Objective Questions I (Only one correct option)

1. NO_2 required for a reaction is produced by the decomposition of N_2O_5 in CCl_4 as per the equation,

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

The initial concentration of N_2O_5 is 3.00 mol L ¹ and it is

2. In the following reaction; xA = yB

$$\log_{10} \quad \frac{d[A]}{\mathrm{dt}} \quad \log_{10} \frac{d[B]}{\mathrm{dt}} \quad 0.3010$$

- **3.** For the reaction of H₂ with I₂, the rate constant is 2.5 10 ⁴ dm³mol ¹s ¹ at 327°C and 1.0 dm³ mol ¹ s ¹ at 527°C. The activation energy for the reaction, in kJ mol ¹ is (R 8.314 JK ¹ mol ¹) (2019 Main, 10 April II) (a) 59 (b) 72 (c) 150 (d) 166
- **4.** A bacterial infection in an internal wound grows as $N(t) = N_0 \exp(t)$, where the time *t* is in hours. A dose of antibiotic, taken orally, needs 1 hour to reach the wound. Once it reaches there, the bacterial population goes down as $\frac{dN}{dt} = 5N^2$. What will be the plot of $\frac{N_0}{N}$ vs *t* after 1 hour?

(2019 Main, 10 April I)



Consider the given plot of enthalpy of the following reaction between A and B. A B C+D

Identify the incorrect statement.

(2019 Main, 9 April II)



- (a) *D* is kinetically stable product.
- (b) Formation of A and B from C has highest enthalpy of activation.
- (c) C is the thermodynamically stable product.
- (d) Activation enthalpy to form C is 5 kJ mol¹ less than that to form D.
- **6.** The given plots represent the variation of the concentration of a reaction *R* with time for two different reactions (i) and (ii). The respective orders of the reactions are

(2019 Main, 9 April I)



7. For a reaction scheme, $A \stackrel{k_1}{=} B \stackrel{k_2}{=} C$, if the rate of formation of *B* is set to be zero then the concentration of *B* is given by (2019 Main, 8 April II)

(a) $k_1 k_2 [A]$ (b) $\frac{k_1}{k_2} [A]$ (c) $(k_1 k_2) [A]$ (d) $(k_1 k_2) [A]$

8. For the reaction, 2A + B = C, the values of initial rate at different reactant concentrations are given in the table below. The rate law for the reaction is (2019 Main, 8 April I)

[A](mol	L ¹)	$[\boldsymbol{B}] \pmod{L^{1}}$	Initial rate (mol L ¹ s ¹)
(0.05	0.05	0.045
(0.10	0.05	0.090
(0.20	0.10	0.72
(a) rate	$k [A][B]^2$	(b) rate	$k \left[A\right]^2 \left[B\right]^2$
(c) rate	k[A][B]	(d) rate	$k [A]^{2}[B]$

9. For a reaction, consider the plot of $\ln k$ versus 1/T given in the figure. If the rate constant of this reaction at 400 K is 10^{-5} s⁻¹, then the rate constant at 500 K is

(2019 Main, 12 Jan II)



- 10 Decomposition of X exhibits a rate constant of 0.05 g/year. How many years are required for the decomposition of 5 g of X into 2.5 g?
 (2019 Main, 12 Jan I)
 (a) 20
 (b) 25
 (c) 40
 (d) 50
- 11. The reaction, 2 X B is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be (2019 Main, 11 Jan II) (a) 7.2 h (b) 18.0 h (c) 12.0 h (d) 9.0 h
- **12.** If a reaction follows the Arrhenius equation, the plot $\ln k vs$ 1/(RT) gives straight line with a gradient (y) unit. The energy required to activate the reactant is

(2019 Main, 11 Jan I)

(a)
$$\frac{y}{R}$$
 unit (b) y unit (c) yR unit (d) y unit

13. For an elementary chemical reaction,

$$A_{2} \xrightarrow{k_{1}} 2A \text{, the expression for } \frac{d[A]}{dt} \text{ is}$$
(2019 Main, 10 Shift II)
(a) $2k_{1}[A_{2}] = k_{1}[A]^{2}$
(b) $k_{1}[A_{2}] = k_{1}[A]^{2}$
(c) $2k_{1}[A_{2}] = 2k_{1}[A]^{2}$
(d) $k_{1}[A_{2}] = k_{1}[A]^{2}$

14. Consider the given plots for a reaction obeying Arrhenius equation $(0^{\circ}C < T < 300^{\circ}C)$: (*k* and E_a are rate constant and activation energy, respectively) (2019 Main, 10 Jan I)



Choose the correct option.

- (a) Both I and II are wrong
- (b) Both I and II are correct
- (c) I is wrong but II is right
- (d) I is right but II is wrong
- **15** For the reaction, 2A B products

When concentration of both (*A* and *B*) becomes double, then rate of reaction increases from 0.3 mol L¹ s¹ to 2.4 mol L¹ s¹.

When concentration of only *A* is doubled, the rate of reaction increases from 0.3 mol L 1 s 1 to 0.6 mol L 1 s 1 . Which of the following is true? (2019 Main, 9 Jan II) (a) The whole reaction is of 4th order (b) The order of reaction w.r.t. *B* is one (c) The order of reaction w.r.t. *B* is 2

(d) The order of reaction w.r.t. A is 2

III.

(a) A and B

(c) C and D

16 The following results were obtained during kinetic studies of the reaction; (2019 Main, 9 Jan I)

	ZA B	Products	
Experiment	[A] (in mol L ¹)	[B] (in mol L ⁻¹)	Initial rate of reaction (in mol L ¹ min ⁻¹)
I.	0.10	0.20	6.93 10 ³
II.	0.10	0.25	6.93 10 ³

0.30

1.386 10²

The time (in minutes) required to consume half of A is (a) 5 (b) 10 (c) 100 (d) 1

0.20

17. Which of the following lines correctly show the temperature dependence of equilibrium constant, *K*, for an exothermic reaction? (2018 Main)



- 18. 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 : (2018 Main)

 (a) 2
 (b) 3
 (c) 1
 (d) 0
- **19.** Two reactions R_1 and R_2 have identical pre- exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kJ mol⁻¹. If k_1 and k_2 are rate constants for reactions R_1 and R_2 ,

respectiv (<i>R</i> 8.3	vely at 300 14 J mol ¹ K	K, then l ¹)	n $\frac{k_2}{k_1}$ is	equal to (2017 Main)
(a) 8	(b) 12	(c) 6	(d) 4

- **20.** Decomposition of H_2O_2 follows a first order reaction. In 50 min, 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 (**2016 Main**) (a) 6.93 10⁴ mol min⁻¹ (b) 2.66 L min⁻¹ at STP (c) 1.34 10⁻² mol min⁻¹ (d) 6.93 10⁻² mol min⁻¹
- 21. Higher order (>3) reactions are rare due to (2015 Main)
 (a) low probability of simultaneous collision of all the reacting species
 - (b) increase in entropy and activation energy as more molecules are involved
 - (c) shifting of equilibrium towards reactants due to elastic collisions(d) loss of active species on collision
- **22.** For the elementary reaction, M N, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is (2014 Adv.) (a) 4 (b) 3 (c) 2 (d) 1
- **23.** For the non-stoichiometric reaction, 2A + B = C + D, the following kinetic data were obtained in three separate experiments, all at 298 K. (2014 Main)

	Initial concentration [A]	Initial concentration [B]	Initial rate of formation of <i>C</i> (mol L ⁻¹ s ⁻¹)
(i)	0.1 M	0.1 M	1.2 10 ³
(ii)	0.1 M	0.2 M	1.2 10 ⁻³
(iii)	0.2 M	0.1 M	2.4 10 ³

The rate law for the formation of C is

(a)
$$\frac{dC}{dt} = k[A][B]$$

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

24. In the reaction, P Q R S, the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is (2013 Adv.)



25. 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)

(a)
$$53.6 \text{ kJ mol}^{-1}$$
 (b) 48.6 kJ mol^{-1} (2013 Main)
(c) 58.5 kJ mol^{-1} (d) 60.5 kJ mol^{-1}

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



27. For a first order reaction, A = P, the temperature (T) dependent rate constant (k) was found to follow the equation :

$$\log k \quad \frac{2000}{T} \quad 6.0$$

the pre-exponential factor A and the activation energy E_a , respectively, are (2009)

(a) 1.0 10^6 s⁻¹ and 9.2 kJ mol⁻¹

- (b) 6.0 s $^{-1}$ and 16.6 kJ mol $^{-1}$
- (c) 1.0 10^6 s⁻¹ and 16.6 kJ mol⁻¹

(d) 1.0 10^6 s⁻¹ and 38.3 kJ mol⁻¹

28. Under the same reaction conditions, initial concentration of 1.386 mol dm ³ of a substance becomes half in 40 s and 20 s through first order and zero order kinetics respectively. Ratio $\frac{k_1}{k_0}$ of the rate constants for first order (k_1) and zero order (k_0) of the reaction is (2008, 3M)

	(2000)
(a) $0.5 \text{ mol}^{-1} \text{ dm}^{-3}$	(b) 1.0 mol dm 3
(c) 1.5 mol dm 3	(d) 2.0 mol 1 dm 3

- **29.** Consider a reaction, $aG \ bH$ products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is (2007, 3M) (a) 0 (b) 1 (c) 2 (d) 3
- Which one of the following statement(s) is incorrect about order of reaction? (2005, 1M)
 (a) Order of reaction is determined experimentally
 - (b) Order of reaction is equal to sum of the power of concentration terms in differential rate law
 - (c) It is not affected with stoichiometric coefficient of the reactants
 - (d) Order cannot be fractional

- **31.** (A) follows first order reaction, (A) product. Concentration of A, changes from 0.1 M to 0.025 M in 40 min. Find the rate of reaction of A when concentration of A is 0.01 M. (2004, 1M) (a) $3.47 \quad 10^{-4} \text{ M min}^{-1}$ (b) $3.47 \quad 10^{-5} \text{ M min}^{-1}$ (c) $1.73 \quad 10^{-4} \text{ M min}^{-1}$ (d) $1.73 \quad 10^{-5} \text{ M min}^{-1}$
- **32.** In a first order reaction the concentration of reactant decreases from 800 mol/dm³ to 50 mol/dm³ in 2 10^4 s. The rate constant of reaction in s ¹ is (2003, 1M) (a) 2 10^4 (b) 3.45 10^{-5} (c) 1.386 10^{-4} (d) 2 10^{-4}
- **33.** Consider the chemical reaction,

$$N_2(g) + 3H_2(g) = 2NH_3(g)$$

The rate of this reaction can be expressed in terms of time derivatives of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions

(a) Rate
$$\frac{d[N_2]}{dt} = \frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$
(2002, 3M)
(b) Rate
$$\frac{d[N_2]}{dt} = 3 \frac{d[H_2]}{dt} = 2 \frac{d[NH_3]}{dt}$$
(c) Rate
$$\frac{d[N_2]}{dt} = \frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$
(d) Rate
$$\frac{d[N_2]}{dt} = \frac{d[H_2]}{dt} = \frac{d[N_2]}{dt} = \frac{d[N_3]}{dt}$$

34. If *I* is the intensity of absorbed light and *C* is the concentration of *AB* for the photochemical process. AB + h AB^* , the rate of formation of AB^* is directly

proportional to (2001, 1M) (a) C (b) I(c) I^2 (d) C I

- **35.** The rate constant for the reaction, $2N_2O_5$ $4NO_2 + O_2$ is 3.0 10 ⁵ s ¹. If the rate is 2.40 10 ⁵ mol L ¹ s ¹, then the concentration of N_2O_5 (in mol L ¹) is (2000, 1M) (a) 1.4 (b) 1.2 (c) 0.04 (d) 0.8
- **36.** The half-life period of a radioactive element is 140 days. After 650 days, one gram of the element will reduce to (1986)

(a)
$$\frac{1}{2}$$
 g (b) $\frac{1}{4}$ g (c) $\frac{1}{8}$ g (d) $\frac{1}{16}$ g

- 37. A catalyst is a substance which (1983, 1M)
 (a) increases the equilibrium concentration of the product
 (b) changes the equilibrium constant of the reaction
 (c) shortens the time to reach equilibrium
 (d) supplies energy to the reaction
- **38.** The specific rate constant of a first order reaction depends on the (1983, 1M)
 - (a) concentration of the reactant
 - (b) concentration of the product
 - (c) time
 - (d) temperature

- **39.** The rate constant of a reaction depends on (1981, 1M) (a) temperature
 - (b) initial concentration of the reactants
 - (c) time of reaction
 - (d) extent of reaction

Objective Questions II

(One or more than one correct option)

40. For a first order reaction A(g) = 2B(g) + C(g) at constant volume and 300 K, the total pressure at the beginning (t = 0) and at time t are p_0 and p_t , respectively. Initially, only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach $1/3^{rd}$ of its initial value. The correct option(s) is (are) (Assume that all these gases behave as ideal gases) (2018 Adv.)



- 41. In a bimolecular reaction, the steric factor *P* was experimentally determined to be 4.5. the correct option(s) among the following is(are) (2017 Adv.)
 (a) The activation energy of the reaction is unaffected by the value of the steric factor
 - (b) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation
 - (c) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally
 - (d) Since *P* 4.5, the reaction will not proceed unless an effective catalyst is used
- **42.** According to the Arrhenius equation, (2016 Adv.) (a) a high activation energy usually implies a fast reaction
 - (b) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy
 - (c) higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant
 - (d) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy
- **43.** For the first order reaction,

 $2N_2O_5(g)$ $4NO_2(g) + O_2(g)$ (2011)

- (a) the concentration of the reactant decreases exponentially with time
- (b) the half-life of the reaction decreases with increasing temperature
- (c) the half-life of the reaction depends on the initial concentration of the reactant
- (d) the reaction proceeds of 99.6% completion in eight half-life duration

- **44.** The following statement (s) is are correct (1999, 3M) (a) A plot of $\log K_p$ vs $\frac{1}{r}$ is linear
 - (b) A plot of log [X] vs time is linear for a first order reaction, x p
 - (c) A plot of $\log p vs \frac{1}{T}$ is linear at constant volume
 - (d) A plot of $p vs \frac{1}{V}$ is linear at constant temperature
- **45.** For the first order reaction,(1998, 2M)(a) the degree of dissociation is equal to $(1 e^{kt})$
 - (b) a plot of reciprocal concentration of the reactant *vs* time gives a straight line
 - (c) the time taken for the completion of 75% reaction is thrice the $\frac{1}{2}$ of the reaction
 - (d) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}
- **46.** A catalyst (1984, 1M)
 - (a) increases the average kinetic energy of reacting molecules
 - (b) decreases the activation energy
 - (c) alters the reaction mechanism
 - (d) increases the frequency of collisions of reacting species

Numerical Value

47. Consider the following reversible reaction,

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

The activation energy of the backward reaction exceeds that of the forward reaction by 2RT (in J mol¹). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of G^{\ominus} (in J mol¹) for the reaction at 300 K is

(Given; $\ln(2) = 0.7 RT = 2500 \text{ J mol}^{-1}$ at 300 K and G is the Gibbs energy) (2018 Adv.)

Passage Based Questions

Passage

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

$$^{14}_{7}$$
N $_{0}n^{1}$ $^{14}_{6}$ C $_{1}p^{1}$

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

$${}^{4}C = {}^{14}_{7}N$$

The half-life period of 14 C is 5770 yr.

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

48. Which of the following option is correct?

(a) In living organisms, circulation of ¹⁴C from atmosphere is high so the carbon content is constant in organism

(2006, 3 4M = 12M)

- (b) Carbon dating can be used to find out the age of earth crust and rocks
- (c) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbons content remains constant in living organisms
- (d) Carbon dating cannot be used to determine concentration of ¹⁴C in dead beings
- **49.** What should be the age of fossil for meaningful determination of its age?
 - (a) 6 yr
 - (b) 6000 yr
 - (c) 60,000 yr
 - (d) It can be used to calculate any age
- **50.** A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the places respectively then
 - (a) the age of fossil will increase at the place where explosion has taken place and $T_1 = T_2 = \frac{1}{2} \ln \frac{C_1}{C_2}$
 - (b) the age of fossil will decrease at the place where explosion has taken place and $T_1 = T_2 = \frac{1}{2} \ln \frac{C_1}{C}$
 - (c) the age of fossil will be determined to be the same
 - (d) $\frac{T_1}{T_2} = \frac{C_1}{C_2}$

Fill in the Blanks

- **51.** In Arrhenius equation, $k = A \exp \left(\frac{E_a / RT}{RT} \right)$. *A* may be termed as the rate constant at (1997, 1M)
- **52.** For the reaction : $N_2(g) + 3H_2(g) = 2NH_3(g)$

Under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is 0.001 kg/h⁻¹. The rate of conversion of H_2 under the same condition is kg/h⁻¹. (1994, 1M)

- **53.** The hydrolysis of ethyl acetate in medium is a order reaction. (1986, 1M)
- 54. The rate of chemical change is directly proportional to(1985, 1M)

formula $\frac{0.05}{t_{1/2}}$

True/False

55. For a first order reaction, the rate of the reaction doubles as the concentration of the reaction (s) doubles. (1986, 1M)

Integer Answer Type Questions

56. An organic compound undergoes first order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{\lfloor t_{1/8} \rfloor}{102}$ = 10.2 (log $c_{1/8} 2 = 0.3$)

$$[t_{1/10}] \qquad (2012)$$

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

The order of the re	eaction is			(201	0)
<i>t</i> (min)	0.0	0.05	0.12	0.18	
[R] (molar)	1.0	0.75	0.40	0.10	

Subjective Questions

58. 2X(g) 3Y(g) 2Z(g)

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

Assuming ideal gas condition. Calculate

(a) order of reaction

(b) rate constant

- (c) time taken for 75% completion of reaction (d) total pressure when $p_x = 700 \text{ mm}$ (2005, 4M)
- **59.** For the given reaction, *A B* Products

Following data are given

Initial conc. (m/L)	Initial conc. (m/L)	Initial rate [mL ⁻¹ s ⁻¹]
$[A]_0$	$[B]_0$	
0.1	0.1	0.05
0.2	0.1	0.1
0.1	0.2	0.05

(a) Write the rate equation.

```
(b) Calculate the rate constant. (2004, 2M)
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- **60.** ⁶⁴Cu (half-life = 12.8 h) decays by emission (38%), emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes. (2002)
- **61.** The rate of first order reaction is $0.04 \text{ mol } L^{-1}s^{-1}$ at 10 min and $0.03 \text{ mol } L^{-1}s^{-1}$ at 20 min after initiation. Find the half-life of the reaction. (2001, 5M)
- **62.** A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol⁻¹. (2000, 3M)

- **63.** The rate constant for an isomerisation reaction, A = B is 4.5 10 ³min. If the initial concentration of A is 1 M, calculate the rate of the reaction after 1 h. (1999, 4M)
- **64.** (i) The rate constant of a reaction is $1.5 \quad 10^7 \text{ s}^{-1}$ at 50 C and 4.5 10^7 s^{-1} at 100 C. Evaluate the Arrhenius parameters A and E_a . (1998, 5M)
 - (ii) For the reaction, $N_2O_5(g)$ $2NO_2(g) + \frac{1}{2}O_2(g)$,

calculate the mole fraction $N_2O_5(g)$ decomposed at a constant volume and temperature, if the initial pressure is 600 mm Hg and the pressure at any time is 960 mm Hg. Assume ideal gas behaviour.

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

$$\log k(s^{-1})$$
 14.34 $\frac{1.25 \quad 10^4 \text{ K}}{T}$

- (i) What is the energy of activation for the reaction?
- (ii) At what temperature will its half-life period be 256 min? (1997, 5M)
- **66.** One of the hazards of nuclear explosion is the generation of Sr^{90} and its subsequent incorporation in bones. This nucleide has a half-life of 28.1 yr. Suppose one microgram was absorbed by a new-born child, how much Sr^{90} will remain in his bones after 20 yr. (1995, 2M)
- **67.** At 380 C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol⁻¹. Calculate the time required for 75% decomposition at 450 C. (1995, 4M)
- **68.** From the following data for the reaction between A and B

[A], (mol/L)	[B], (mol/L)	Initial rate (mol $L^{-1}s^{-1}$) at		
		300 K	320 K	
2.5 10 4	3.0 10 5	5.0 10 4	$2.0 \ 10^{-3}$	
5.0 10 4	6.0 10 ⁵	4.0 10 ⁻³	_	
1.0 10 3	6.0 10 ⁵	1.6 10 ²		

Calculate

(i) the order of the reaction with respect to A and with respect to B.

(1994, 5M)

- (ii) the rate constant at 300 K.
- (iii) the pre-exponential factor.
- **69.** The gas phase decomposition of dimethyl ether follows first order kinetics

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

The reaction is carried out in a constant volume container at 500 C and has a half-life of 14.5 min. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min? Assume ideal gas behaviour. (1993, 4M)

- **70.** A first order reaction, A = B, requires activation energy of 70 kJ mol⁻¹. When a 20% solution of A was kept at 25 C for 20 min, 25% decomposition took place. What will be the percentage decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature. (1993, 4M)
- **71.** Two reactions (i) A products (ii) B products, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 min. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300 K.

(1992, 3M)

- **72.** The nucleidic ratio, ${}_{1}^{3}$ H to ${}_{1}^{1}$ H in a sample of water is 8.0 10 18 : 1. Tritium undergoes decay with a half-life period of 12.3 yr. How many tritium atoms would 10.0 g of such a sample contain 40 yr after the original sample is collected. (1992, 4M)
- **73.** The decomposition of N_2O_5 according to the equation,

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

is a first order reaction. After 30 min from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg. On complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction. (1991, 6M)

- **74.** In Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are 4 10^{13} s⁻¹ and 98.6 kJ mol⁻¹ respectively. If the reaction is of first order, at what temperature will its half-life period be 10 min? (1990, 3M)
- **75.** An experiment requires minimum beta activity produced at the rate of 346 beta particles per minute. The half-life

period of ${}_{42}$ Mo⁹⁹, which is a beta emitter, is 66.6 h. Find the minimum amount of ${}_{42}$ Mo⁹⁹ required to carry out the experiment in 6.909 h. (1989, 5M)

76. A first order gas reaction has $k = 1.5 = 10^{-6}$ per second at 200 C. If the reaction is allowed to run for 10 h, what percentage of the initial concentration would have change in the product? What is the half-life of this reaction?

(1987, 5M)

- **77.** While studying the decomposition of gaseous N_2O_5 , it is observed that a plot of logarithm of its partial pressure *versus* time is linear. What kinetic parameters can be obtained from this observation? (1985, 2M)
- 78. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 yr. What is the rate constant (in yr ¹) for the decay? What fraction would remain after 11540 yr? (1984, 3M)
- 79. A first order reaction is 20% complete in 10 min. Calculate (i) the specific rate constant of the reaction, and (ii) the time taken for the reaction to go to 75% completion. (1983, 2M)
- **80.** Rate of reaction, *A B* products is given below as a function of different initial concentrations of *A* and *B*

[A] mol/L	[B] (mol/L)	Initial rate $(mol L^{-1} min^{-1})$
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to *A* and *B*. What is the half-life of *A* in the reaction ? (1982, 4M)

1.	(b)	2.	(c)	3.	(d)	4.	(a)
5.	(d)	6.	(d)	7.	(b)	8.	(a)
9.	(c)	10.	(d)	11.	(b)	12.	(d)
13.	(c)	14.	(b)	15.	(c)	16.	(b)
17.	(a)	18.	(a)	19.	(d)	20.	(a)
21.	(a)	22.	(b)	23.	(d)	24.	(d)
25.	(a)	26.	(a)	27.	(d)	28.	(a)
29.	(d)	30.	(d)	31.	(a)	32.	(c)
33.	(a)	34.	(d)	35.	(d)	36.	(d)
37.	(c)	38.	(d)	39.	(a)	40.	(a,d)
41.	(a,c)	42.	(b,c,d)	43.	(a,b,d)	44.	(a,b,d)
45.	(a,d)	46.	(b,c)	47.	(+8500J/ mol	l)	

Answers

48.	(c) 49. (b)	50. (a) 5 1	I. T
52.	0.0015 53. acidic fir	st or basic, second	
54.	concentration of reactant(s	s) at that instant	
55.	T 56. (9)	57. (0)	
58.	(960 mm Hg) 61. (25 min)	62. (100 kJ mol ⁻¹)	1
63.	$(3.26 10^{-3} \text{ mol } \text{L}^{-1} \text{ min}^{-1})$	66. $(6.1 10^{-7} \text{ g})$	
67.	(20.74 min) 69. (0.75 atm	n) 70. (67 %)	
71.	$(3.26 \ 10^{2} \min^{-1})$	72. (5.6 10 ⁵)	
73.	$(5.2 \ 10^{3} \min^{-1})$	74. (311.34 K)	
75.	$(3.56 10^{-16} \text{ g})$	78. (0.25)	
80.	(1.386 min)		

Hints & Solutions

Key Idea The rate of a chemical reaction means the speed with which the reaction takes place. For R Ρ Rate of disappearance of R[*R*] Decrease in conc. of RTime taken t Rate of appearance of PIncrease in conc. of P [P]Time taken t Given, $[N_2O_5]_{initial}$ 3.00 mol L⁻¹ After 30 min, $[N_2O_5]$ 2 .75 mol L⁻¹ $2N_2O_5(g)$ $4NO_2(g) \quad O_2(g)$ *t* 0 3.0 M t 30 2.75 M From the equation, it can be concluded that 1 $[N_2O_5]$ <u>1</u> $[NO_2]$ $\overline{2}$ 4 t t [N₂O₅] (2.75 3.00) mol L¹ 0.25 30 30 t and $\frac{[NO_2]}{t} 2 \frac{(N_2O_5)}{t} \frac{[NO_2]}{t} 2$ $\frac{0.25}{30}$

2. In the given reaction;
$$x A y B$$

$$\log_{10} \frac{d[A]}{dt} \quad \log_{10} \frac{d[B]}{dt} \quad 0.3010$$

Value of log2 0.3010 Substituting 0.3010 by log2

1.

$$\log_{10} \quad \frac{d[A]}{dt} \quad \log_{10} \frac{d[B]}{dt} \quad \log_2$$

Using logarithm rules,

$$\frac{-d[A]}{dt} = 2 \quad \frac{d[B]}{dt} = \frac{1}{2} \quad \frac{d[A]}{dt} = \frac{d[B]}{dt} \qquad \dots (i)$$

Using the rate equation (i) to determine the reaction involved is 2A B

Option that fits correct in the above reaction is (c).
$$2C_2H_4$$
 C_4H_8 .

3. Key Idea The Arrhenius equation for rate constants at two different temperatures is
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \frac{T_2 - T_1}{T_1 T_2} \quad \text{[where, } T_2 - T_1\text{]}$$
where, k_1 and k_2 are rate constants at temperatures T_1 and T_2 , respectively.
R Gas constant, E_a Activation energy

For the reaction,
$$H_2 + I_2$$
 2HI
Given k_1 2.5 10 ⁴ dm³mol ¹s ¹
 T_1 (273 327) K 600 K
 k_2 1 dm³mol ¹s ¹ at T_2 (273 527) K 800 K
Now, $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \frac{T_2}{T_1 T_2}$
 $\log \frac{1}{2.5 \ 10^4} = \frac{E_a}{2.303 \ 8.314 \ 10^3} \frac{800 \ 600}{600 \ 800}$
 $\log \frac{(10 \ 10^3)}{2.5} = \frac{E_a}{0.019} \frac{200}{48 \ 10^4}$
 $\log 4 \ 3\log 10 \ \sim E_a \ 0.022$
 $E_a = \frac{2 \ \log 2 \ 3}{0.022}$
 $= \frac{3.6}{0.022} \ \simeq 163.6 \text{kJ mol}^{-1}$

4. The expression for bacterial growth is

$$\frac{N}{N} = \frac{N}{0} e^{t}$$

From 0 to 1 hour $N(t) = N_0 e^t$

From 1 hour onwards, $\frac{dN}{dt} = 5N^2$

On differentiating the above equation from N to N we get.

$$\frac{N}{N} \frac{dN}{2} \frac{dN}{5} \frac{dt}{dt} \qquad [\because \text{At 1 hour, } N = eN_0]$$

$$\frac{1}{N} \frac{1}{eN_0} = 5(t = 1)$$

Multiply both sides by N_0 , we get

$$\frac{N_0}{N} = \frac{1}{e} = 5N_0(t-1) \text{ or}, \frac{N_0}{N} = 5N_0(t-1) = \frac{1}{e}$$
$$\frac{N_0}{N} = 5N_0t = \frac{1}{e} = 5N_0$$

On comparing the above equation with equation of straight line, y mx c

We get
$$m = 5N_0, c = \frac{1}{e} = 5N_0$$

Plot of $\frac{N_0}{N}$ vs t is shown aside.



5. Only statement (d) is incorrect. Corrected statement is "Activation enthalpy to form *C* is 15 kg mol⁻¹ more than 5 kg mol⁻¹ that is required to form *D*." It can be easily explained by following graph.



Activation enthalpy (or energy) is the extra energy required by the reactant molecules that result into effective collision between them to form the products.

In first order reaction, the rate expression depends on the concentration of one species only having power equal to unity.
 nR products

$$\frac{d[R]}{dt} \quad k[R]$$

On integration, $\ln[R] kt \ln[R_0]$ or $\ln(R) \ln(R_0) kt$ y c mxm slope k (negative) c intercept $\ln(r_0)$

The graph for first order reactions is



In zero order reaction,

$$\begin{bmatrix} R \end{bmatrix} \quad \text{product}$$
$$\frac{d[R]_{t}}{dt} \quad k \text{ or } \quad d[R]_{t} \quad k dt$$

On integrating, $[R]_t$ kt c

If
$$t = 0, [R]_t = [R]_0$$
$$[R]_t = kt = [R]_0$$
$$[R]_t = [R]_0 = kt$$

Thus, the graph plotted between $[r]_t$ and t gives a straight line with negative slope (k) and intercept equal to $[R]_0$. The graph for zero order reaction is



7.
$$A \stackrel{K_1}{=} B \stackrel{K_2}{=} C$$

Rate of formation of *B* is
 $\frac{d[B]}{dt} = k_1[A] = k_2[B]$
 $0 = k_1[A] = k_2[B]$ \because Given, $\frac{d[B]}{dt} = 0$
 $k_2[B] = k_1[A]$
Concentration of *B*, $[B] = \frac{k_1}{k_2}[A]$
8. Let the rate equation be $k [A]^{k} [B]^{\nu}$

From Ist values,

0.045 $k[0.05]^x [0.05]^y$...(i) From 2nd values,

- 0.090 $k[0.10]^x [0.05]^y$...(ii)
- From 3rd values, $0.72 \quad k[0.20]^{x} [0.10]^{y} \qquad \dots (iii)$

On dividing equations (i) by (ii), we get

$$\frac{0.045}{0.09} \quad \frac{0.05}{0.10} \stackrel{x}{}^{x}$$

$$\frac{0.05}{0.10} \stackrel{1}{}^{1} \quad \frac{0.05}{0.10} \stackrel{x}{}^{x}$$
Similarly on dividing Eq. (ii) by (iii) we get
$$\frac{0.09}{0.72} \quad \frac{0.1}{0.2} \stackrel{x}{}^{2} \quad \frac{0.05}{0.10} \stackrel{y}{}^{y}$$

$$\frac{0.01}{0.08} \quad \frac{0.1}{0.2} \quad \frac{0.05}{0.1} \stackrel{y}{}^{y}$$

$$0.25 \quad \frac{0.05}{0.10} \stackrel{y}{}^{y}$$

$$0.25 \quad [0.5]^{y}$$

$$[0.5]^{2} \quad [0.5]^{y}$$

$$y \quad 2$$
Hence, the rate law for the reaction

Rate $k [A] [B]^2$

9. The temperature dependence of a chemical reaction is expressed by Arrhenius equation,

$$k \quad Ae^{-E_{\hat{a}}/RT} \qquad \qquad \dots (i)$$

Taking natural logarithm on both sides, the Arrhenius equation becomes,

$$\ln k \quad \ln A \quad \frac{E_a}{RT}$$

where, $\frac{E_a}{R}$ is the slope of the plot and $\ln A$ gives the intercept.

Eq. (i) at two different temperatures for a reaction becomes,

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} - \frac{1}{T_1} - \frac{1}{T_2} \qquad \dots (ii)$$

In the given problem,

$$\begin{array}{ccc} T_1 & 400 \text{K}, \ T_2 & 500 \text{K} \\ k_1 & 10 & 5 \text{ s} & 1, \ k_2 & ? \end{array}$$

 $\frac{E_a}{R}$ (Slope) 4606

On substituting all the given values in Eq. (ii), we get

$$\ln \frac{k_2}{10^{-5}} \quad 4606 \quad \frac{1}{400} \quad \frac{1}{500}$$
$$\ln \frac{k_2}{10^{-5}} \quad 2.303$$
$$\frac{k_2}{10^{-5}} \quad 10 \quad k_2 \quad 10^{-4} \text{ s}$$

Therefore, rate constant for the reaction at 500 K is 10 4 s 1 .

10. Given, rate constant (k) 0.05 g/year

Thus, from the unit of k, it is clear that the reaction is zero order. Now, we know that

1

 $\frac{a_{\rm o}}{2k}$ half-life $(t_{1/2})$ for zero order reaction

where, a_o initial concentration, k rate constant $t_{1/2} = \frac{5 \text{ g}}{2 \text{ 0.05 g / year}} = 50 \text{ years}$

Thus, 50 years are required for the decomposition of 5 g of Xinto 2.5 g.

11. For zero order reaction,

$$\begin{bmatrix} A_0 \end{bmatrix} \begin{bmatrix} A_t \end{bmatrix} kt \qquad \dots(i)$$
where, $\begin{bmatrix} A_0 \end{bmatrix}$ initial concentration
$$\begin{bmatrix} A_t \end{bmatrix}$$
 final concentration at time 't'
k rate constant

Also, for zero order reaction,
$$t_{1/2} = \frac{[A_0]}{2k}$$

60

Given,
$$t_{1/2} = 6$$
 h and $[A_0] = 0.2$ M
 $6 = \frac{0.2}{2k}$
 $0.2 = 1$

or.

Now, from Eq. (i)

$$\begin{bmatrix} A_0 \\ [A_0] \\ [A_t] \\ kt \end{bmatrix} = kt$$

Given, $\begin{bmatrix} A_0 \\] \\ 0.5 \\ M, \begin{bmatrix} A_t \\] \\ 0.2 \\ M \end{bmatrix} = 0.2 M$
$$0.5 \quad 0.2 \quad \frac{1}{60} \quad t \qquad \because k$$

$$0.3 \quad \frac{1}{60} \quad t$$

$$t \quad 0.3 \quad 60 \quad 18h$$

1 60

12. The temperature dependence of rate of a chemical reaction is expressed by Arrhenius equation as,
$$k = Ae^{E^{-}/RT}$$
 ...(i)

R Gas constant, E_a Activation energy

Taking log on both sides of the Eq. (i), the equation $\frac{E_a}{RT}$ becomes $\ln k \quad \ln A$



- On comparing with equation of straight line (y mx c), the nature of the plot of $\ln k vs \frac{1}{RT}$ will be:
- (i) Intercept $C \ln A$
- (ii) Slope/gradient m E_a y E_a y

So, the energy required to activate the reactant, (activation energy of the reaction, E_a is y)

13. The elementary reaction,
$$A_2 \xrightarrow[k_1]{k_1} 2A$$

follows opposing or reversible kinetics, (i) Rate of the reaction,

$$\begin{array}{ccc} r & r_{\text{forward}} & r_{\text{backward}} \\ & k_1 [A_2] & k_1 [A]^2 & \dots (i) \end{array}$$

(ii) Again, rate of the reaction can be expressed as, $d[A_2] = 1 d[A]$

$$r \quad \frac{d[A_2]}{dt} \quad \frac{1}{2} \frac{d[A_2]}{dt}$$

So, the rate of appearance of A, i.e.

$$\frac{d[A]}{dt} = 2r - 2k_1[A_2] - 2k_1[A]^2 \text{ [from Eq. (i)]}$$

14. The Arrhenius equation is,

$$k \quad A.e^{E_a/RT}$$

where, k rate constant,

A Arrhenius constant, E_a activation energy,

and T temperature in K

From the equation, it is clear that k decreases exponentially with E_a . So, the plot-I is correct.

In the plot-II, k is plotted with temperature (in °C but not in K). So, at 0°C, k = 0 and k will increase exponentially with temperature upto 300°C. Therefore, the plot-II is also correct.

15. For the reaction, 2A = Bproducts.

Let, the rate expression is

$$r \quad [A]^{a}[B]^{b}$$
Expt 1 $\frac{r_{2}}{r_{1}} \quad \frac{2A}{A}^{a} \quad \frac{2B}{B}^{b}$

$$\frac{2.4}{0.3} \quad 2^{a} \quad 2^{b} \quad 2^{3} \quad 2^{a \quad b}$$

$$3 \quad a \quad b \qquad \dots (i)$$

Expt 2
$$\frac{r_2}{r_1} = \frac{2A}{A} \begin{bmatrix} a & B \\ B & B \end{bmatrix}^b$$

 $\frac{0.6}{0.3} = 2^a = 1 = 2^1 = 2^a = a = 1 = \dots..(ii)$

From Eq. (i), 1 b 3 b 2 Order of the reaction (n) a b 1 2 3 Order of the reaction wrt. A = 1Order of the reaction wrt. B = 2**16.** Let, the rate expression is $r [A]^a [B]^b$. From experiment I, $\frac{r_2}{r_1} = \frac{0.1}{0.1}^{a} = \frac{0.25}{0.20}^{b}$ $\frac{6.93 \quad 10^{-3}}{6.93 \quad 10^{-3}} \quad 1 \quad \frac{5}{4}^{-b}$ $1 \quad \frac{5}{4}^{b} \qquad \frac{5}{4}^{0} \quad \frac{5}{4}^{b} \qquad \frac{5}{4}^{b} \qquad b \quad 0$ From experiment II, $\frac{r_3}{r_1} = \frac{0.2}{0.1}^{a} = \frac{0.30}{0.20}^{b}$ $\frac{1.386 \quad 10^{-2}}{0.693 \quad 10^{-2}} \quad (2)^a \quad (1.5)^0$ 2 2^a 1 2^1 2^a a 1 $r [A]^{1}[B]^{0} r [A]$ So, Order of the reaction (n) 1 Now, let for the 1st experiment, $r_1 \quad k \quad [A]$ $k = \frac{r_1}{\lceil A \rceil} = \frac{6.93 \times 10^{-3}}{0.1} = 6.93 \times 10^{-2} \text{ s}^{-1}$

$$t_{50} = \frac{0.693}{k} = \frac{0.693}{6.93 \times 10^{-2}} = 10 \text{ s}$$

17. From thermodynamics,

$$\ln k \quad \frac{H}{RT} \quad \frac{S}{R} \qquad \qquad \dots (i)$$

...(ii)

Mathematically, the equation of straight line is

y c mxAfter comparing Eq. (ii) with (i) we get,

slope
$$\frac{H}{R}$$
 and intercept $\frac{S}{R}$

Now, we know for exothermic reaction H is negative ()ve. But here,

Slope
$$\frac{H}{R}$$
 is positive

So, lines A and B in the graph represent temperature dependence of equilibrium constant K for an exothermic reaction as shown below



18. For the reaction,

so,

$$CH_3CHO(g)$$
 $CH_4 + CO$

Let order of reaction with respect to CH_3CHO is *m*. Its given, $r_1 = 1$ torr/sec. when CH_3CHO is 5% reacted i.e. 95% unreacted. Similarly, $r_2 = 0.5$ torr/sec when CH_3CHO is 33% reacted i.e., 67% unreacted.

Use the formula, $r (a x)^m$

where $(a \ x)$ amount unreacted

$$\frac{r_1}{r_2} = \frac{(a - x_1)^m}{(a - x_2)^m} \text{ or } \quad \frac{r_1}{r_2} = \frac{a - x_1}{a - x_2}^m$$

Now putting the given values

$$\frac{1}{0.5}$$
 $\frac{0.95}{0.67}^{m}$ 2 $(1.41)^{m}$ or m 2

19. According to Arrhenius equation

$$k \quad Ae^{-E_a/RT}$$

where, A collision number or pre-exponential factor.

- *R* gas constant
- *T* absolute temperature
- E_a energy of activation

For reaction
$$R_1, k_1 = Ae^{-E_{a_1}/RT}$$
 ...(i)

For reaction
$$R_2$$
, $k_2 = Ae^{-E_{a_2}/RT}$...(ii)

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{k_2}{k_1} = e^{\frac{(E_{a_2} - E_{a_1})}{RT}} \dots (iii)$$

[: Pre-exponential factor 'A' is same for both reactions]

Taking ln on both the sides of Eq. (iii), we get

$$\ln \frac{k_2}{k_1} = \frac{E_{a_1} E_{a_2}}{RT}$$

Given, $E_{a_1} = E_{a_2} = 10 \text{ kJ mol}^{-1} = E_{a_2} = 10,000 \text{ J mol}^{-1}$

$$\ln \frac{k_2}{k_1} = \frac{10,000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} - 300 \text{ K}} = 4$$

20. For first order reaction, $k = \frac{2.303}{t} \log \frac{a}{a \times x}$

Given,

$$t = 50 \min, a = 0.5 \text{ M}, a = x = 0.125 \text{ M}$$

 $k = \frac{2.303}{50} \log \frac{0.5}{0.125} = 0.0277 \min^{-1}$

Now, as per reaction

$$\frac{2H_2O_2}{\frac{1}{2}\frac{d[H_2O_2]}{dt}} = \frac{2H_2O + O_2}{\frac{1}{2}\frac{d[H_2O_2]}{dt}} = \frac{1}{2}\frac{d[H_2O]}{dt} = \frac{d[O_2]}{dt}$$
Rate of reaction, $\frac{d[H_2O_2]}{dt} = k[H_2O_2]$
 $\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}k[H_2O_2] = \dots(i)$

When the concentration of H₂O₂ reaches 0.05 M, $\frac{d[O_2]}{dt} = \frac{1}{2} = 0.0277 \quad 0.05$ $\frac{d[O_2]}{dt} = 6.93 \quad 10^{-4} \text{ mol min}^{-1}$

or

Alternative Method

In fifty minutes, the concentration of H₂O₂ decreases from 0.5 to 0.125 M or in one half-life, concentration of H₂O₂ decreases from 0.5 to 0.25 M. In two half-lives, concentration of H_2O_2 decreases from 0.5 to 0.125 M or $2t_{1/2}$ 50 min

or
$$\frac{d[O_2]}{dt} = \frac{1}{2} \frac{d[H_2O_2]}{dt} = \frac{k[H_2O_2]}{2} = \frac{k[H_2O_2]}{2} = 6.93 \cdot 10^{-4} \text{ mol min}^{-1}$$

- 21. The main conditions for the occurrence of a reaction is proper orientation and effective collision of the reactants. Since, the chances of simultaneous collision with proper orientation between two species in high order reactions are very rare, so reaction with order greater than 3 are rare.
- **22.** For the elementary reaction, M

Rate law can be written as

Rate
$$[M]^n$$

Rate $k[M]^n$...(i)
the concentration of $[M]$

N

When we double the concentration of [M],

rate becomes 8 times, hence new rate law can be written as

8 Rate
$$k [2M]^n$$
 ...(ii)

$$\frac{\text{Rate}}{8 \text{ Rate}} \frac{k [M]^n}{k [2M]^n} = \frac{1}{8} \frac{1}{[2]^n}$$

$$[2]^n = 8 [2]^3 = n = 3$$

23. This problem can be solved by determining the order of reaction w.r.t. each reactant and then writing rate law equation of the given equation accordingly as

$$R = \frac{dC}{dt} = k[A]^{x}[B]^{y}$$

where, x order of reaction w.r.t Ay order of reaction w.r.t B $12 \ 10^{3} \ k(01)^{x}(01)^{y}$

1.2 10
$$k(0.1)(0.1)^{y}$$

1.2 10 $k(0.1)^{x}(0.2)^{y}$
2.4 10 $k(0.2)^{x}(0.1)^{y}$
 $R = k[A]^{1}[B]^{0}$

As shown above, rate of reaction remains constant as the concentration of reactant (B) changes from 0.1 M to 0.2 M and becomes double when concentration of A change from 0.1 to 0.2, (i.e. doubled).

24. PLAN Time of 75% reaction is twice the time taken for 50% reaction if it is first order reaction w.r.t. P. From graph, [Q] decreases linearly with time, thus it is zeroth order reaction w.r.t. Q

	$\frac{dx}{dt}$ $bk[P]^a[Q]^b$					
Order w.r.t	P	а	1			
Order w.r.t	Q	b	0			
Thus, overall order of	the r	eact	tion	1	0	1

25. From Arrhenius equation, $\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} = \frac{1}{T_2} = \frac{1}{T_1}$

Given,

[from Eq. (i)]

$$T_1 = 300 \text{ K}$$

On putting values,

log

$$2 \quad \frac{E_a}{2.303 \quad 8.314} \quad \frac{1}{310} \quad \frac{1}{300} \\ E_a \quad 53.603 \text{ kJ/mol}$$

 $\frac{k_2}{k_1}$ 2 T_2 310 K

26. According to Arrehnius equation, rate constant increases exponentially with temperature :

$$k \quad Ae^{E_a/RT}$$

27. The logarithmic form of Arrhenius equation is

$$\log k \quad \log A \quad \frac{E_a}{2.303 \ RT}$$

Given:
$$\log k = 6$$

Comparing the above two equations :

$$\log A = 6 \qquad A = 10^6$$

$$\frac{E_a}{2.303R} = 2000$$

$$E_a = 2000 = 2.303 = 8.314 \text{ J}$$

$$38.3 \text{ kJ} = \text{mol}^{-1}$$

28. For first order reaction $t_{1/2} = \frac{\ln 2}{k_1} = 40 \text{ s}$...(i)

For zero order reaction
$$t_{1/2} = \frac{[A]_0}{2k_0}$$
 20s ...(ii)

and

 $\frac{1}{2} \quad \frac{[A]_0}{2k_0} \quad \frac{k_1}{\ln 2}$ $\frac{k_1}{k_0} \quad \frac{\ln 2}{[A]_0}$ $\frac{0.693}{1.386}$

29. Rate $[G]^m [H]^n$

 \therefore Rate is double on doubling the concentration of G and maintaining H constant, m 1, i.e. R [G].

Also, when both concentration of G and H are doubled, rate increases by a factor of 8. Here rate is increasing by a factor of 2 due to G (first order in G), therefore, factor due to H is 4. D [11]2

$$\begin{array}{cccc} R & \lfloor H \rfloor^{r} \\ \text{Overall order} & m & n & 1 & 2 & 3 \end{array}$$

- **30.** Order of a reaction can take any real value, i.e. negative, integer, fraction etc.
- **31.** For first order reaction,

$$k \quad \frac{2.303}{t} \quad \log \frac{a}{a \ x} \quad \frac{2.303}{40} \log \frac{0.1}{0.025} \quad 3.46 \quad 10^{-2}$$

Rate [k] A 3.46 10⁻² 0.01 3.46 10⁻⁴

32. For a first order reaction,
$$kt = \ln \frac{\lfloor A \rfloor_0}{\lfloor A \rfloor}$$

$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{1}{2 \cdot 10^4} \ln \frac{800}{50} = \frac{4 \ln 2}{2 \cdot 10^4} \mathrm{s}^{-1}$$

1.386 = 10⁻⁴ \mathrm{s}^{-1}

33. For any general reaction,

$$aA \quad bB \qquad cC \quad dD$$
Rate
$$\frac{1}{a} \frac{d[A]}{dt} \qquad \frac{1}{b} \frac{d[B]}{dt}$$

$$\frac{1}{c} \frac{d[C]}{dt} \qquad \frac{1}{d} \frac{d[D]}{dt}$$
For
$$N_2 + 3H_2 \qquad 2NH_3$$
Rate
$$\frac{d[N_2]}{dt} \qquad \frac{1}{3} \frac{d[H_2]}{dt} \qquad \frac{1}{2} \frac{d[NH_3]}{dt}$$

- **34.** Rate will be directly proportional to both concentration and intensity, i.e. rate of formation of $AB^* C I$.
- **35.** The unit of rate constant (t^{-1}) indicating that the decomposition reaction following first order kinetics.

Rate
$$k[N_2O_5]$$

[N₂O₅] $\frac{\text{Rate}}{k} = \frac{2.40 \cdot 10^{-5}}{3 \cdot 10^{-5}} = 0.8 \text{ M}$

36. 560 days $\frac{560}{140}$ 4 half-lives.

Amount of reactant remaining after n-half-lives

$$\frac{1}{2}^{n}$$
 initial amount $\frac{1}{2}^{4}$ 1.0 g $\frac{1}{16}$ g

- **37.** A catalyst increases the rate of reaction but by the same factor to both forward and backward directions. Hence, a catalyst shorten the time required to reach the equilibrium.
- **38.** Specific rate constant of reaction depends on temperature.
- **39.** The rate constant (k) of all chemical reactions depends on temperature.

k
$$Ae^{E_a/RT}$$

where, A pre-exponential factor, E_a activation energy.

40. Given for the reaction (at T=300 K and constant volume = V) A(g) 2B(g) C(g)

at
$$t = 0$$
 $p_0 = -$
at $t = t$ $p_0 = x$ $2x = x$
at $t = t_{1/3}$ $p_0 = \frac{2p_0}{3} = \frac{p_0}{3} = \frac{4p_0}{3} = \frac{2p_0}{3}$

We can calculate,

or

$$p_t \quad p_0 \quad x \quad 2x \quad x \quad p_0 \quad 2x$$

$$2x \quad p_t \quad p_0 \quad \text{or} \quad x \quad \frac{p_t \quad p_0}{2}$$

Now for first order reaction,

 $t \quad \frac{1}{k} \ln \frac{p_0}{(p_0 \quad x)}$

Putting the value of *x* in the equation,

$$t \quad \frac{1}{k} \ln \frac{p_0}{p_0} \quad \frac{p_t \quad p_0}{2} \quad \frac{1}{k} \ln \frac{2p_0}{2p_0 \quad p_t \quad p_0}$$

or
$$kt = \ln \frac{2p_0}{(3p_0 - p_t)}$$

or $kt = \ln 2p_0 + \ln (3p_0 - p_t)$
or $\ln (3p_0 - p_t) = kt = \ln 2p_0$

It indicates graph between $\ln (3p_0 \quad p_t) vs \ 't'$ will be a straight line with negative slope, so option (a) is correct

$$t_{1/3} = \frac{1}{k} \ln \frac{p_0}{p_0/3} = \frac{1}{k} \ln 3$$

It indicates $t_{1/3}$ is independent of initial concentration so, option (b) is incorrect.

Likewise, rate constant also does not show its dependence over initial concentration. Thus, graph between rate constant and $[A]_0$ will be a straight line parallel to X-axis.

41. If steric factor is considered, the corrected Arrhenius equation will be

 $k \quad pAe^{\frac{E_a}{RT}}$ where A frequency factor by Arrhenius.

 $\therefore p$ 1, pA A hence, (a) is correct.

Activation energy is not related to steric factor.

12. Rate constant,
$$k A e^{E_a/RT}$$

where, E_a activation energy and A pre-exponential factor

- (a) If E_a is high, it means lower value of k hence, slow reaction. Thus, incorrect.
- (b) On increasing temperature, molecules are raised to higher energy (greater than E_a), hence number of collisions increases. Thus, correct.

(c)
$$\log k \quad \log A \quad \frac{E_a}{RT} \qquad \frac{d(\log k)}{dT} \quad \frac{E_a}{RT^2}$$

Thus, when E_a is high, stronger is the temperature dependence of the rate constant. Thus, correct.

- (d) Pre-exponential factor (*A*) is a measure of rate at which collisions occur. Thus, correct.
- **43.** (a) For a first order reaction, the concentration of reactant remaining after time t is given by $[A] = [A]_0 e^{-kt}$ Therefore, concentration of reactant decreases exponentially with time.
 - actant $t \rightarrow t$ ime. $t \rightarrow t$ ate constant (k) and therefore
 - (b) Rise in temperature increases rate constant (k) and therefore decreases half-life (t_{1/2}) as

$$t_{1/2} \quad \frac{\ln 2}{k}$$

- (c) Half-life of first order reaction is independent of initial concentration.
- (d) For a first order reaction, if 100 moles of reactant is taken initially, after *n* half-lives, reactant remaining is given by

$$\% A = 100 \quad \frac{1}{2}^{n} \quad 100 \quad \frac{1}{2}^{8} \quad 0.3906$$

A reacted 100 - 0.3906 = 99.6%

44. Equilibrium constant is related to temperature

$$\log K_p$$
 constant $\frac{H}{2.3 RT}$

Plot of $\log K_p$ vs 1/T will be a straight line. For the first order reaction X = P

$$\log \frac{[X]_0}{[X]} \frac{kt}{2.3} \qquad \log [X] \quad \log [X_0] \quad \frac{kt}{2.3}$$

i.e. $\log[X]vs$ 't' will give a straight line.

Also at constant temperature, pV constant

Plot of p vs - will give a straight line.

45. For a first order reaction :

1

$$kt \ln \frac{1}{1}$$
 where, degree of dissociation.
 $e^{kt} = 1 e^{kt}$

Also $\frac{1}{[A]} = \frac{e^{kt}}{[A]_0}$, i.e. plot of reciprocal of concentration of

reactant vs time will be exponential.

Time for 75%
$$\frac{1}{k} \ln \frac{100}{100-75} - \frac{2 \ln 2}{k} - 2 (t_{1/2})$$

The Arrhenius equation is :

$$\ln k \quad \ln A \quad \frac{E_a}{RT}$$

The dimensions of k and A must be same. For first order reaction, dimensions of k is t^{-1} .

- **46.** A catalyst lowers the activation energy by enabling the reaction to continue through an alternative path, i.e. catalyst changes the reaction mechanism. However, catalyst does not affect either average kinetic energies of reactants or the collision frequency.
- **47.** For the reaction,

$$\begin{array}{ccc} A(g) & B(g) \overleftrightarrow{\longrightarrow} AB(g) \\ \text{Given} & E_{a_b} & E_{a_f} & 2RT & \text{or} & E_{a_b} & E_{a_f} & 2RT \\ \text{Further} & & & & \\ \end{array}$$

$$A_f \quad 4A_b \quad \text{or} \quad \frac{A_f}{A_b} \quad 4$$

Now, rate constant for forward reaction,

$$k_c A_c e^{E_{a_f}/RT}$$

Likewise, rate constant for backward reaction,

$$k_b \quad A_b e^{E_{a_b}/RT}$$

At equilibrium,

Rate of forward reaction Rate of backward reaction

i.e.,

$$k_{f} \quad k_{b} \quad \text{or} \quad \frac{f}{k_{b}} \quad k_{eq}$$

$$k_{eq} \quad \frac{A_{f}e^{-E_{af}/RT}}{A_{b}e^{-E_{ab}/RT}} \quad \frac{A_{f}}{A_{b}}e^{-(E_{af}-E_{ab})/RT}$$

k.

so

After putting the given values

$$k_{eq} = 4e^2$$
 (as $E_{a_b} = E_{a_f} = 2RT$ and $\frac{A_f}{A_b} = 4$)

Now, G RT ln
$$K_{eq}$$
 2500 ln(4 e^2)
2500 (ln 4 ln e^2) 2500 (1.4 2)
2500 3.4 8500 J/mol
Absolute value 8500 J/mol

iving plants maintain an equilibrium bet

- **48.** Living plants maintain an equilibrium between the absorption of C^{14} (produced due to cosmic radiation) and the rate of decay of C^{14} present inside the plant. This gives a constant amount of C^{14} per gram of carbon in a living plant.
- **49.** Fossil whose age is closest to half-life of C-14 (5770 yr) will yield the most accurate age by C-14 dating.

$$50. \quad T \quad \ln \frac{N_0}{N}$$

where N_0 Number of C^{14} in the living matter and N Number of C^{14} in fossil. Due to nuclear explosion, amount of C^{14} in the near by area increases. This will increase N_0 because living plants are still taking C-14 from atmosphere, during photosynthesis, but N will not change because fossil will not be doing photosynthesis.

T(age) determined in the area where nuclear explosion has occurred will be greater than the same determined in normal area.

Also,
$$T_1 = \ln \frac{C_1}{C}$$
 $T_2 = \ln \frac{C_2}{C}$ $T_1 = T_2 = \frac{1}{2} - \ln \frac{C_1}{C_2}$

C Concentration of C-14 in fossil.

51.
$$k \quad Ae^{E_a/Rl}$$
: At $T \quad , k \quad A$
52. $\frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$
 $-\frac{d[H_2]}{dt} = \frac{3}{2} \frac{d[NH_3]}{dt} = \frac{3}{2} \quad 0.001 \quad 0.0015 \text{ kg}$

- **53.** acidic, first or basic, second.
- 54. Rate is directly proportional to concentration of reactants.
- **55.** *R* [Reactant]

On doubling the concentration of reactant, rate would be double.

56. For a first order process $kt \ln \frac{[A]_0}{[A]}$

where, $[A]_0$ initial concentration.

[A] concentration of reactant remaining at time "t".

$$kt_{1/8} = \ln \frac{[A]_0}{[A]_0/8} = \ln 8 \qquad \dots(i)$$

 h^{-1} .

and
$$kt_{1/10} = \ln \frac{[A]_0}{[A]_0/10} = \ln 10$$
 ...(ii)

Therefore,
$$\frac{t_{1/8}}{t_{1/10}} = \frac{\ln 8}{\ln 10} \log 8 = 3 \log 2 = 3 = 0.3 = 0.9$$

 $\frac{t_{1/8}}{\ln 10} = 10 = 0.9 = 10 = 9$

 $t_{1/10}$

58. (a) Partial pressure becomes half of initial in every 100 min, therefore, order = 1.

(b)
$$k = 100 \quad \ln \frac{800}{400} \quad \ln 2 \quad k = 6.93 \quad 10^{-3} \text{ min}^{-1}$$

(c) For 75% reaction; time required 2 half-life 200 min
(d) 2X (g) 3Y (g) 2Z (g)
800 x
$$\frac{3}{2}x$$
 x
Total pressure 800 $\frac{3}{2}x$
Also 800 x 700 x 100
Total pressure 800 $\frac{3}{2}$ 100 950 mm Hg
59. $\frac{(Rate)_1}{(Rate)_2} = \frac{0.05}{0.10} \frac{1}{2} = \frac{1}{2}a^a a$ 1; order w.r.t A.
Order w.r.t B 0
(a) Rate k [A]
(b) k $\frac{Rate}{[A]} = \frac{0.05}{0.10}$ 0.5 s ¹
60. $29 Cu^{64} - \frac{38\%}{k_3} = 1^0 - 30 Zn^{64}$
 $29 Cu^{64} - \frac{19\%}{k_2} = 1^0 - 28 Ni^{64}$
 $29 Cu^{64} - \frac{16^0}{k_3} - \frac{43\%}{k_3} - \frac{38}{28} - \frac{7}{11}$
71, 72 and 73 are the corresponding partial half-lives.
Also k k₁ k₂ k₃
 $\frac{\ln 2}{T} - \frac{\ln 2}{T_1} - \frac{\ln 2}{T_2} - \frac{\ln 3}{T_3}$
 $\frac{1}{T} - \frac{1}{T_1} - \frac{1}{T_2} - \frac{1}{T_3} - \frac{1}{T_1} - \frac{1}{271} - \frac{43}{38T_1}$
 $\frac{1}{T_1} - \frac{1}{2} - \frac{43}{38}$
 $\frac{1}{T_1} - \frac{1}{2} - \frac{43}{38}$
 $\frac{1}{T_1} - \frac{1007}{38} - \frac{100}{38} - 12.8 - 33.68 h$
 $T_2 = 2T_1 - 67.36 h$
 $T_3 - \frac{38T_1}{43} - \frac{38 - 33.68}{43} - 29.76 h$
61. R k [A]
R_1 k [A]_1 and R_2 k [A]_2
R_1 k [A]_1 b A_3
 $\frac{\ln 2}{t_{1/2}} - 10 - \ln \frac{4}{3}$
 $t_{1/2} - \frac{10 \log 3}{\log 4} - \frac{3}{6} - \frac{3}{6} - \frac{3}{25} - \frac{5}{10} - \frac{1}{10} - \frac{3}{10} -$

62. k_{500} A e^{E_1/RT_1} k_{400} A e E_2/RT_2 $kt \quad \ln \frac{[A]_0}{[A]}$ 63. 4.5 10⁻³ 60 $\ln \frac{1}{[A]}$ [A] 0.76 M Rate k[A] 4.5 10³ 0.76 3.42 10 3 mol L 1 min 1 **64.** (i) $\ln \frac{k_2}{k_1} = \frac{E_a}{R} = \frac{T_2 - T_1}{T_1 T_2}$ $\ln \quad \frac{4.5 \quad 10^7}{1.5 \quad 10^7} \quad \frac{E_a}{8.314} \quad \frac{50}{323 \quad 373}$ E_a 22 kJ Also $\ln k \ln A = \frac{E_a}{RT}$ At 50°C : $\ln A = \ln (1.5 \ 10^7) = \frac{22 \ 1000}{8.314 \ 323} = 8.33$ $A = 4.15 = 10^3 \text{ s}^{-1}$ (ii) $N_2O_5(g)$ $2NO_2(g) + \frac{1}{2}O_2(g)$ Partial pressure of $N_2O_5(g)$ remaining = 600 - 240 $= 360 \, \text{mm}$ Mole fraction $\frac{360}{960}$ 0.375 **65.** (i) The Arrhenius equation is $\log k \quad \log A \quad \frac{E_a}{2.303 RT}$ Comparing with the given equation : 1.25 $10^4 \frac{E_a}{2.303R} E_a$ 239.33 kJ mol⁻¹ (ii) When half-life 256 min, $k \quad \frac{\ln 2}{t_{1/2}} \quad \frac{0.693}{256 \quad 60} \text{ s}^{-1} \quad 4.5 \quad 10^{-5} \text{ s}^{-1}$ $\frac{1.25 \cdot 10^4}{T} = 14.34 - \log 4.5 \cdot 10^{-5} = 16.68$ $T = \frac{1.25 \cdot 10^4}{16.68} = 669 \text{ K}$

66.

$$k_{t} = \ln \frac{w_{0}}{w}$$

$$\frac{\ln 2}{28.1} = 20 = \ln \frac{10^{-6} \text{ g}}{w} \qquad w = 6.1 = 10^{-7} \text{ g}$$

67. For 1st order reaction :

67. For 1st order reaction :

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

$$\ln \frac{k}{(450 \text{ C})} = \ln \frac{t_{1/2}}{(380 \text{ C})} = \frac{E_a}{R} = \frac{450}{727} = \frac{380}{653}$$

$$\ln \frac{360}{t_{1/2}} = \frac{200}{8.314} = \frac{70}{727} = \frac{3.54}{653}$$

$$t_{1/2} = \frac{450^\circ\text{C}}{10.37} = \frac{10.37}{10} = \frac{3.54}{10.37}$$
68. Comparing the data of experiment number 2 and 3 :

$$R = 1.6 = 10^{-2} = -1.0 = 10^{-3}$$

 $\frac{R_3}{R_2} \quad \frac{1.6 \quad 10^{-2}}{4 \quad 10^{-3}} \quad \frac{1.0 \quad 10^{-3}}{5 \quad 10^{-4}}$

$$m$$
 2, order w.r.t. *A*
Now comparing the data of experiment number 1 and 2 :

$$\frac{R_2}{R_1} = \frac{4 \cdot 10^{-3}}{5 \cdot 10^{-4}} = \frac{5 \cdot 10^{-4}}{2.5 \cdot 10^{-4}} = \frac{6.0 \cdot 10^{-5}}{3.0 \cdot 10^{-5}}^{n}$$

8 (2)² (2)ⁿ n 1, order w.r.t. B.

(i) Order with respect to A = 2, order with respect to B = 1.

(ii) At 300 K, $R = k [A]^2 [B]$

$$k \quad \frac{R}{[A]^2 [B]} \quad \frac{5.0 \quad 10^{-4}}{(2.5 \quad 10^{-4})^2 (3.0 \quad 10^{-5})}$$

2.66 \quad 10^8 s^{-1} L^2 mol^{-2}

(iii) From first experiment :

Now

Rate (320 K)
$$k$$
 (320 K) (2.5 10⁴)² (3.0 10⁵)
2 10³

$$k (320 \text{ K}) = \frac{2}{(2.5 \times 10^{-4})^2} \frac{(3.0 \times 10^{-5})}{(3.0 \times 10^{-5})^2}$$

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

$$\ln \frac{k}{k} \frac{(320 \text{ K})}{(300 \text{ K})} = \frac{E_a}{R} \frac{T_2}{T_1 T_2}$$

$$\ln \frac{1.066}{2} \frac{10^9}{(1.08)^2} = \frac{E_a}{8.214} \frac{20}{200}$$

2.66
$$10^{\circ}$$
 8.314 300 320
 E_a 55.42 kJ mol⁻¹
ln k ln A $\frac{E_a}{RT}$

At 300 K :
 ln (2.66

$$10^8$$
)
 ln A
 $\frac{55.42}{8.314}$
 10^3

 Solving :
 ln A
 41.62
 A
 1.2
 10^{18}

69. CH₃ O CH₃(g) CH₄(g) + H₂(g) + CO (g)
At 12 min : 0.40 p p p p
Total pressure 0.4 2p
Also k 12 ln
$$\frac{0.40}{0.40 p}$$
 $\frac{\ln 2}{14.5}$ 12 1.77 p 0.175
Total pressure 0.4 + 2p = 0.4 + 2 0.175 = 0.75 atm

70.
$$\ln \frac{k}{k} \frac{(40 \text{ C})}{(25 \text{ C})} = \frac{E_a}{R} \frac{15}{298 313}$$

 $\frac{70 \ 1000}{8.314} = \frac{15}{298 \ 313} = 1.35$
 $\frac{k}{k} \frac{(40 \text{ C})}{(25 \text{ C})} = 3.87$
Also $k (25^{\circ}\text{C}) = \frac{1}{20} \ln \frac{100}{75} = \frac{1}{20} \ln \frac{4}{3}$
 $k (40 \text{ C}) = 3.87 - k (25^{\circ}\text{C})$
 $3.87 - \frac{1}{20} \ln \frac{4}{3} = 55.66 - 10^{-3} \text{ min}^{-1}$
Now $k (40^{\circ}\text{C}) = 20 - \ln \frac{100}{100 - x}$
 $55.66 - 10^{-3} = 20 - \ln \frac{100}{100 - x}$
 $x = 67\%$

71. (i) $A \stackrel{k_A}{\longrightarrow}$ Product

(ii)
$$B \xrightarrow{k_B}$$
 Product
For (i) $\frac{E_a}{R} \frac{10}{300 \ 310}$ ln 2
 E_a (i) 9300 R ln 2 53.6 kJ
 E_a (ii) $\frac{E_a}{2}$ (i) 26.8 kJ
At 310 K $t_{1/2}$ (i) 30 min
 \therefore Rate of (ii) 2 rate of (i)
 $t_{1/2}$ (ii) 15 min
Now for reaction (ii) :
ln $\frac{k_B (310)}{k_B (300)}$ ln $\frac{t_{1/2} (300)}{t_{1/2} (310)} = \frac{E_a (ii)}{R} \frac{10}{300 \ 310}$
ln $\frac{t_{1/2} (300)}{15} = \frac{\ln 2}{2} t_{1/2} (300) 21.2 min$
 $k_B (300) = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{21.2} - 3.26 \ 10^{-2} min^{-1}$

72. Initially :

$$N \begin{pmatrix} {}_{1}\text{H}^{3} & {}_{1}\text{H}^{1} \end{pmatrix} = \frac{10}{8} & 2 & 6 & 10^{23} & \frac{20}{3} & 10^{23} \\ 1 & \frac{N \begin{pmatrix} {}_{1}\text{H}^{1} \end{pmatrix}}{N \begin{pmatrix} {}_{1}\text{H}^{3} \end{pmatrix}} & \frac{20 & 10^{23}}{3N \begin{pmatrix} {}_{1}\text{H}^{3} \end{pmatrix}} \\ 1 & \frac{1}{8 & 10^{-18}} & \frac{20 & 10^{23}}{3N \begin{pmatrix} {}_{1}\text{H}^{3} \end{pmatrix}} & 1.25 & 10^{17} \\ N \begin{pmatrix} {}_{1}\text{H}^{3} \end{pmatrix} & \frac{20 & 10^{23}}{3 & 1.25 & 10^{17}} & 5.33 & 10^{6} \\ kt & \ln \frac{N_{0}}{N} & \frac{\ln 2}{12.3} & 40 & \ln \frac{5.33 & 10^{6}}{N} \\ N & 5.6 & 10^{5} \end{pmatrix}$$

73. For the reaction :

$$2N_2O_5$$
 $4NO_2 + O_2$
If p_0 is the initial pressure, the total pressure after completion of reaction would be $\frac{5}{2} p_0$.

584.5
$$\frac{5}{2} p_0 \qquad p_0$$
 233.8 mm

Let the pressure of N_2O_5 decreases by 'p' amount after 30 min. Therefore,

$$2N_2O_5 4NO_2 + O_2$$
At 30 min : $p_0 \ p \ 2p \ \frac{p}{2}$
Total pressure $p_0 \ \frac{3}{2} \ p \ 284.5$

$$p \ \frac{2}{3} (284.5 \ 233.8) \ 33.8$$
Now, $kt \ \ln \frac{p_0}{p_0 \ p}$

$$k \ \frac{1}{30} \ln \frac{233.8}{233.8 \ 33.8} \min^{-1} \ 5.2 \ 10^{-3} \min^{-1}$$

-

74. Arrhenius equation is :

$$\log k \quad \log A \quad \frac{E_a}{2.303 RT}$$
when $t_{1/2} = 10 \min_{k} k \quad \frac{\ln 2}{t_{1/2}} = \frac{0.693}{10 \ 60} = 1.115 = 10^{-3} \text{ s}^{-1}$

$$\frac{E_a}{2.303 RT} \quad \log A \quad \log k$$

$$\log \frac{A}{k} \quad \log \frac{4 \quad 10^{13}}{1.115 \quad 10^{-3}} = 16.54$$

$$T \quad \frac{E_a}{2.303 R \quad 16.54} \quad \frac{98.6 \quad 1000}{2.303 \quad 16.54 \quad 8.314}$$

$$311.34 \text{ K}$$

75. The minimum rate of decay required after 6.909 h is 346 particles min⁻¹.

$$N = \frac{\text{Rate } kN}{k}$$

$$N = \frac{\text{Rate } kN}{k} = \frac{346 - 66.6 - 60}{0.693} = 1.995 = 10^6 \text{ atoms}$$

$$kt = \ln \frac{N_0}{N} = \frac{\ln 2}{66.6} = 6.909 = \ln \frac{N_0}{N} = 0.0715$$

$$\frac{N_0}{N} = 1.074$$

$$N_0 = 1.074 = N = 1.074 = 1.995 = 10^6$$

$$2.14 = 10^6 = 10^6$$

Mass of Mo required $\frac{2.14 \ 10^{\circ}}{6.023 \ 10^{23}}$ 99 3.56 10 ¹⁶ g

76. $k = 1.5 = 10^{-6} \text{ s}^{-1}$

$$kt = \ln \frac{100}{100 \ x}$$
$$\ln \frac{100}{100 \ x} = 1.5 \quad 10^{-6} \ s^{-1} = 10 \quad 60 \quad 60 \ s = 0.0054$$

$$\frac{100}{100 \ x} = 1.055$$

x 5.25% reactant is converted into product.
Half-life $\frac{\ln 2}{k} = \frac{0.693}{1.5 \ 10^{-6}} = 462000 \ \text{s} = 128.33 \ \text{h}$
For a first order process : $\ln \frac{[A]_0}{[A]} \ kt = \ln [A] \ \ln [A]_0 \ kt$
If the reactant is in gaseous state
and $kt_{1/10} = \ln \frac{[A]_0}{[A]_0/10} \ \ln 10 \qquad \dots$ (ii)
Therefore, $\frac{t_{1/8}}{t_{1/10}} = \frac{\ln 8}{\ln 10} \ \log 8 \ 3\log 2 \ 3 \ 0.3 \ 0.9$
 $= \frac{t_{1/8}}{t_{1/10}} \ 10 \ 0.9 \ 10 \ 9$

 $\ln p \quad \ln p_0 \quad kt \qquad \dots(i)$ where p is the partial pressure of reactant remaining unreacted at instant 't' and p_0 is its initial partial pressure.

Also, from equation (i), $\ln p vs t$ would give a straight line. Therefore, decomposition of N₂O₅ following first order kinetics.

78.
$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5770} \text{ yr}^{-1} = 1.2 = 10^{-4} \text{ yr}^{-1}$$

Also $kt = \ln \frac{1}{f} = \frac{\ln 2}{5770} = 11540 = \ln 4$ $f = \frac{1}{4} = 0.25$

79. For a first order reaction,

77.

$$kt \quad \ln \frac{\lfloor A \rfloor_0}{\lfloor A \rfloor}$$

Г **/** Л

where $[A]_0$ Initial concentration of reactant

[*A*] Concentration of reactant remaining unreacted at time *t*.

(i)
$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{1}{10} \ln \frac{100}{100 \ 20} = \frac{1}{10} \ln \frac{5}{4}$$

 $\frac{2.303 \ (\log 5 \ 2 \ \log 2)}{10} \ \min^{-1} = 0.023 \ \min^{-1}$
(ii) $t = \frac{1}{k} \ln \frac{100}{25} = \frac{2 \ln 2}{k} = \frac{2 \ 0.693}{0.023} = 60 \ \min$

80. Looking at the rate data of experiment number 1 and 2 indicates that rate is doubled on doubling concentration of A while concentration of B is constant. Therefore, order with respect to A is 1. Similarly, comparing data of experiment number 1 and 3, doubling concentration of B, while concentration of A is constant, has no effect on rate.

Therefore, order with respect to B is zero.

Rate
$$k [A]$$

 $k \frac{0.005}{0.010} = 0.5 \text{ min}^{-1} = \frac{0.693}{t_{1/2}}$
 $t_{1/2} = \frac{0.693}{0.5} = 1.386 \text{ min}$