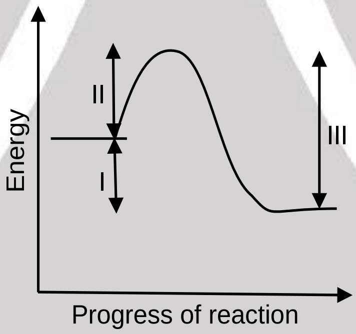
I. The reaction is not elementary

II. The reaction is of second order

III. $-d[H_2]/dt = -d[NH_3]/dt$ **[NSEC-2017]**

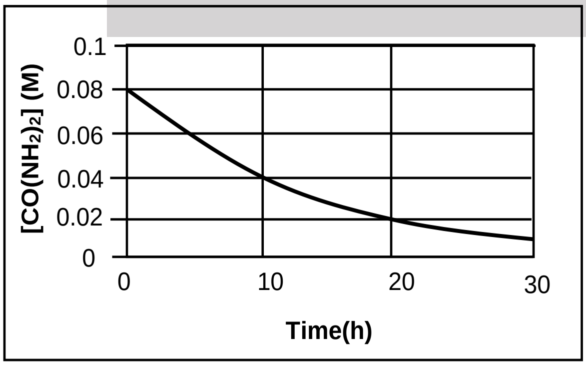
(A) II only (B) I and II (C) II and III (D) I, II and III

61. Which of the energy values marked as I, II and III in the following diagram, will change by the addition of a suitable catalyst? **[NSEC-2018]**



(A) II only (B) I and II (C) II and III (D) III only

62. Urea, $CO(NH_2)_2$, decomposes at 90ºC as $CO(NH_2)_2(aq) \rightarrow NH_4^+(aq) + OCN^-(aq)$. Experimental data obtained for the reaction is given in the following plot



From the graph it can be inferred that **[NSEC-2018]**

(A) average rate of the reaction is the same for successive time intervals of 10 h
(B) unit of rate constant of the reaction is h^{-1}
(C) rate constant of the reaction is the lowest at 30 h
(D) the reaction is of zero order

63. The rate of the reaction between two reactants X and Y can be expressed as $R = k[X]^2[Y]$. In an experiment, the initial rate of the reaction was found to be R_1 when the initial concentrations of X and Y are $[X_0]$ and $[Y_0]$. Another experiment was performed in which $[X_0]$ was taken as ½ $[X_0]$. What should be $[Y_0]$ in this experiment to get the initial rate as $0.5R_1$? **[NSEC-2018]**
(A) 4 $[Y_0]$ (B) 1/2 $[Y_0]$ (C) 2 $[Y_0]$ (D) $[Y_0]$

PART - III : HIGH LEVEL PROBLEMS (HLP)

THEORY

COMPLICATIONS IN 1st ORDER REACTION

REVERSIBLE 1ST ORDER REACTION (both forward and backward)

	$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}}$	B
$t = 0$	a	0
$t = t$	$a - x$	x
$t = t_{eq.}$	$a - x_{eq.}$	$x_{eq.}$

$x_{eq.}$ = eq conc. of product

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0$$ (∵ At equilibrium conc. is not changed)

$$\frac{d[A]}{dt} = -k_f[A] + k_b[B]$$

$$\frac{d[B]}{dt} = -k_b[B] + k_f[A]$$

$$\frac{d(a-x)}{dt} = -k_f(a-x) + k_bx$$

$$-\frac{dx}{dt} = -k_f a + (k_f + k_b)x$$

$$\int_0^x \frac{dx}{k_f a - (k_f - k_b)x} = \int_0^t dt$$

$$-\frac{\ell n[k_f a - (k_f + k_b)x]_0^x}{k_f + k_b} = t$$

$$\Rightarrow \quad \frac{1}{k_f + k_b}\left(-\ell n\left(\frac{k_f a - (k_f + k_b)x]}{k_f a}\right)\right) = t \quad \Rightarrow \quad \frac{1}{k_f + k_b}\,\ell n\left(\frac{k_f a}{k_f a - (k_f + k_b)x]}\right) = t$$

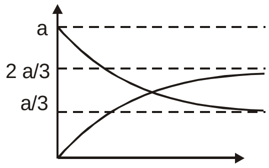
$$\boxed{x = \frac{k_f a}{k_f + k_b}\left(1 - e^{-(k_f + k_b)t}\right)}$$ (remember)

$$K_{eq.} = \frac{k_f}{k_b} = \frac{[B]_{eq.}}{[A]_{eq.}} = \frac{x_{eq.}}{(a - x_{eq.})}$$

$$\frac{k_f + k_b}{k_f} = \frac{a}{x_{eq.}}$$

$$x = x_{eq.}\left(1 - e^{-(k_f + k_b)t}\right) \quad (t \to \infty,\ x \to x_{eq.})$$

$$\boxed{k_f + k_b = \frac{1}{t}\,\ell n\left(\frac{x_{eq.}}{x_{eq.} - x}\right)}$$ (remember)



Where $X_{eq} = a \times \left[\frac{k_f}{k_f + k_b}\right]$

$$X_{eq} = \frac{k_f \times a}{k_f + k_b}.$$

if $\frac{k_f}{k_b} = 2$

SEQUENTIAL 1ST ORDER REACTION OR CONSECUTIVE FIRST-ORDER REACTIONS

	$A \xrightarrow{k_1}$	$B \xrightarrow{k_2}$	C	all first order equation
t = 0	a	0	0	
t	a – x	y	z	

Calculate $[A]_t$, $[B]_t$ and $[C]_t$

For → A

$$\frac{-d[A]}{dt} = r_1 = k_1 [A]$$

$$\frac{-d[A]}{[A]} = k_1\, dt$$

☞ $[A]_t = [A]_0\, e^{-k_1 t}$

$a - x = a\, e^{-k_1 t}$

☞ $x = a(1 - e^{-k_1 t})$

For → B

$r_2 = k_2 [B]$

$$\frac{dy}{dt} = k_1 a e^{-kt} - k_2 y$$

$$\frac{dy}{dt} + k_2 y = k_1 a e^{-kt}$$

$$dy + k_2 y dt = k_1\, a e^{-kt}\, dt$$

$$e^{k_2 t}\, dy + k_2 y\, e^{k_2 t} = k_1 a e^{-k_1 t}.e^{k_2 t} dt$$

$$\int_0^t d(k_2 y e^{k_2 t}) = \int_0^t k_1 a e^{(k_2 - k_1)t} dt$$

$$k_2 y\, e^{k_2 t} = \left(\frac{k_1 a}{k_2 - k_1}\right) e^{(k_2 - k_1)t} + y$$

At t = 0 y = 0

$$y = -\left(\frac{k_1 a}{k_2 - k_1}\right)$$

☞ $\boxed{y = \frac{k_1 a}{k_2 - k_1}\{e^{-k_1 t} - e^{-k_2 t}\}}$ (remember)

Calculate time at which concentration of B will be maximum

$$\frac{dy}{dt} = 0$$

$$-k_1\, e^{-k_1 t} + k_2\, e^{-k_2 t} = 0$$

$$e^{-k_2 t} = \frac{k_1}{k_2} e^{-k_1 t}$$

$$e^{k_1 t} = \frac{k_1}{k_2} e^{k_2 t} \quad \Rightarrow \quad k_1 t = \ell n \frac{k_1}{k_2} + k_2 t$$

☞ $\boxed{t_{max.} = \frac{1}{(k_1 - k_2)}\ell n\frac{k_1}{k_2}}$ (remember)

$$[B]_{max} = a \times \left[\frac{k_2}{k_1}\right]^{\frac{k_2}{k_1 - k_2}} = [A_0]\left[\frac{k_2}{k_1}\right]^{\frac{k_2}{k_1 - k_2}}$$

CASE-I $k_1 >> k_2$

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

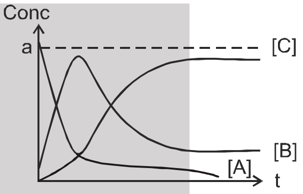
a

$\downarrow$ a – x x

☞ $[A] = a\,e^{-k_1 t}$ (conc. is minimum)

☞ $[B] = a\,e^{-k_2 t}$

☞ $[C] = a\,(1 - e^{-k_2 t})$



∴ $k_1t >> k_2\,t$

$k_1 > k_2$

∴ $k_1t << -\,k_2\,t$

∴ $e^{-k_1 t} << e^{-k_2 t}$

$y = \frac{k_1 a}{k_1}\,(-e^{-k_1 t}) = a\,e^{-k_2 t} = [B]$

Effective half life is $t_{1/2}$ for B.

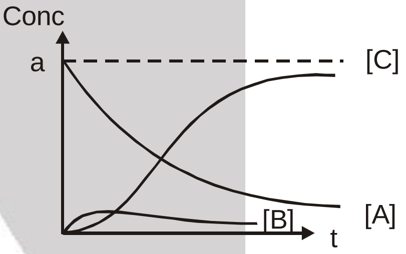
CASE-II : $k_2 >> k_1$

$[B]_t \rightarrow 0$

☞ $[A] = a\,e^{-k_1 t}$

☞ $[C] = a\,(1 - e^{-k_1 t})$

$y = \frac{k_1}{k_2}\,a\,e^{-k_1 t} = \frac{k_1}{k_2}\,[A]$ $\left(\frac{k_1}{k_2} \rightarrow 0\right)$



CASE-III : If in sequential equation, $k_1 = k_2 = k$

$y = kate^{-kt}$

$z = a(1 - e^{-kt}) - kate^{-kt}$

Solved Examples

Ex.1 Starting from the equation for radioactive decay i.e. $-\frac{dN}{dt} = \lambda N$, derive the expression, mean life = $\frac{1}{\lambda}$.

Sol. (i) $-\frac{dN}{dt} = \lambda N$. This on integration gives (with $N = N_0$, at $t = 0$); $N = N_0\,e^{-\lambda t}$

$$\text{Mean life} = \left[\frac{\int_{t=0}^{\infty} t\,dN}{\int_{t=0}^{\infty} dN}\right] = \frac{\int_{t=0}^{\infty} t\frac{dN}{dt}dt}{\int_{t=0}^{\infty} \frac{dN}{dt}dt} = \frac{\int_{t=0}^{\infty} (-\lambda N_0)e^{-\lambda t}t\ \ dt}{\int_{t=0}^{\infty} (-\lambda N_0)e^{-\lambda t}\ \ dt} = \frac{1}{\lambda}. \qquad \therefore \text{Mean life} = \frac{1}{\lambda}$$

Ex.2 In the case of first order consecutive reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ (Product), one may show that the concentration of B is given by $C_B = \frac{k_1 C_A^0}{(k_2 - k_1)}\left[e^{-k_1 t} - e^{-k_2 t}\right]$.

The usual assumptions are $C_A = C_A{}^0$ at t = 0 while $C_B = C_C = 0$ at t = 0. Show that C_B has its maximum value at time $t = \left(\frac{2.303}{k_2 - k_1}\right)\log\left(\frac{k_2}{k_1}\right)$.

Sol. $\dfrac{dC_B}{dt} = \dfrac{k_1 C_A^{\circ}}{(k_2 - k_1)}\left[k_2 e^{-k_2 t} - k_1 e^{-k_1 t}\right]$

equating this zero $\quad k_2 e^{-k_2\,t} = k_1 e^{-k_1\,t}$

$\therefore \quad \dfrac{k_2}{k_1} = e^{(k_2 - k_1)\,t} \qquad \therefore \quad \ell n\left(\dfrac{k_2}{k_1}\right) = (k_2 - k_1)\,t \qquad \therefore \quad t = \left(\dfrac{2.303}{k_2 - k_1}\right)\log\left(\dfrac{k_2}{k_1}\right)$

SUBJECTIVE QUESTIONS

1. For the reaction A → B, the rate law expression is $-\dfrac{d[A]}{dt} = K[A]^{1/2}$. If initial concentration of A is A_0.

Calculate : (a) integrated form of the rate law expression
(b) nature of plot of $[A]^{1/2}$ vs time.
(c) half life period.

2. **(a)** Let there be as first-order reaction of the type, A B + C. Let us assume that all three species are gases. We are required to calculate the value of rate constant based on the following data.

Time	0	t	∞
Partial pressure of A	P_0	P_t	–

(b) Let there be a first order reaction, A B + C. Let us assume all three are gases. We are required to calculate the value of rate constant based on the following data.

Time	0	t	∞
Total pressure	P_0	P_t	–

Calculate the expression of rate constant.

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

Time	0	t	∞
Total pressure of B + C	–	P_t	P_∞

Calculate the expression of rate constant.

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

Time	0	t	∞
Total pressure of B	–	P_t	P_∞

Calculate the expression of rate constant.

3. For a first order reversible reaction $A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$, the initial concentration of A and B are $[A]_0$ and zero respectively. If concentrations at equilibrium are $[A]_{eq.}$ and $[B]_{eq.}$ derive an expression for the time taken by B to attain concentration equal to $[B]_{eq/2}$.

4. For a gaseous reaction A ⟶ products, the half-life of the first order decomposition at 400 K is 150 minutes and the energy of activation is 65.0 kJ mole^{-1}. What fraction of molecules of A at 400 K have sufficient energy to give the products ?

5. At some temperature, the rate constant for the decomposition of HI on a gold surface is 0.1 Ms^{-1}.

$2HI \longrightarrow H_2(g) + I_2(g)$

What is the order of the reaction? How long will it take for the concentration of HI to drop from 2M to 0.5M

ONLY ONE OPTION CORRECT TYPE

6. A certain reaction $A + B \longrightarrow C$, the first order with respect to each reactant k = 10^{-3}. Determine the final concentration of A after 100 s, if the initial concentration of A was 0.1 M and that of B was 0.2 M.
(A) 0.098 M (B) 0.088 M (C) 0.078 M (D) 0.068 M

7. At a given temperature, $k_1 = k_2$ for the reaction, $A + B \rightleftharpoons C + D$.

If $\left[\frac{dx}{dt}\right] = k_1[A][B] - k_2[C][D]$ in which set of the concentration reaction ceases?

	[A]	[B]	[C]	[D]		[A]	[B]	[C]	[D]
(A)	0.1 M	0.2 M	0.3 M	0.4 M	(B)	0.4 M	0.25 M	0.2 M	0.5 M
(C)	0.2 M	0.2 M	0.3 M	0.2 M	(D)	0.2 M	0.2 M	0.4 M	0.2 M

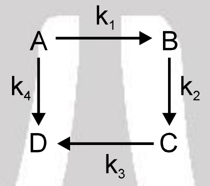
8. For the complex, $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2^+]$

$$\left(\frac{dx}{dt}\right) = 2 \times 10^7\ L^2\ mol^{-2}\ s^{-1}\ [Ag^+]\ [NH_3]^2 - 1 \times 10^{-2}\ s^{-1}\ [Ag(NH_3)_2^+]$$

Hence, ratio of rate constants of the forward and backward reactions is :

(A) $2 \times 10^7\ L^2\ mol^{-2}$ (B) $2 \times 10^9\ L^2\ mol^{-2}$ (C) $1 \times 10^{-2}\ L^2\ mol^{-2}$ (D) $0.5 \times 10^{-9}\ L^2\ mol^{-2}$

9. Consider the elementary reaction sequence shown in figure. Which of the following equations are correct?



(A) $\frac{d[A]}{dt} = -k_1[A] + k_4[D]$ (B) $\frac{d[C]}{dt} = k_2[B] - k_3[C]$

(C) $\frac{d[D]}{dt} = k_4[D] + k_3[D]$ (D) Nothing can be said about order of reactions in this problem

10. The steady state concentration of the activated molecule [A*] in the following sequence of steps is given by :

$$A + A \xrightarrow{K_1} A + A^*$$

$$A^* + A \xrightarrow{K_2} 2A$$

(A) $\frac{K_2[A]}{K_1}$ (B) $\frac{K_1[A]}{K_2}$ (C) $K_1K_2[A]$ (D) $\frac{K_1K_2}{[A]}$

11. The α activity in 1 g sample of ^{226}Ra ($t_{1/2}$ = 1600 years) is equal to :

(A) 2.19×10^{12} dpm (B) 2.19×10^{14} dpm (C) 2.19×10^{16} dpm (D) 4.96×10^{12} dpm

12. In the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$\left(\frac{dx}{dt}\right) = 1 \times 10^2\ [N_2]\ [H_2]^3 - 1 \times 10^{-3}\ [NH_3]^2$ and at some instant if $\frac{[N_2]\ [H_2]^3}{[NH_3]^2} = 10^{-5}\ M^2$

then at this instant value of $\left(\frac{dx}{dt}\right)$ is :

(A) 0 (B) 1×10^5 (C) 1×10^{-5} (D) 1×10^{-3}

13. A (aq) → B (aq) + C (aq) is a first order reaction.

Time	t	∞
moles of reagent	n_1	n_2

Reaction progress is measure with the help of titration of reagent 'R'.If all A, B and C reacted with reagent and have 'n' factors $\left[\text{n factors; eq.wt.} = \frac{\text{mol.wt}}{n}\right]$ in the ratio of 1 : 2 : 3 with the reagent.The k in terms of t, n_1 and n_2 is :

(A) $k = \frac{1}{t}\ln\left(\frac{n_2}{n_2 - n_1}\right)$ (B) $k = \frac{1}{t}\ln\left(\frac{2n_2}{n_2 - n_1}\right)$ (C) $k = \frac{1}{t}\ln\left(\frac{4n_2}{n_2 - n_1}\right)$ (D) $k = \frac{1}{t}\ln\left(\frac{4n_2}{5(n_2 - n_1)}\right)$

14. For A $\xrightarrow[K_1]{}$ B $\xrightarrow[K_2]{}$ C, at what time will B be present in greatest concentration ?

(A) $\frac{k_1}{K_2 - K_1}$ (B) $\frac{1}{K_1 - K_2}\ln\frac{k_1}{k_2}$ (C) $\frac{1}{K_2 - K_1}\ln\frac{k_1}{k_2}$ (D) None of these

15. A $\xrightarrow{K=2\times10^{-5}\,s^{-1}}$ B $\xrightarrow{K=8\times10^{-6}\,s^{-1}}$ C $\xrightarrow{K=3\times10^{-3}\,s^{-1}}$ D

The rate determing step of the reaction is -

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

16. A reaction is catalysed by H^+ ion;and in the rate law the dependence of rate is of first order with respect to the concentration of H^+ ions, in presence of HA rate constant is 2×10^{-3} min^{-1} and in presence of HB rate constant is 1×10^{-3} min^{-1}. HA and HB have relative strength as :

(A) 0.5 (B) 0.002 (C) 0.001 (D) 2

MATCH THE COLUMN

17. Match the order of reaction (in List **I**) with its property (in List **II**) :

	List I (order)		**List II (Property)**
(A)	Zero	(p)	Half life $\propto \frac{1}{a^2}$
(B)	First	(q)	Half life $\propto \frac{1}{a}$
(C)	Second	(r)	Half life is doubled on doubling the initial concentration
(D)	Third	(s)	50% reaction takes same time even if concentration is halved or doubled.

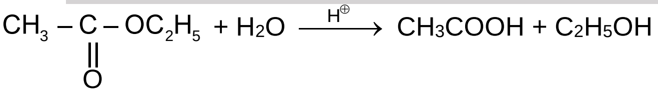
NUMERICAL VALUE TYPE

18. A 1 mL sample of a bacterial culture at 37ºC is taken, and diluted to 10 L. A 1mL sample of the diluted culture is spread on a culture plate. Ten minutes later, another 1mL sample taken from the original culture diluted and spread in the same way. The two plates are incubated for 24 hours. The first sample exhibits 48 colonies of bacteria, the second 72 colonies. If we assume that each colony originates with a single bacterium, what is the approx generation time in minute (time required for doubling the population).

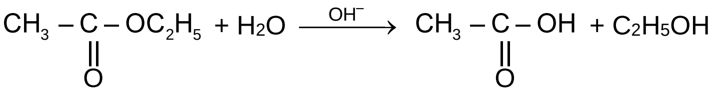
19. Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. Due to this, some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.025 M $KMnO_4$ solution under acidic conditions. Calculate the rate constant for decomposition of H_2O_2 in hr^{-1}. Report your answer as k × 100. [$\ln\frac{20}{17.5} = 0.1335$]

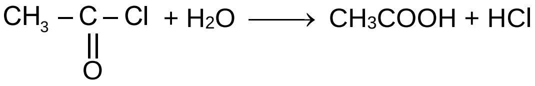
ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

20. Which of the following are example of Pseudo uni molecular reaction?

(A) 
$CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + H_2O \xrightarrow{H^{\oplus}} CH_3COOH + C_2H_5OH$

(B) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\oplus}} C_6H_{12}O_6$ (glucose) + $C_6H_{12}O_6$ (fructose)

(C) 
$CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + H_2O \xrightarrow{OH^-} CH_3-\underset{\underset{O}{\|}}{C}-OH + C_2H_5OH$

(D) 
$CH_3-\underset{\underset{O}{\|}}{C}-Cl + H_2O \longrightarrow CH_3COOH + HCl$

21. A reaction takes place in three steps. The rate constant of the three steps are k_1, k_2 and k_3 respectively. The overall rate constant $k = \frac{k_1 k_3}{k_2}$

The energy of activation for the three steps are 40, 30 and 20 KJ respectively. Therefore :

(A) Overall energy of activation is 10 KJ

(B) Overall energy of activation is 30 KJ

(C) The reaction mechanism is $2A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} A^* + A$; $A^* \xrightarrow[\text{rds}]{K_3}$ product and overall order is one.

(D) The reaction mechanism is $A \xrightarrow{K_1} B$; $B \xrightarrow{K_2} C$; $C \xrightarrow{K_3}$ product and overall order is one

22. The rate expression for the reaction :

$NH_4CNO \rightleftharpoons NH_2CONH_2$ can be derived from the mechanism :

i. $NH_4CNO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_4NCO$ (Fast)

ii. $NH_4NCO \xrightarrow{k_3} NH_3 + HNCO$ (Fast)

iii. $NH_3 + HNCO \xrightarrow{k_4} NH_2CONH_2$ (Slow)

Which of the following statement(s) is/are correct about the rate expression ?

(A) $\frac{d_{(urea)}}{dt} = \frac{k_1 k_3}{k_2}[NH_4CNO]$

(B) $\frac{d_{(urea)}}{dt} = \frac{k_1 k_3}{k_2 k_4}[NH_4CNO]$

(C) $\frac{d_{(urea)}}{dt} = k[NH_4CNO]$

(D) $\frac{d_{(urea)}}{dt} = \frac{k_1 \times k_2}{k_3 \times k_4}[NH_4CNO]$

PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr. **Max. Marks : 63**

Important Instructions

A. General :

1. The test is of 1 hour duration.
2. The Test Booklet consists of 21 questions. The maximum marks are 63.

B. Question Paper Format :

3. Each part consists of five sections.
4. Section-1 contains 8 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5. Section-2 contains 4 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6. Section-3 contains 5 questions. The answer to each of the questions is numerical value, ranging from 0 to 9 (both inclusive).
7. Section-4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8. Section-5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme :

9. For each question in Section-1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (– 1) mark will be awarded.
10. For each question in Section-2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.

11. For each question in Section-3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)

This section contains 8 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

1.✍ 60 % of a first order reaction was completed in 60 min. The time taken for decompose to half of their original amount will be :

(A) ≈ 30 min (B) ≈ 45 min (C) ≈ 20 min (D) ≈ 40 min

2. The decomposition of H_2O_2 can be followed by titration with $KMnO_4$ and is found to be a first order reaction. The rate constant is 4.5×10^{-2}. In an experiment, the initial titre value was 25 mL. The titre value will be 5 mL after a lapse of

(A) $4.5 \times 10^{-2} \times 5$ min (B) $\frac{\log_e 5}{4.5 \times 10^{-2}}$ min (C) $\frac{\log_e 5/4}{4.5 \times 10^{-2}}$ min (D) None of the above

3. In a second order reaction, 20% of a substance is dissociated in 40 min. The time taken by 80% of its dissociation is :

(A) 160 min (B) 640 min (C) 200 min (D) 320 min

4. A simple mechanism for enzyme-catalysed reaction is given by the following set of equations

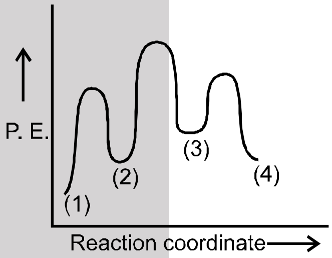
$\underset{\text{(enzyme)}}{E} + \underset{\text{(reactant)}}{S} \rightleftharpoons \underset{\text{(intermediate-1)}}{ES}$

$\underset{\text{(intermediate-1)}}{ES} \rightleftharpoons \underset{\text{(intermediate-2)}}{EP}$

$\underset{\text{(intermediate-2)}}{EP} \rightleftharpoons \underset{\text{(enzyme)}}{E} + \underset{\text{(product)}}{P}$

This is known as the Michaelis–Menten mechanism. The potential energy diagram is shown in the fig. Which of the following sets of identifications is correct ?

(Assume that the temperature and pressure are constant).



	(1)	(2)	(3)	(4)
(A)	E + P.	EP	ES	E + S
(B)	ES	Activated complex	EP	Activated complex
(C)	EP	Activated complex	ES	Activated complex
(D)	E + S	ES	EP	E + P

5. In a reaction carried out at 500 K, 0.001 % of the total number of collisions are effective. The energy of activation of the reaction is approximately

(A) 15.8 kcal mol^{-1} (B) 11.5 kcal mol^{-1} (C) 12.8 kcal mol^{-1} (D) zero

6.✍ A reaction, the rate constant is expressed as $k = Ae^{-40000/T}$. The energy of the activation is

(A) 40000 cal (B) 88000 cal (C) 80000 cal (D) 8000 cal

7. For the decomposition of $H_2O_2(aq)$ it was found that V_{O_2} (t = 15 min.) was 100 mL (at 0ºC and 1 atm) while V_{O_2} (maximum) was 200 mL (at 0ºC and 2 atm). If the same reaction had been followed by the titration method and if $V_{KMnO_4}^{(cM)}$ (t = 0) had been 40 mL, what would $V_{KMnO_4}^{(cM)}$ (t = 15 min) have been ?

(A) 30 mL (B) 25 mL (C) 20 mL (D) 15 mL

8. Consider the following reactions at 300 K.

$A \rightarrow B$ (uncatalysed reaction)

$A \xrightarrow{\text{catalyst}} B$ (catalyst reaction)

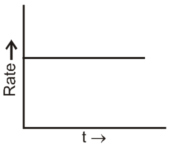
The activation energy is lowered by 8.314 KJ mol^{-1} for the catalysed reaction. How many times the rate of this catalysed reaction greater than that of uncatalysed reaction ? (Given $e^{3.33} = 28$)

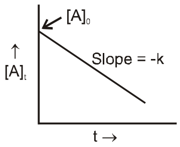
(A) 15 times (B) 38 times (C) 22 times (D) 28 times

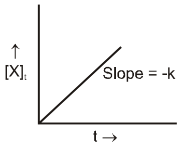
Section-2 : (One or More than one options correct Type)

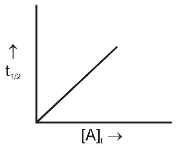
This section contains 4 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

9.✍ Which of the following graphs represents zero order if A $\longrightarrow$ P
At t = 0 $\Rightarrow [A]_0$
At t = t $\Rightarrow [A]_t$

(A)


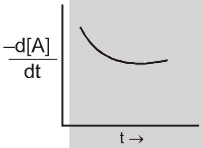
(B)


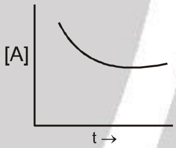
(C)


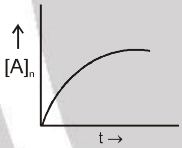
(D)


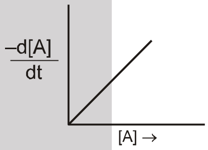
10.✍ In a hypothetical reaction X $\rightarrow$ Y, the activation energy for the forward and backward reactions in 15 and 9 kJ mol^{-1}, respectively. The potential energy of X is 10 kJ mol^{-1}. Then Plot of $t_{1/2}$ vs. concentration
(A) The heat of reaction of 6 kJ
(B) The potential energy of Y is 16 kJ.
(C) The threshold energy of the reaction is 25 kJ
(D) The reaction is endothermic.

11. Which of the following plots are correctly made for the reaction nA $\rightleftharpoons$ $(A)_n$ if it obeys first order reaction ?

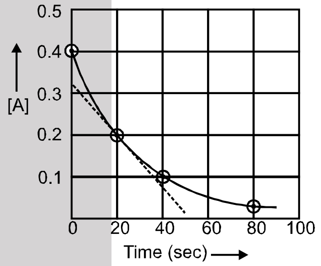
(A)


(B)


(C)


(D)


12.✍ A certain reaction A $\rightarrow$ B follows the given concentration (Molarity)-time graph. Which of the following statements is/are true ?
(A) The reaction is second order with respect to A
(B) The rate for this reaction at 20 s will be 7×10^{-3} M s^{-1}.
(C) The rate for this reaction at 80 s will be 1.75×10^{-3} M s^{-1}
(D) The [B] will be 0.35 M at t = 60 s



Section-3 : (Numerical Value Type.)

This section contains 5 questions. Each question, when worked out will result in numerical value from 0 to 9 (both inclusive).

13.✍ At some temperature, the rate constant for the decomposition of HI on a gold surface is 0.08 M.s^{-1}.

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

What is the order of the reaction ? How long will it take for the concentration of HI to drop from 1.50 M to 0.30 M ?

14. Identify the reaction order from the following rate constant :
$k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1}.

15.✍ $3A + B \longrightarrow C + D$
Mechanism of given reaction is :
Step 1 : $A + B \xrightarrow{k_1} E$
Step 2 : $E + 2A \xrightarrow{k_2} C + D$
What is the total order of reaction considering steady state approximation.

16.✍ A reaction take place at 300K. When catalyst is added rate of reaction increases. Calculate the change in temp (in ºC) which would have same effect on rate of reaction as that of catalyst. (Assume catalyst change the activation energy by 20%).

17. Consider the following chemical reaction and the corresponding kinetic data showing the initial reaction rate as a function of the initial concentrations of the reactants :

$$H_3AsO_4(aq) + 2H_3O^+(aq) + 3I^-(aq) \rightarrow HAsO_2(aq) + I_3^-(aq) + 4H_2O(liq)$$

Initial Rate × 10^{-5} (M/sec)	**[H_3AsO_4]**	**[H_3O^+]**	**[I^-]**
3.7	0.001	0.01	0.10
7.4	0.001	0.01	0.20
7.4	0.002	0.01	0.10
3.7	0.002	0.005	0.20

Using the data, establish the correct reaction composite order.

SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Questions 18 to 20

Study the two photochemical reactions and answer the question at the end.

For the overall reaction between A and B to yield C and D, two mechanisms are proposed :

I. $A + B \;\; AB^* \longrightarrow C + D$, $k_1' = 1 \times 10^{-5}\ M^{-1}\ s^{-1}$

II. $A \longrightarrow A^* \longrightarrow E$, $k_1 = 1 \times 10^{-4}\ s^{-1}$

$E + B \longrightarrow C + D$, $k_2 = 1 \times 10^{10}\ M^{-1}\ s^{-1}$

(species with * are short-lived)

18. Rate according to mechanism I when concentration of each reactant is 0.1 M will be :

(A) $1 \times 10^{-7}\ Ms^{-1}$ (B) $1 \times 10^{-6}\ Ms^{-1}$ (C) $1 \times 10^{-5}\ Ms^{-1}$ (D) $1 \times 10^{-4}\ Ms^{-1}$

19. Rate according to mechanism II when concentration of each reactant is 1 M will be:

(A) $1 \times 10^{-4}\ Ms^{-1}$ (B) $1 \times 10^{10}\ Ms^{-1}$ (C) $1 \times 10^{-6}\ Ms^{-1}$ (D) $1 \times 10^{-10}\ Ms^{-1}$

20. At what concentration of B, rates of two mechanism are equal :

(A) 1 M (B) 5 M (C) 7 M (D) 10 M

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

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21.✍ Match order of the reaction (in List–I) with the corresponding rate constant (in List–II) and select the correct answer using the code given below the lists.

	List I (order)		**List II (rate constant)**
(P)	Zero	(1)	$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$
(Q)	First	(2)	$k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$
(R)	Second	(3)	$k = \frac{x}{t}$
(S)	Third	(4)	$k = \frac{1}{t}\log_e\left(\frac{a}{(a-x)}\right)$

Code :

	P	Q	R	S		P	Q	R	S
(A)	3	4	2	1	(B)	1	2	4	3
(C)	3	1	2	4	(D)	2	3	1	4

Practice Test-2 ((IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ans.										
Que.	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Ans.										
Que.	**21**									
Ans.										

APSP Answers

PART - I

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

PART - II

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)				

PART - III

1.	(C)	**2.**	(C)	**3.**	(C)	**4.**	(B)	**5.**	(D)
6.	(A)	**7.**	(C)	**8.**	(B)	**9.**	(C)	**10.**	(A)
11.	(C)	**12.**	(A)	**13.**	(B)	**14.**	(A)	**15.**	(B)
16.	(C)	**17.**	(B)	**18.**	(C)	**19.**	(D)	**20.**	(C)
21.	(C)	**22.**	(D)	**23.**	(A)	**24.**	(D)	**25.**	(C)
26.	(B)	**27.**	(B)	**28.**	(D)	**29.**	(C)	**30.**	(A)
31.	(C)	**32.**	(B)	**33.**	(A)	**34.**	(D)	**35.**	(C)
36.	(C)	**37.**	(B)	**38.**	(B)	**39.**	(A)	**40.**	(B)
41.	(D)	**42.**	(B)	**43.**	(C)	**44.**	(D)	**45.**	(D)
46.	(B)	**47.**	(C)	**48.**	(A)	**49.**	(B)	**50.**	(C)
51.	(C)	**52.**	(A)	**53.**	(A)	**54.**	(D)	**55.**	(D)
56.	(A)	**57.**	(C)	**58.**	(A)	**59.**	(C)	**60.**	(B)
61.	(C)	**62.**	(B)	**63.**	(C)				

PART - IV

1. **(a)** $\sqrt{A_t} = \left(\sqrt{A_0} - \frac{k}{2}t\right)$ **(b)** straight line with slope – $\frac{k}{2}$ (c) $\frac{\sqrt{2}(\sqrt{2}-1)}{K}\sqrt{[A]_0}$

2. **(a)** $k = \frac{1}{t}\ln\left(\frac{P_0}{P_t}\right)$ **(b)** $k = \frac{1}{t}\ln\left(\frac{P_0}{2P_0 - P_t}\right)$ **(c)** $k = \frac{1}{t}\ln\left(\frac{P_\infty}{P_\infty - P_t}\right)$ **(d)** $k = \frac{1}{t}\ln\left[\frac{P_\infty}{P_\infty - P_t}\right]$

3. $t = \dfrac{0.693}{K_f + K_b}$

4. $\dfrac{K}{A} = e^{-Ea/RT} = 3.13 \times 10^{-6}$. = Fraction of Molecule Having Sufficient Energy. **5.** t = 7.5 sec

6. (A) **7.** (B) **8.** (B) **9.** (B) **10.** (B)

11. (A) **12.** (A) **13.** (D) **14.** (B) **15.** (C)

16. (D) **17.** (A) → (r) ; (B) → (s) ; (C) → (q) ; (D) → (p) **18.** 17

19. 80 **20.** (AB) **21.** (BC) **22.** (AC)

PART - V

1. (B) **2.** (B) **3.** (B) **4.** (D) **5.** (B)

6. (C) **7.** (A) **8.** (D) **9.** (ABCD) **10.** (ABCD)

11. (ABCD) **12.** (BD)

13. From the unit of k given, the reaction is of zero order.
As this reaction is of the type 2A → Products, we apply,
$k_0 = \dfrac{x}{nt}$ where n = 2 or $k_0 = \dfrac{a-(a-x)}{nt}$ or $0.08 = \dfrac{1.50 - 0.30}{2t}$ ⇒ t = 7.5 s

14. Second order **15.** 2 **16.** 75 **17.** 4 **18.** (A)

19. (A) **20.** (D) **21.** (A)

APSP Solutions

PART - I

1.

	A(g)	+	2B(g)	→	C(g)
t = 0	0.4 atm		1 atm		0 atm
t = t	(0.4 –0.3)atm		(1 – 0.6)atm		0.3 atm

Since reaction is elementary.
So, Rate of reaction w.r.t. A & B will be of order equal to stoichiometric coefficient
Rate = K [A] $[B]^2$
$\text{Rate}_{(\text{Initial})} = K\,[0.4]\,[1]^2$
$\text{Rate}_{(\text{after } t = t)} = K\,[0.1][0.4]^2$

$$\frac{R_{(t=t)}}{R_{(t=o)}} = \frac{K[0.1][0.4]^2}{K[0.4][1]} = \frac{1}{25}$$

2. Rate constant change on changing temperature.

3. As $t_{50\%}$ is constant. Hence order of reaction is 1.

$t_{50\%} = \dfrac{0.693}{K}$

n = 1, $t_{1/2} = \dfrac{0.693}{K}$

4. $K_{eq} = \dfrac{k_f}{k_b} = \dfrac{[CH_3]^2}{[C_2H_6]}$ ∴ $[CH_3] = \dfrac{10^{-4}}{10} = 10^{-5}$ M

$\dfrac{1.57 \times 10^{-3}}{k_b} = \dfrac{(10^{-5})^2}{1}$ ⇒ $k_b = 1.57 \times 10^{7}\ \text{L mol}^{-1}\text{s}^{-1}$

5. $k = \frac{2.303}{t}\log\left(\frac{C_{A_0}}{C_A}\right)$

$2.303 \times 1 = 2.303 \log\left(\frac{C_{A_0}}{C_A}\right)$

$\frac{C_{A_0}}{C_A} = 10 \qquad \therefore \qquad CA \Rightarrow \frac{1}{10} = 0.1$

rate after 1 min $r_1 = k.C_A \qquad \Rightarrow \qquad 2.0303 \times 0.1 \Rightarrow 0.2303\ \text{min}^{-1}$

6. $r_1 = k[A]^2 [B]$; $r_2 = k[2A]^2 [2B] = 8 r_1$

7. $A \longrightarrow B + 2C + 3D$

	A	B	2C	3D	
Optical rotation	–	θ_1	θ_2	θ_3	
t=0	a	0	0	0	Optical rotation at t = 0 is zero.
t=t	a–x	x	2x	3x	Optical rotation at time = t is $(x.\theta_1 + 2x.\theta_2 + 3x.\theta_3)$.
t=∞	0	a	2a	3a	Optical rotation at time = ∞ is $(a.\theta_1 + 2a.\theta_2 + 3a.\theta_3)$.

$(x.\theta_1 + 2x.\theta_2 + 3x.\theta_3) = r_t$; $\qquad (a.\theta_1 + 2a.\theta_2 + 3a.\theta_3) = r_\infty$

$x = \frac{r_t}{\theta_1 + 2\theta_2 + 3\theta_3}$; $\qquad a = \frac{r_\infty}{\theta_1 + 2\theta_2 + 3\theta_3}$

$k = \frac{1}{t}\ln\left[\frac{a}{a-x}\right] = \frac{1}{t}\ln\left[\frac{r_\infty}{r_\infty - r_t}\right]$

8. First step is slow (require large activation energy) second step is fast (less activation energy) and overall reaction exothermic, so product energy level should be less as compare to reactants.

9. $r_1 = k[A]\,[B]^2 = k[0.6]\,[0.80]^2$

After reaction

$$\begin{array}{ccccccc} A & + & 2B & \longrightarrow & C & + & D \\ 0.6 - 0.2 & & 0.8 - 0.4 & & 0.2 & & 0.2 \\ 0.4 & & 0.4 & & 0.2 & & 0.2 \end{array}$$

$\frac{r_2}{r_1} = \frac{k(0.4)(0.4)^2}{(0.6)(0.8)^2} = \frac{1}{6}$

10.✍ We know $\quad -\frac{d(BrO_3^-)}{dt} = -\frac{1}{5}\frac{d(Br^-)}{dt} = -\frac{1}{6}\frac{d(H^+)}{dt} = +\frac{d(Br_2)}{dt}$

Then by this relation $\quad \frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

11. Rate = k $[\text{conc}]^n \longrightarrow$ Independent of conc. of A.

12. More is the activation energy less is the rate of reaction.

13. $t_{1/2} = \frac{t}{4}$; $t_{1/2} = T \ln 2 \qquad$ so $\frac{t}{4} = T \ln 2$; $t = 4T \ln 2$

14. Slow step is the rate determining step (RDS) and (N_2O_2) is the reactive intermediate.

$\therefore \qquad r = k_2 [N_2O_2] [O_2] \qquad$ .....(i)

From reversible reaction, $[N_2O_2]$ is

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

substitute $[N_2O_2]$ in equation (i),

$r = k_2\left(\frac{k_1}{k_{-1}}\right) [NO]^2 [O_2]$

Hence, rate constant = $k_2\left(\frac{k_1}{k_{-1}}\right)$

15. For nth order, $t_{1/2} \propto (1)^{1-n}$.

$\Rightarrow \quad \dfrac{t_{1/2}}{(a)^{1-n}}$ or $t_{1/2} \times (a)^{n-1} = \text{Constant}$

$\therefore$ Given $t_{1/2} \times (a)^{n-1} = \text{Constant}$

$\Rightarrow \quad (a)^{n-1} = (a)^2 \quad \Rightarrow \quad n - 1 = 2 \quad \Rightarrow \quad n = 3$

Hence, third order reaction.

16. It is fact.

17. For zero order reaction, $t_{1/2} \propto (a)^1$

18. $\lambda = \lambda_1 + \lambda_2$; $\lambda = \dfrac{0.693}{22}$ and $\dfrac{\lambda_1}{\lambda_2} = \dfrac{2}{98}$

$\lambda_1 = 0.00063 \text{ year}^{-1}$; $\lambda_2 = 0.03087 \text{ year}^{-1}$

19. $\lambda_A N_A = \lambda_B N_B$ ($\because$ rate of disintegration are same)

$\dfrac{N_A}{N_B} = \dfrac{\lambda_B}{\lambda_A} = \dfrac{2}{1}$

20. ${}_{84}Po^{218} \longrightarrow {}_{82}Pb^{214} + {}_{2}He^{4}$; ${}_{82}Pb^{214} \longrightarrow {}_{83}Bi^{214} + {}_{-1}e^{0}$

Pb^{214} to reach maximum number of nuclei

$$t_{maximum} = \frac{1}{\lambda_1 - \lambda_2} \ln \frac{\lambda_1}{\lambda_2} = 247.5 \text{ sec.} \quad \text{where, } \lambda_1 = \frac{0.693}{183} \text{ ; } \lambda_2 = \frac{0.693}{161}$$

25. $0.2 \text{ M} \xrightarrow[t_{1/2}=5 \text{ hr}]{} 0.1 \text{ M} \xrightarrow[t_{1/2}=5 \text{ hr}]{} 0.05 \text{ M}$

From $0.2 \text{ M} \xrightarrow[t = 10 \text{ hr}]{} 0.05 \text{ M}$

So $t_{1/2}$ is constant which is characteristic of first order reaction. Hence, $t_{1/2} \propto (1)^0$.

PART - II

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1. $K = (\text{mol L}^{-1})^{1-n} \text{ sec}^{-1}$, n = 0, 1.

2. Order is the sum of the power of the concentrations terms in rate law expression. $R = [A] . [B]^2$
Thus, order of reaction = 1 + 2 = 3.

3. $H_2 + I_2 \rightarrow 2HI$
When 1 mole of H_2 and 1mole of I_2 reacts, 2 moles of HI are formed in the same time interval.

Thus the rate may be expressed as $\dfrac{-\Delta[H_2]}{\Delta t} = \dfrac{-\Delta[I_2]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[HI]}{\Delta t}$

The negative sign signifies a decrease in concentration of the reactant with increase of time.

4. $\text{Rate1} = k\,[A]^n\,[B]^m$
On doubling the concentration of A and halving the concentration of B
$\text{Rate2} = k\,[2A]^n\,[B/2]^m$

Ratio between new and earlier rate. $\dfrac{k[2A]^n\ [B/2]^m}{k\ [A]^n\ [B]^m} = 2^n \times \left(\dfrac{1}{2}\right)^m = 2^{n-m}$

5. $\text{Rate}_1 = k\,[NO]^2\,[O_2]$
When volume is reduced to 1/2, concentration become two times,

$\text{Rate}_2 = k\,[2NO]^2\,[2O_2]$ $\quad \dfrac{\text{Rate}_1}{\text{Rate}_2} = \dfrac{k[NO]^2[O_2]}{k[2NO]^2[2O_2]}$ or $\dfrac{\text{Rate}_1}{\text{Rate}_2} = \dfrac{1}{8}$ $\quad \therefore \quad \text{Rate}_2 = 8\ \text{Rate}_1$.

6. In Arrhenius equation, $k = Ae^{-Ea/RT}$
k = rate constant, A = frequency factor
T = temperature, R = gas constant, E_a = energy of activation.
This equation can be used for calculation of energy of activation.

7. The concentration of the reactant decreases from 0.8 M to 0.4 M in 15 minutes, i.e., $t_{1/2}$ = 15 minute. Therefore, the concentration of reactant will fall from 0.1 M to 0.025 in two half live. i.e., $2t_{1/2} = 2 \times 15$ = 30 minutes.

8. $2A + B \longrightarrow C$ rate = k [A] [B]

The value of k (velocity constant) is always independent of the concentration of reactant and it is a function of temperature only.

9. $t_{1/2}$ = 4 hours $n = \frac{T}{t_{1/2}} = \frac{24}{4} = 6$; $N = N_0\left(\frac{1}{2}\right)^N$

or, $N = 200 \times \left(\frac{1}{2}\right)^6 = 200 \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = 3.125g.$

10. For endothermic reaction, ΔH = +ve $\Delta H = E_f - E_b$, it means $E_b < E_f$.

11. Generally, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation. Thus, a reaction involving two different reactants can never be unimolecular.

12. Given rate = k $[CO]^2$

Thus, according to the rate law expression doubling the concentration of CO increases the rate by a factor of 4.

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

$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$ [rate determining step]

Rate of the reaction (r) = k $[NOBr_2]$ [NO]

where $[NOBr_2] = K_c [NO] [Br_2]$

$r = k.\ K_C.\ [NO]\ [Br_2]\ [NO]$

$r = k'\ [NO]^2\ [Br_2].$

The order of the reaction with respect to NO(g) = 2.

14. $\Delta H_R = E_f - E_b = 180 - 200 = -20$ kJ mol^{-1}

The correct answer for this question should be –20kJ mol^{-1}. But no option given is correct. Hence we can ignore sign and select option

15. Let A be the activity for safe working.

Given $A_o = 10A$ $A_o \times N_o$ and $A \times N$

$$t = \frac{2.303}{\lambda} \log \frac{N_o}{N} = \frac{2.303}{\lambda} \log \frac{A_o}{A}$$

$$= \frac{2.303}{\frac{0.693}{30}} \log \frac{10A}{A} = \frac{2.303 \times 30}{0.693} \log 10 = \frac{2.303 \times 30}{0.693} = 99.69 \text{ days} \approx 100 \text{ days.}$$

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

$$-\frac{1}{1/2}\frac{d(A)}{dt} = \frac{1}{2}\frac{d(B)}{dt}$$

$$\boxed{-\frac{d(A)}{dt} = \frac{1}{4}\frac{d(B)}{dt}}$$

17. In first order reaction for X% complation

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

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log\left(\frac{100}{100 - 99}\right)$$

$$\frac{0.693}{6.93} = \frac{2.303 \times 2}{t}$$

So, t = 46.06 min.

18. A $\longrightarrow$ product

For zero order reaction

$t_{1/2} \propto \frac{1}{a^{n-1}}$ a = initial concentration of reactant

$t_{1/2} \propto a$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{a_1}{a_2} \; ; \; \frac{1}{(t_{1/2})_2} = \frac{2}{0.50}$$

$$t_{1/2} = \frac{0.5}{2} = 0.25 \text{ h.}$$

19. Mechanism (1) rate = K $[Cl_2]$ $[H_2S]$

Mechanism (2) rate = K_1 $[Cl_2]$ $[HS^-]$

$$K_{eq} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$[HS^-] = \frac{K_{eq}[H_2S]}{[H^+]}$$

$$\text{Rate} = K_1 K_{Eq.} \frac{[Cl_2]\left[H_2S\right]}{[H^+]}$$

$\therefore$ Mechanism (1) is consistent with this rate equation.

20. $$\frac{\text{Rate at } 50^o\text{C}}{\text{Rate at } T_1{}^o\text{C}} = (2)^{\frac{\Delta T}{T_1}} = (2)^{\frac{50}{10}} = 2^5 = 32 \text{ times}$$

21. $K_1 = A_1 e^{-Ea_1/RT}$

$K_2 = A_2 e^{-Ea_2/RT}$

$$\frac{K_1}{K_2} = \frac{A_1}{A_2} e^{(E_{a_2} - E_{a_1})/RT}$$

$K_1 = K_2 A \times e^{E_{a_1}/RT}$

22. $$K = \frac{1}{40} \ln \frac{0.1}{0.025} = \frac{1}{40} \ln 4$$

$$R = K[A]^1 = \frac{1}{40} \ln 4(.01) = \frac{2\ln 2}{40}(.01) = 3.47 \times 10^{-4}$$

23. $$\log \frac{K_2}{K_1} = \frac{-E_a}{2.030R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$\frac{K_2}{K_1} = 2$; T_2 = 310 K T_1 = 300 K

$$\Rightarrow \log 2 = \frac{-E_a}{2.303 \times 8.134}\left(\frac{1}{310} - \frac{1}{300}\right) \quad \Rightarrow E_a = 53598.6 \text{ J/mol} = 53.6 \text{ KJ/mol}$$ Ans is (1)

24. $1.2 \times 10^{-3} = K\,(0.1)^x\,(0.1)^y$ $\Rightarrow$ $1.2 \times 10^{-3} = K\,(0.1)^x\,(0.2)^y$

$2.4 \times 10^{-3} = K\,(0.2)^x\,(0.1)^y$ $\Rightarrow$ $R = K\,[A]^1\,[B]^0$

25. Higher order (> 3) reactions are rare due to low probability of simultaneous collision of all the reacting species.

26. In 50 minutes, concentration of H_2O_2 becomes $\frac{1}{4}$ of initial.

$\Rightarrow$ $2 \times t_{1/2} = 50$ minutes

- $t_{1/2} = 25$ minutes
- $K = \frac{0.693}{25}$ per minute

$$r_{H_2O_2} = \frac{0.693}{25} \times 0.05 = 1.386 \times 10^{-3}$$

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

$r_{O_2} = \frac{1}{2} \times r_{H_2O_2}$; $r_{O_2} = 0.693 \times 10^{-3}$

$r_{O_2} = 6.93 \times 10^{-4}$ mol/minute × litre

27. $k_1 = Ae^{-Ea_1/RT}$; $k_2 = Ae^{-(Ea_1-10)/RT}$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{10}{RT} = \frac{10}{8.314 \times 10^{-3} \times 300} = 4$$

28. Rate = K (pressure)^n

$R_1 = K(P_1)^n$

$R_2 = K(P_2)^n$

$\frac{R_1}{R_2} = \left[\frac{P_1}{P_2}\right]^n$ $P_1 = 363 - \frac{363 \times 5}{100} = 344.85$, $P_2 = 363 - \frac{363 \times 33}{100} = 243.21$

$$\frac{1}{0.5} = \left(\frac{344.85}{243.21}\right)^n$$

$2 = (\sqrt{2})^n$; (n = 2)

PART - IV

1. **(a)** $A \longrightarrow B$

$$\frac{-d[A]}{dt} = K\,[A]^{\frac{1}{2}}$$

$A \longrightarrow B$

$t = 0$ $a = C_O$

$t = t$ $(a-x) = C_t$

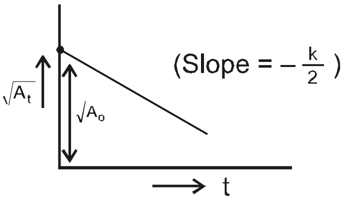
$$\frac{-d[A]}{dt} = K\,[A]^{\frac{1}{2}}$$

$$\int_{A_0}^{A_t} \frac{1}{(A_t)^{\frac{1}{2}}}\,.dA_t = -\int_{o}^{t} K\,dt$$

$$\left[\frac{(A_t)^{\frac{1}{2}}}{\left(\frac{1}{2}\right)}\right]_{C_O}^{C_t} = -kt \qquad 2\,[(C_t)^{\frac{1}{2}} - (C_O)^{\frac{1}{2}}] = -kt$$

$$(A_t)^{\frac{1}{2}} - (A_o)^{\frac{1}{2}} = \frac{kt}{2} \qquad = \sqrt{A_t} - \sqrt{A_o} - \frac{kt}{2} \qquad \sqrt{A_t} = \sqrt{A_o} - \frac{kt}{2}$$

(b) $\sqrt{A_t} = \left(\frac{-k}{2}\right) t + \sqrt{A_o}$



(c) For Half life $A_t = \left(\frac{A_0}{2}\right)$

$$\sqrt{\frac{A_0}{2}} = \sqrt{A_0} - \frac{kt_{1/2}}{2} \Rightarrow \frac{kt_{1/2}}{2} = \sqrt{A_0} - \sqrt{\frac{A_0}{2}}$$

$$t_{\frac{1}{2}} = \frac{2}{k}\left[\frac{\sqrt{2}\,\sqrt{A_0}-\sqrt{A_0}}{\sqrt{2}}\right] \quad \Rightarrow \quad t_{\frac{1}{2}} = \frac{2}{k}\left[\frac{\sqrt{2}-1}{\sqrt{2}}\right] = \sqrt{A_0} = \frac{\sqrt{2}\,(\sqrt{2}-1)\sqrt{A_0}}{k}\ t_{1/2}$$

2. **(a)**

$$\begin{array}{lllll} & A & \longrightarrow B & + \quad C & \\ t=0 & a & 0 & 0 & a\,P_0 \\ t=t & a\text{-}x & x & x & (a-x)\,P_t \end{array}$$

$$Kt = \ln\left(\frac{a}{a-x}\right) \Rightarrow \quad k = \frac{1}{t}\ln\left(\frac{P_0}{P_t}\right)$$

(b)

$$\begin{array}{llllll} & A & \longrightarrow B & + \quad C & & \\ t=0 & a & 0 & 0 & a \propto P_0 & \\ t=t & a\text{-}x & x & x & (a+x) \propto P_t & \Rightarrow \quad x \propto (P_t - P_0) \end{array}$$

$$Kt = \ln\left(\frac{a}{a-x}\right) \quad \Rightarrow \quad k = \frac{1}{t}\ln\left(\frac{P_0}{P_0-(P_t-P_0)}\right) \quad \Rightarrow \quad k = \frac{1}{t}\ln\left(\frac{P_0}{2P_0-P_t}\right)$$

(c)

$$\begin{array}{llllll} & A & \longrightarrow B & + \quad C & & \\ t=0 & a & 0 & 0 & & \\ t=t & a\text{-}x & x & x & 2x \propto P_t & \Rightarrow \quad x \propto \frac{P_t}{2} \\ t=\infty & 0 & a & a & 2a \propto P_\infty & \Rightarrow \quad a \propto \frac{P_\infty}{2} \end{array}$$

$$Kt = \ln\left(\frac{a}{a-x}\right) \qquad \Rightarrow \quad k = \frac{1}{t}\ln\left(\frac{P_\infty}{P_\infty-P_t}\right)$$

(d)

$$\begin{array}{llll} & A(g) \longrightarrow & B(g) \quad + & C(s) \\ t=0 & a & 0 & 0 \\ t=t & a\text{-}x & x & x \\ t=\infty & 0 & a & a \end{array}$$

$P_t = x$; $P_\infty = a$

$$k = \frac{1}{t}\ln\left[\frac{a}{a-x}\right] \quad ; \quad k = \frac{1}{t}\ln\left[\frac{P_\infty}{P_\infty-P_t}\right]$$

3.

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$$

$$\begin{array}{lll} t=0 & [A]_0 & 0 \\ t=t & [A]_0 - x & x \\ t=t_{eq} & [A_0] - x_{eq} = [A]_{eq}\ ; & X_{eq} = [B]_{eq}. \end{array}$$

$$(K_f + K_b) = \frac{1}{t}\ln\left(\frac{x_{eq}}{x_{eq}-x}\right) \quad \Rightarrow \quad (K_f + K_b) = \frac{1}{t}\ln\left(\frac{[B]_{eq}}{[B]_{eq} - \frac{[B]_{eq}}{2}}\right)$$

$$(K_f + K_b) = \frac{1}{t}\ln 2 \quad \Rightarrow \quad t = \frac{\ln 2}{K_f + K_b}$$

5. From the unit of k given, the reaction is of zero order. As this reaction is of the type 2A → Products, we apply

$k_0 = \frac{x}{nt}$ where n = 2 or $k_0 = \frac{a-(a-x)}{nt}$ or $0.1 = \frac{(2-0.5)}{2t}$

t = 7.5 sec

6.

	A	+	B	$\longrightarrow$	C
t = 0	a = 0.1 M		b = 0.2 M		0
t = 100s	a – x		b – x		x

From question, r = k[A][B] and hence

$$k_t = \frac{1}{b-a}\ln\frac{a(b-x)}{b(a-x)}$$

or, $$10^{-3} \times 100 = \frac{1}{0.2-0.1} \times 2.303 \times \log\frac{0.1(0.2-x)}{0.2(0.1-x)}$$

$x \approx 0.002$ $\quad\therefore\quad$ [A] = 0.1 – x = 0.098 M

7. $A + B \rightleftharpoons C + D$

$$\left[\frac{dx}{dt}\right] = 0$$

$k_1[A][B] - k_2[C][D] = 0$; $\qquad k_1[A][B] = k_2[C][D]$

[A] [B] = [C] [D]

$0.4 \times 0.25 = 0.2 \times 0.5 \quad\Rightarrow\quad 1 = 1.$

8. Equation : $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2^+]$

Given, $$\frac{dx}{dt} = 2 \times 10^7\ L^2\ mol^{-2}\ s^{-1}\ [Ag^+]\ [NH_3]^2 - 1 \times 10^{-2}\ s^{-1}\ [Ag(NH_3)_2^+]$$

For equilibrium $\frac{dx}{dt} = 0$

$$2 \times 10^7\ [Ag^+]\ [NH_3]^2 - 1 \times 10^{-2}\ [Ag(NH_3)_2^+] = 0$$

$$\frac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2} = \frac{2\times10^7}{1\times10^{-2}} = 2 \times 10^9\ L^2\ mol^{-2}.$$

9. In given sequence of Rxn $\frac{d[C]}{dt} = k_2[B] - K_3[C]$

10. $A + A \xrightarrow{K_1} A + A^*$ $\qquad A^* + A \xrightarrow{K_2} 2A$

Rate of decomposition $\qquad A = K_1[A]^2$

Rate of formation $\qquad A = K_2[A][A^*]$

At equilibrium rate of decomposition = rate of formation

$$K_1[A]^2 = K_2[A][A^*]$$

$$[A^*] = \frac{K_1}{K_2}[A]$$

11. Activity = $\lambda N_0 = \frac{0.693}{t_{1/2}} \times \frac{1}{226} \times N_A$

12. Given Rxn

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$\frac{dx}{dt} = 1 \times 10^2\ [N_2]\ [H_2]^3 - 1 \times 10^{-3}\ [NH_3]^2$$

when $\frac{dx}{dt} = 0$ $\qquad$ then $\frac{[N_2][H_2]^3}{[NH_3]^2} = 10^{-5}$

Hence the reaction will be at equilibrium at the given instant.

13.

	A (aq)	$\longrightarrow$	B (aq)	+	C (aq)
t=0	a		0		0
t=t	a–x		x		x
t=∞	0		a		a

$(a - x) + 2x + 3x \propto n_1$

$a + 4x \propto n_1$ $\qquad$ .....(i)

$2a + 3a \propto n_2$

$a \propto \frac{n_2}{5}$ .....(ii)

$$k = \frac{1}{t}\ln\left[\frac{a}{a-x}\right] \quad \Rightarrow \quad k = \frac{1}{t}\ln\frac{\left(\frac{n_2}{5}\right)}{\left(\frac{n_2-n_1}{4}\right)} = \frac{1}{t}\ln\frac{4(n_2)}{5(n_2-n_1)}$$

14. $y = \frac{k_1 a}{k_2-k_1}\left[e^{-k_1t}-e^{-k_2t}\right]$

$\frac{dy}{dt} = 0.$

$-k_1e^{-k1t} + k_2e^{-k2t} = 0$ So, $t_{max} = \frac{1}{K_1-K_2}\ln\frac{k_1}{k_2}$

15. Slow step is rate determining step.

16. We know

Rate = k [conc.]

Given Rxn catalysed by HA and HB

Rate constant $k_A = k_1\,[H^+]_A$

$k_B = k_1\,[H^+]_B$

Then relative strength of acids A and B is

$$\frac{k_A}{k_B} = \frac{[H^+]_A}{[H^+]_B}$$

$$\frac{2}{1} = \frac{[H^+]_A}{[H^+]_B} = \text{strength of } \frac{[\text{Acid A}]}{[\text{Acid B}]}$$

17. $t_{1/2} \propto \frac{1}{(\text{initial conc.})^{\text{order}-1}}$

18. $t_1 = \frac{1}{k}\ln\left(\frac{a+x_1}{a}\right)$

$t_2 = \frac{1}{k}\ln\left(\frac{a+x_1}{a}\right)$

$(t_2 - t_1) = \frac{1}{k}\ln\left(\frac{a+x_2}{a+x_1}\right)$

$k = \frac{1}{t_2-t_1}\ln\left(\frac{a+x_2}{a+x_1}\right)$

$k = \frac{1}{10}\ln\left(\frac{72}{48}\right)$

$k = \frac{1}{10}\ln\left(\frac{3}{2}\right)$

$k = \left(\frac{\ln 3 - \ln 2}{10}\right)$

$\frac{\ln 2}{(t_{1/2})} = \left(\frac{\ln 3-\ln 2}{10}\right)$

$\frac{0.80}{(t_{1/2})} = \frac{0.48-0.30}{10}$

$$\frac{0.30}{(t_{1/2})} = \frac{0.18}{10}$$

$$t_{1/2} = \frac{30 \times 10}{18} = 17 \text{ minutes (Approx.)}$$

19. Molarity of $H_2O_2 = \frac{11.x}{11.2} = \frac{20}{11.2} = 1.786$

For titration, $[M_1V_1]\ V.F_1 = [M_2V_2]\ V.F_2$

$M_1 \times 10 \times 2 = 0.025 \times 25 \times 5$

$M_1 = 0.15625$

Now molarity of diluted solution = 0.15625

So molarity of original solution = 1.563

So, $K = \frac{1}{t} \ln \left(\frac{C_0}{C_t}\right)$

$$K = \frac{2.303}{6} \log\left(\frac{1.786}{1.563}\right)$$

$K = 80\ \text{sec}^{-1}$

21. $K = \frac{K_1K_3}{K_2}$

$$Ae = \frac{-(E_a)_{overall}}{RT} = \frac{A_1e^{-\frac{E_1}{RT}} \times A_3e^{-\frac{E_3}{RT}}}{A_2e^{-\frac{E_2}{RT}}}$$

$$Ae\ \frac{-(E_a)_{overall}}{RT} = \left(\frac{A_1A_3}{A_2}\right)\ e^{-\frac{[E_1+E_3-E_2]}{RT}}$$

$(E_a)_{overall} = E_1 + E_3 - E_2 = 30$ KJ/mole

$$2A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} A^* + A \qquad \text{[Fast]}$$

$$\frac{K_1}{K_2} = \frac{[A^*][A]}{[A]^2} \text{ or } [A^*] = \frac{K_1}{K_2}[A]$$

$$\text{rate} = K_3[A^*] = \frac{K_1K_3}{K_2}[A]$$

22. $\frac{d}{dt}[NH_2CONH_2] = k_4[NH_3][HNCO]$ from (iii)

Applying steady state approximation to HNCO or NH_3

$$\frac{d[HNCO]}{dt} = O = k_3\,[NH_4NCO] - k_4[NH_3][HNCO]$$

$$\therefore \quad \frac{k_3}{k_4} = \frac{[NH_3][HNCO]}{[NH_4CNO]}$$

$$\frac{d[urea]}{dt} = k_4 \times [NH_3][HNCO] = k_4 \times \frac{k_3}{k_4}\,[NH_4NCO]$$

Also, $[NH_4NCO] = \frac{k_1}{k_2} \times [NH_4CNO]$

$$\therefore \quad \frac{d[urea]}{dt} = k_3 \times \frac{k_1}{k_2} \times [NH_4CNO] = k[NH_4CNO]$$

PART - V

1.

$$t_{1/2} = \frac{0.69}{k} = \frac{0.3 \times 2.3}{k}$$

$$t_{60\%} = \frac{2.3}{k}\log\frac{100}{100-60} = \frac{2.3}{k}\log\frac{10}{4}$$

$$k = \frac{2.3}{60}\log\frac{10}{4}$$

$$\frac{0.3 \times 2.3}{t_{1/2}} = \frac{2.3}{60}\log\frac{10}{4}$$

$$\frac{0.3}{t_{\frac{1}{2}}} = \frac{1}{60}[1-2\log 2] = \frac{1}{60}[1-0.6]$$

$$\frac{0.3}{t_{1/2}} = \frac{0.4}{60} \qquad \therefore \qquad t_{1/2} = \frac{60 \times 0.3}{0.4} = 45\,\text{min}$$

Use direct relation

$$t_{1/2} = 0.3,\ t_{x\%} = \left(\log\frac{100}{100-x}\right)$$

$$t_{60\%} = \log\frac{10}{4} = (0.4)$$

$$\frac{t_{1/2}}{t_{60\%}} = \frac{0.3}{0.4} \qquad \therefore \qquad t_{1/2} = t_{60\%} \times \frac{0.3}{0.4} = \frac{60 \times 3}{4} = 45\ \text{min}$$

2. Use the formula

$$t = \frac{2.303}{k}\log\frac{V_0}{V_t} = \frac{1}{k}\ln\frac{V_0}{V_t} = \frac{1}{4.5 \times 10^{-2}\,\text{min}^{-1}}\ln\frac{25\,\text{mL}}{5\,\text{mL}} = \frac{\log_e 5}{4.5 \times 10^{-2}}\,\text{min}$$

3. For second order reaction,

When x = 20%, (a – x) = 80%, a = 100%

$$k_2 = \frac{1}{t}.\frac{x}{a(a-x)} = \frac{1}{40} \times \frac{20}{100 \times (100-20)} = \frac{1}{2 \times 100 \times 80}$$

When x = 80%, (a – x) = 20%

$$k_2 = \frac{1}{t} \times \frac{80}{100 \times 20} = \frac{1}{25}t$$

From equations (i) and (ii),

$$t = \frac{2 \times 100 \times 80}{25} = 640\,\text{min}$$

4. Intermediate and product have less potential energy than activated complex.

5. The fraction of molecules having energy equal to or greater than E_a is :

$$x = \frac{n}{N} = e^{-E_a/RT}\left(x = \frac{n}{N} = 0.001\% = \frac{0.001}{100} = 10^{-5}\right)$$

$$\therefore \qquad \log x = \frac{-E_a}{2.3 \times RT} \quad (R = 2\text{cal mol}^{-1}\ \text{K}^{-1},\ T = 500\ \text{K})$$

$$\log 10^{-5} = \frac{-E_a}{2.3 \times 2 \times 500}$$

$E_a = 11.5 \times 103$ cal mol^{-1} = 11.5 kcal mol^{-1}

6.

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

$k = Ae^{-40000/RT}$ ....(ii)

from (i) and (ii)

$$\frac{E_a}{RXT} = \frac{40000}{T}$$

$E_a = 40,000 \times 2$ cal ⇒ $E_a = 80,000$ cal

7. V_{O_2} (t = 15 min.) = 100 ml (at 1 atm, 0ºC)

$\therefore$ $x \propto 100$ ml

V_{O_2} $(t = \infty)$ = 200 ml (at 2 atm, 0ºC)

= 400 ml (at 1 atm, 0ºC)

$\therefore$ $a \propto 400$ ml

i.e., in 15 min 25% of reaction proceeds. Hence V_{KMnO_4} will be $\frac{3}{4} \times 40 = 30$ mL.

8. $A \rightarrow B$ (uncatalysed reaction)

$A \xrightarrow{\text{catalyst}} B$ (catalyst reaction)

$K = A\,e^{-E_a/RT}$

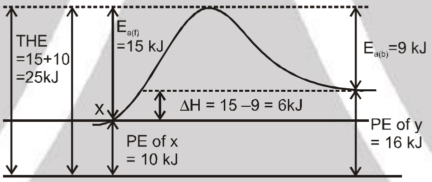
$K_{cat.} = A\,e^{-E_{a(cat.)}/RT}$

$$\frac{K_{cat.}}{K} = e^{(E_a - E_a^{'})\times\frac{1}{RT}}$$

$$\frac{K_{cat.}}{K} = e^{\frac{8.314\times10^3}{8.314\times300}} = e^{3.33} = 28 \text{ times}$$

9. $t_{1/2} \propto (a)^{1-n}$; $[A]_t = [A]_0 - kt$ and $X = kt$ are integrated form of zero order.

10. For reaction $X \rightarrow Y$



$E_{a(f)} = 15$ kJ mol^{-1}, $E_{a(b)} = 9$ kJ mol^{-1}

Heat of reaction $E_{a(f)} - E_{a(b)} = 15 - 9 = 6$ kJ mol^{-1}

Potential energy of Y is = 10 + 6 = 16 kJ

Thershold energy of the reaction = PE of X + $E_{a(f)}$ = 10 kJ + 15 kJ = 25 kJ

The reaction is endothermic beacuse $E_{a(f)} > E_{a(b)}$

12. Use initial rate law method, let the reaction be first order,

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

(B) At t = 20 s, $k_1 = \frac{2.303}{20}\log\left(\frac{0.4}{0.2}\right)$

and at t = 40 s, $k_2 = \frac{2.303}{40}\log\left(\frac{0.4}{0.1}\right) = k_1$

⇒ Assumption is corret ($k_1 = k_2$)

Rate at 20s = $k[A] = \frac{0.693}{20} \times 0.2 = 0.0063 \approx 7 \times 10^{-3}$ Ms^{-1}

Clearly, half life $t_{1/2} = 20$s

(D) In 60 s, number of life = $\frac{60}{20} = 3$

⇒ [B] at 60 s = $0.4 - 0.4\left(\frac{1}{2}\right)^3 = 0.35$ M

13. From the unit of k given, the reaction is of zero order.

As this reaction is of the type 2A → Products, we apply,

$k_0 = \frac{x}{nt}$ where n = 2 or $k_0 = \frac{a-(a-x)}{nt}$ or $0.08 = \frac{1.50-0.30}{2t}$

t = 7.5 s

15. From steady state approximation

$\frac{dE}{dt} = K_1 [A] [B] – K_2[E] [A]^2 = 0$

$[E] = \frac{K_1[A][B]}{K_2[A]^2} = \frac{k_1}{k_2}\frac{[B]}{[A]}$ So $-\frac{dB}{dt} = k_1[A] [B]$

or $-\frac{dA}{dt} = k_1[A] [B] + 2k_2[E] [A]^2 = k_1[A] [B] + 2 k_2 \times \frac{k_1}{k_2}\frac{[B]}{[A]}[A]^2 = 3k_1[A][B]$

$-\frac{1}{3}\frac{dA}{dt} = k_1[A] [B]$

16. $\ell n\frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$ ....(i)

$\ell n\frac{K_C}{K_1} = \frac{E_a-E_{ac}}{RT_1}$ for effect of catalyst new $K_C = K_2$

$\ell n\frac{K_2}{K_1} = \frac{E_a-E_{ac}}{RT_1}$ ....(ii)

from (i) and (ii) $\frac{E_a-E_{ac}}{RT_1} = \frac{E_a}{R}.\left(\frac{1}{T_1},\frac{1}{T_2}\right)$

$\frac{1}{T_1} - \frac{1}{T_2} = \frac{E_a-E_{ac}}{E_a.T_1}$

$\frac{1}{300} - \frac{1}{T_2} = \frac{100-80}{100\times 300} = \frac{20}{100\times 300} = \frac{1}{1500}$

$\frac{1}{T_2} = \frac{1}{300} - \frac{1}{1500} = \frac{5-1}{1500} = \frac{4}{1500}$

$T_2 = 375$ change in temp = 375 – 300 = 75 Ans.

17. Assume rate law

$r = K[H_3AsO_4]^x [H_3O^+]^y [I^-]^z$

Solving by the help of various experiements

x = 1, y = 2 and z = 1 total order = 4

18. (I). Rate law for mechanism I

Rate = k_1^1 [A] [B]

Rate = 1×10^{-5} [.1] [.1] = 1×10^{-7} m/sec.

19. (II). Rate = $1 \times 10^{-4} \times [1] = 1 \times 10^{-4}$

20. (III). Rate I = Rate II

$k_1^1 [A] [B] = k_1 [A]$

$B = \frac{k_1}{k_1^1} = 10$ M

21. Zero order, $x = kt$

First order, $K = \frac{1}{t}\ln\frac{a}{(a-x)}$

Second order, $K = \frac{1}{t}\left[\frac{1}{(a-x)}-\frac{1}{a}\right]$

Third order, $K = \frac{1}{2t}\left[\frac{1}{(a-x)^2}-\frac{1}{a^2}\right]$