CHAPTER



Chemical Kinetics

- 1. 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 (a) 2 (b) 3 (c) 1 (d) 0
 - (2018)
- 2. N_2O_5 decomposes to NO_2 and O_2 and follows first order kinetics. After 50 minutes, the pressure inside the vessel increases from 50 mm Hg to 87.5 mm Hg. The pressure of the gaseous mixture after 100 minutes at constant temperature will be

(a) 116.25 mm Hg	(b) 175.0 mm Hg
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(c) 106.25 mm Hg (d) 136.25 mm Hg.

(Online 2018)

For a first order reaction, $A \rightarrow P$, $t_{1/2}$ (half-life) is 10 days. 3. The time required for $\frac{1}{4}$ th conversion of A (in days) is $(\ln 2 = 0.693, \ln 3 = 1.1)$ (d) 2.5 (a) 5 (b) 4.1 (c) 3.2

If 50% of a reaction occurs in 100 second and 75% of the 4. reaction occurs in 200 second, the order of this reaction is

(a)	1	(b)	2	(c) zero (d) 3	
				(Online	2018)

Two reactions R_1 and R_2 have identical pre-exponential 5. 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 respectively at 300 K, then $\ln(k_2/k_1)$ is equal to $(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$ (a) 6 (b) 4

(c) 8 (d) 12 (2017)The rate of a reaction A doubles on increasing the temperature

6. from 300 K to 310 K. By how much, the temperature of reaction B should be increased from 300 K so that rate doubles if activation energy of the reaction B is twice to that of reaction A. (a)

The rate of a reaction quadruples when the temperature 7. changes from 300 K to 310 K. The activation energy of this reaction is

(Assume activation energy and pre-exponential factor are independent of temperature;

 $\ln 2 = 0.693$; $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)

(a) 53.6 kJ mol^{-1} (b) 26.8 kJ mol⁻¹ (d) 214.4 kJ mol⁻¹

(c) 107.2 kJ mol⁻¹

(Online 2017)

(2016)

- 8. Decomposition of H_2O_2 follows a first order reaction. In fifty minutes the concentration of H₂O₂ decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H₂O₂ reaches 0.05 M, the rate of formation of O₂ will be (a) $6.93 \times 10^{-2} \text{ mol min}^{-1}$
 - (b) $6.93 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$

(c)
$$2.66 \text{ Lmin}^{-1}$$
 at STP

(d) $1.34 \times 10^{-2} \text{ mol min}^{-1}$

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

$$\begin{aligned} \mathbf{O}_{3(g)} + \mathbf{Cl}^{\bullet}_{(g)} &\to \mathbf{O}_{2(g)} + \mathbf{ClO}^{\bullet}_{(g)}; \ k_{i} = 5.2 \times 10^{9} \text{ L mol}^{-1} \text{ s}^{-1} \\ &\dots(i) \\ \mathbf{ClO}^{\bullet}_{(g)} + \mathbf{O}^{\bullet}_{(g)} &\to \mathbf{O}_{2(g)} + \mathbf{Cl}^{\bullet}_{(g)}; \ k_{ii} = 2.6 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1} \\ &\dots(ii) \end{aligned}$$

The closest rate constant for the overall reaction

- $O_{3(g)} + O_{(g)}^{\bullet} \rightarrow 2O_{2(g)}$ is (a) $1.4 \times 10^{20} \text{ L mol}^{-1} \text{ s}^{-1}$ (b) $3.1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (c) $5.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (d) $2.6 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (Online 2016)
- 10. The rate law for the reaction below is given by the expression k[A] [B]

 $A + B \rightarrow \text{Product}$ If the concentration of B is increased from 0.1 to 0.3 mole, keeping the value of A at 0.1 mole, the rate constant will

be
(a)
$$3 k$$
 (b) $9 k$ (c) $k/3$ (d) k
(Online 2016)

- 11. Higher order (>3) reactions are rare due to
 - (a) shifting of equilibrium towards reactants due to elastic collisions
 - (b) loss of active species on collision
 - (c) low probability of simultaneous collision of all the reacting species
 - (d) increase in entropy and activation energy as more molecules are involved.

(2015)

- 12. The reaction, $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$ follows first order kinetics. The pressure of a vessel containing only N_2O_5 was found to increase from 50 mm Hg to 87.5 mm Hg in 30 min. The pressure exerted by the gases after 60 min. will be (assume temperature remains constant)
 - (a) 106.25 mm Hg (b) 116.25 mm Hg
 - (c) 125 mm Hg (d) 150 mm Hg

(Online 2015)

13. $A + 2B \rightarrow C$, the rate equation for this reaction is given as Rate = k[A][B].

If the concentration of A is kept the same but that of B is doubled what will happen to the rate itself?

- (b) The same (a) Halved
- (c) Doubled (d) Quadrupled

(Online 2015)

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

Initial	Initial	Initial rate of							
concentration	concentration	formation of C							
[A]	[<i>B</i>]	$(mol L^{-1}s^{-1})$							
0.1 M	0.1 M	1.2×10^{-3}							
0.1 M	0.2 M	1.2×10^{-3}							
0.2 M	0.1 M	$2.4 imes 10^{-3}$							

The rate law for the formation of C is

(a)
$$\frac{dC}{dt} = k[A]$$
 (b) $\frac{dC}{dt} = k[A][B]$
(c) $\frac{dC}{dt} = k[A]^2[B]$ (d) $\frac{dC}{dt} = k[A][B]^2$ (2014)

- 15. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be $(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \text{ and } \log 2 = 0.301)$ (b) 53.6 kJ mol⁻¹ (a) 60.5 kJ mol^{-1}
 - (d) 58.5 kJ mol⁻¹ (c) 48.6 kJ mol^{-1} (2013)
- 16. For a first order reaction, $(A) \rightarrow$ products, the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M is
 - (a) 3.47×10^{-4} M/min (b) 3.47×10^{-5} M/min

(c)
$$1.73 \times 10^{-4}$$
 M/min (d) 1.73×10^{-5} M/min (2012)

17. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about

18. Consider the reaction : LUS . . C1

$$Cl_{2(aq)} + H_2S_{(aq)} \longrightarrow S_{(s)} + 2H^{+}_{(aq)} + 2Cl^{-}_{(aq)}$$

The rate of reaction for this reaction is
rate = $k[Cl_2][H_2S]$
Which of these mechanism is/are consistent with the

his rate equation?

- A. $Cl_2 + H_2S \longrightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow) $Cl^+ + HS^- \longrightarrow H^+ + Cl^- + S$ (fast)
- $H_2S \Leftrightarrow H^+ + HS^-$ (fast equilibrium) B. $Cl_2 + HS^- \longrightarrow 2Cl^- + H^+ + S \text{ (slow)}$

- (a) A only (b) B only (c) Both A and B (d) Neither A nor B
- (2010)
- 19. 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? (a) 1 h (b) 4 h (c) 0.5 h (d) 0.25 h

(2010)

- 20. The half-life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be $(\log 2 = 0.301)$
 - (a) 230.3 minutes (b) 23.03 minutes
 - (c) 46.06 minutes (d) 460.6 minutes (2009)
- **21.** For a reaction $\frac{1}{2}A \rightarrow 2B$ rate of disappearance of A is related to the rate of appearance of B by the expression

(a)
$$-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$$
 (b) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$
(c) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$ (d) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (2008)

- 22. Consider the reaction, $2A + B \rightarrow$ products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is
 - (a) s^{-1} (b) L mol⁻¹ s⁻¹
 - (c) no unit (d) mol $L^{-1} s^{-1}$. (2007)
- 23. The energies of activation for forward and reverse reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol⁻¹ and 200 kJ mol⁻¹ respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol⁻¹. The enthalpy change of the reaction $(A_2 + B_2 \rightarrow 2AB)$ in the presence of a catalyst will be (in kJ mol⁻¹) (a) 20 (b) 300 (c) 120 (d) 280

24. The following mechanism has been proposed for the reaction of NO with Br, to form NOBr. $NO_{(a)} + Br_{\gamma(a)} \longrightarrow NOBr_{\gamma(a)}$

$$NOBr_{2(g)} + NO_{(g)} \rightarrow 2NOBr_{(g)}$$

If the second step is the rate determining step, the order of the reaction with respect to NO(9) is

(a) 1 (b) 0 (c)
$$3$$
 (d) 2 (2006)

- 25. Rate of a reaction can be expressed by Arrhenius equation as : $k = Ae^{-E/RT}$. In this equation, E represents
 - (a) the energy above which all the colliding molecules will react
 - (b) the energy below which colliding molecules will not react
 - the total energy of the reacting molecules at a (c) temperature, T
 - (d) the fraction of molecules with energy greater than the activation energy of the reaction. (2006)

- **26.** 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
 - (a) remain unchanged
 - (b) tripled
 - (c) increased by a factor of 4
 - (d) doubled. (2006)
- 27. $t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to 3/4 of its initial value. If the rate constant for a first order reaction is k, the $t_{1/4}$ can be written as
 - (a) 0.10/k (b) 0.29/k
 - (c) 0.69/k (d) 0.75/k (2005)
- 28. A reaction involving two different reactants can never be
 - (a) unimolecular reaction (b) first order reaction
 - (c) second order reaction (d) bimolecular reaction.
- **29.** The rate equation for the reaction $2A + B \rightarrow C$ is found to be: rate = k[A][B]. The correct statement in relation to this reaction is that the
 - (a) unit of k must be s^{-1}
 - (b) $t_{1/2}$ is a constant
 - (c) rate of formation of C is twice the rate of disappearance of A
 - (d) value of k is independent of the initial concentrations of A and B.

(2004)

(2005)

- **30.** 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
 - (a) 30 minutes (b) 15 minutes (c) 7.5 minutes (d) 60 minutes. (2004)
- **31.** In the respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the following statements is correct?
 - (a) k is equilibrium constant.
 - (b) A is adsorption factor.
 - (c) E_a is energy of activation.
 - (d) *R* is Rydberg constant. (2003)

32. For the reaction system:

$$2\mathrm{NO}_{(g)} + \mathrm{O}_{2(g)} \to 2\mathrm{NO}_{2(g)},$$

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_2 , the rate of reaction will

- (a) diminish to one-fourth of its initial value
- (b) diminish to one-eighth of its initial value
- (c) increase to eight times of its initial value
- (d) increase to four times of its initial value. (2003)
- **33.** 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

(a)
$$\frac{1}{2^{m+n}}$$
 (b) $(m+n)$
(c) $(n-m)$ (d) $2^{(n-m)}$ (2003)

- **34.** The formation of gas at the surface of tungsten due to adsorption is the reaction of order
 - (a) 0
 (b) 1
 (c) 2
 (d) insufficient data.

35. The differential rate law for the reaction, $H \rightarrow H \rightarrow 2H$

$$H_{2} + I_{2} \rightarrow 2HI \text{ is}$$
(a) $-\frac{d[H_{2}]}{dt} = -\frac{d[I_{2}]}{dt} = -\frac{d[HI]}{dt}$
(b) $\frac{d[H_{2}]}{dt} = \frac{d[I_{2}]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$
(c) $\frac{1}{2}\frac{d[H_{2}]}{dt} = \frac{1}{2}\frac{d[I_{2}]}{dt} = -\frac{d[HI]}{dt}$
(d) $-2\frac{d[H_{2}]}{dt} = -2\frac{d[I_{2}]}{dt} = \frac{d[HI]}{dt}$ (2002)

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

(a) 3 (b) 6 (c) 5 (d) 7 (2002)

37. Units of rate constant of first and zero order reactions in terms of molarity M unit are respectively
(a) s⁻¹, M s⁻¹
(b) s⁻¹, M
(c) M s⁻¹, s⁻¹
(d) M, s⁻¹
(2002)

ANSWER KEY																							
1.	(a)	2.	(c)	3.	(b)	4.	(a)	5.	(b)	6.	(d)	7.	(c)	8.	(b)	9.	(c)	10.	(d)	11.	(c)	12.	(a)
13.	(c)	14.	(a)	15.	(b)	16.	(a)	17.	(c)	18.	(a)	19.	(d)	20.	(c)	21.	(c)	22.	(b)	23.	(a)	24.	(d)
25.	(b)	26.	(c)	27.	(b)	28.	(a)	29.	(d)	30.	(a)	31.	(c)	32.	(c)	33.	(d)	34.	(a)	35.	(d)	36.	(a)
37.	(a)																						

1. (a) :
$$r \propto (a - x)^n (n = \text{order of reaction}, (a - x) = \text{unreacted})$$

 $\frac{r_1}{r_2} = \left(\frac{a - x_1}{a - x_2}\right)^n \implies \frac{1}{0.5} = \left(\frac{100 - 5}{100 - 33}\right)^n = \left(\frac{95}{67}\right)^n$
 $2 = (1.41)^n = (\sqrt{2})^n \implies n = 2$
2. (c) : N_2O_5 $\implies 2NO_2 + 1/2 O_2$
At $t = 0$ 50 mm Hg 0 0
At $t = 50$ min 50 $-p_1$ 2 p_1 $\frac{p_1}{2}$
Total pressure at $t = 50$ min is
 $50 - p_1 + 2p_1 + \frac{p_1}{2} = 87.5$ mm Hg
 $50 + 1.5 p_1 = 87.5 \implies p_1 = \frac{37.5}{1.5} = 25$ mm Hg
Since, $t = 50$ min. is the half- life period for the reaction.
Thus, $t = 100$ min $50 - p_2$ $2p_2$ $\frac{p_2}{2}$
 $\therefore 50 - p_2 = \frac{25}{2}$ (At 2nd half-life)
 $p_2 = 37.5$ mm Hg
Total pressure at $t = 100$ min $= 50 - p_2 + 2p_2 + \frac{p_2}{2}$
3. (b) : For a first order reaction, $t_{1/2} = \frac{0.693}{k}$
 $k = \frac{0.693}{10}$
 $k = \frac{2.303}{0.693} \times 10 \log \frac{4}{3} = \frac{2.303}{0.693} \times 10 \times 0.1249 = 4.152 \approx 4.1$ days
4. (a) : $t_{1/2} = 100$ second (50% reaction)
After 200 seconds.
Thus, it follows first order kinetics as half-life is independent
of concentration and follows the relation $t_{3/4} = 2 \times t_{1/2}$
5. (b) : According to the Arrhenius equation, $k = Ae^{-E_d/RT}$
For reaction R_1 ; $k_1 = Ae^{-E_{a1}/RT}$

 $\ln k_1 = \ln A - \frac{E_{a_1}}{RT}$ For reaction R_2 ; $k_2 = Ae^{-E_{a_2}/RT}$ $\ln k_2 = \ln A - \frac{E_{a_2}}{RT}$ Now, $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_{a_1}}{RT} - \frac{E_{a_2}}{RT} = \frac{E_{a_1} - E_{a_2}}{RT} = \frac{\Delta E_a}{RT}$ ed) $= \frac{10 \times 10^{3} \text{ J mol}^{-1}}{8.314 \times 300} = 4$ 6. (d) : For reaction *A*, *T*₁ = 300 K, *T*₂ = 310 K, *k*₂ = 2 *k*₁ $\log \frac{k_{2}}{k_{1}} = \frac{E_{a_{1}}}{2.303R} \left(\frac{1}{T_{1}} - \frac{1}{T_{2}} \right)$ $\therefore \quad \log \frac{2k_{1}}{k_{1}} = \log 2 = \frac{E_{a_{1}}}{2.303R} \left\{ \frac{1}{300} - \frac{1}{310} \right\} \qquad \dots (i)$ For reaction *B*, *T*₁ = 300 K, *T*₂ = ?, *k*₂ = 2*k*₁, *E_{a2}* = 2*E_{a1} \therefore \quad \log \frac{2k_{1}}{k_{1}} = \log 2 = \frac{2E_{a_{1}}}{2.303R} \left\{ \frac{1}{300} - \frac{1}{T_{2}} \right\} \qquad \dots (ii)From eq. (i) and (ii), we get \frac{2E_{a_{1}}}{2.303R} \left\{ \frac{1}{300} - \frac{1}{T_{2}} \right\} = \frac{E_{a_{1}}}{2.303R} \left\{ \frac{1}{300} - \frac{1}{310} \right\} \Rightarrow \quad 2 \left\{ \frac{1}{300} - \frac{1}{T_{2}} \right\} = \left\{ \frac{1}{300} - \frac{1}{310} \right\} \Rightarrow \quad T_{2} = \frac{300 \times 310}{610} \times 2 = 304.92 \text{ K} \therefore \quad \text{Increased temperature} = (304.92 - 300) = 4.92 \text{ K}7. (c) : \ln \frac{k_{2}}{k_{1}} = \frac{E_{a}}{R} \left(\frac{1}{T_{1}} - \frac{1}{T_{2}} \right) \ln 4 = \frac{E_{a}}{R} \left(\frac{1}{300} - \frac{1}{310} \right) \Rightarrow \ln 4 = \frac{E_{a}}{R} \left(\frac{10}{300 \times 310} \right) E_{a} = \frac{1.386 \times 8.314 \times 300 \times 310}{10} = 107165.79 \text{ J mol}^{-1} = 107.165 \text{ kJ mol}^{-1}8. (b) : Decomposition of H_{2}O_{2} is represented as*

 $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ Concentration of H_2O_2 decreases from 0.5 M to 0.125 M in 50 minutes *i.e.*, reduced to 1/4.

So, it can be represented as

$$0.5 \xrightarrow{t_{1/2}} 0.25 \xrightarrow{t_{1/2}} 0.125$$

$$50 \text{ min}$$

 $\Rightarrow 2t_{1/2} = 50 \text{ min} \Rightarrow t_{1/2} = 25 \text{ min}$ Now, for a first order reaction, $= \frac{53 > 8}{647} = \frac{53 > 8}{7:} \text{ y uz}^{-6}$

Rate of H_2O_2 decomposition = $k[H_2O_2]$

$$=\frac{53>8}{7:}\times -55:.=638 \Rightarrow \times 65^{-8} \text{ y } \{\text{xS}^{-6} \text{ y } \text{ w}^{-6}\}$$

Rate of formation of $W_7 = \frac{6}{7} \times \text{rate of } H_2O_2$ decomposition

$$= \frac{6}{7} \times 633 \Rightarrow \times 65^{-8} = 6.93 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$$

9. (c) : Overall rate of a reaction depends upon rate of the slowest step. Hence, the overall rate constant of the reaction will be closest to the rate constant of the slower step *i.e.*, the one having lower value of k.

10. (d): Rate constant varies with temperature only and it is independent of concentration of reactants.

11. (c) : The reactions of higher order are very rare because of the less chances of the molecules to come together simultaneously and collide.

12. (a) : For first order reaction, rate = $k[N_2O_5]$ $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$ 50 - 2P + 4P - PAt t = 0, pressure : At t = 30 min, pressure : 50 - 2PTotal pressure = 50 - 2P + 4P + P = 50 + 3P = 87.5 mm Hg \therefore P = 12.5 mm Hg \therefore $P_0 = 50$ and $P_t = 25$ for N₂O₅ reactant $k = \frac{2.303}{t} \log\left(\frac{P_0}{P_t}\right) = \frac{73858}{85 \text{ y u}} x(s\left(\frac{15}{7}\right)) = \frac{73858}{5 \text{ y u}} x(s\left(\frac{15}{7}\right))$ where x is the pressure at t = 60 min. On solving, x = 12.5 mm Hg = 50 - 2P:. P = 18.75 mm Hg:. Total pressure (at t = 60 min) = 50 + 3P = 106.25 mm Hg13. (c) : $A + 2B \rightarrow C$ Rate $(R_1) = k[A][B]$...(i) Rate $(R_{2}) = k[A][2B]$...(ii) $\frac{o_7}{o_6} = 7 \quad \Rightarrow R_2 = 2R_1$ 14. (a): For the reaction, $2A + B \rightarrow C + D$ Rate of reaction = $-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$ Now, rate of reaction, $\frac{d[C]}{dt} = k[A]^{x}[B]^{y}$ From table, $1.2 \times 10^{-3} = k(0.1)^x (0.1)^y$...(i) $1.2 \times 10^{-3} = k(0.1)^x (0.2)^y$...(ii) $2.4 \times 10^{-3} = k(0.2)^x (0.1)^y$ 2.4 × 10⁻³ = $k(0.2)^x (0.1)^y$...(11) On dividing equation (i) by (ii), we get $\frac{1.2 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k(0.1)^x (0.1)^y}{k(0.1)^x (0.2)^y}$...(iii) $1 = \left(\frac{1}{2}\right)^y \implies y = 0$ On dividing equation (i) by (iii), we get $\frac{1.2 \times 10^{-3}}{2.4 \times 10^{-3}} = \frac{k(0.1)^x (0.1)^y}{k(0.2)^x (0.1)^y}$ $\left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^x \implies x = 1$ Hence, $\frac{d[C]}{dt} = k[A]^{1}[B]^{0} = k[A]$ **15.** (b) : As $r = k[A]^n$ $\frac{r_2}{r_1} = \frac{k_2}{k_1}$; Since $\frac{r_2}{r_1} = 2$ (Given) $\therefore \quad \frac{k_2}{k_1} = 2$ $\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

$$\log 2 = \frac{E_a}{2.303 \times 8.314 \times 10^{-3}} \left[\frac{310 - 300}{310 \times 300} \right]$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 10^{-3} \times 93 \times 10^3}{10} = 53.6 \text{ kJ mol}^{-1}$$

16. (a) : For the first order reaction, $k = \frac{2.303}{t} \log \frac{a}{a - x}$
 $a = 0.1 \text{ M}, a - x = 0.025 \text{ M}, t = 40 \text{ min}$
 $k = \frac{2.303}{40} \log \frac{0.1}{0.025} = \frac{2.303}{40} \log 4 = 0.0347 \text{ min}^{-1}$
[A] \longrightarrow product
Thus, rate = $k[A]$
rate = 0.0347 × 0.01 M min^{-1} = 3.47 × 10^{-4} M min^{-1}

17. (c):
$$\frac{\text{Rate at } 50^{\circ}\text{C}}{\text{Rate at } T_1^{\circ}\text{C}} = 2^{\frac{50}{10}} = 2^5 = 32 \text{ times.}$$

18. (a): The rate equation depends upon the rate determining step. The given rate equation is only consistent with the mechanism A.

19. (d) : For a zero order reaction, $t_{1/2}$ is given as

$$t_{1/2} = \frac{[A_0]}{2k} \implies k = \frac{[A_0]}{2t_{1/2}}$$

Given, $t_{1/2} = 1$ hr, $[A_0] = 2$ M
 $\therefore k = \frac{2}{2 \times 1} = 1$ mol L⁻¹ hr⁻¹

Integrated rate law for zero order reaction is $[A] = -kt + [A_0]$ Here, $[A_0] = 0.5$ M and [A] = 0.25 M

 $\Rightarrow 0.25 = -t + 0.5 \Rightarrow t = 0.25$ hours

20. (c) : Given, $t_{1/2} = 6.93$ min $\lambda = \frac{0.693}{1000}$ (for 1st order reaction)

$$=\frac{0.693}{6.93}$$

Since reaction follows 1st order kinetics, $t = \frac{2.303}{\lambda} \log \frac{[A_0]}{[A]}$ where $[A_0]$ = initial concentration and [A] = concentration of A at time t.

: Reaction is 99% complete.

$$\therefore \quad \frac{[A_0]}{[A]} = \frac{100}{1}$$

or $t = \frac{2.303 \times 6.93}{0.693} \times \log(100) = 23.03 \times 2\log(10) = 46.06$ minutes.

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

22. (b) : Rate = $k [A]^x [B]^y$ When [B] is doubled, keeping [A] constant half-life of the reaction does not change.

Now, for a first order reaction
$$t_{1/2} = \frac{0.693}{k}$$

i.e. $t_{1/2}$ is independent of the concentration of the reactant. Hence the reaction is first order with respect to *B*. Now when [A] is doubled, keeping [B] constant, the rate also doubles. Hence the reaction is first order with respect to *A*.

 \therefore Rate = $[A]^{l} [B]^{l}$

 \therefore order = 2

Now for a *n*th order reaction, unit of rate constant is $(L)^{n-1} \pmod{1^{-n} s^{-1}}$ when n = 2, unit of rate constant is $L \mod^{-1} s^{-1}$.

23. (a) : $\Delta H_R = E_f - E_b = 180 - 200 = -20 \text{ kJ mol}^{-1}$

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

24. (d) : $NO_{(g)} + Br_{2(g)} \implies NOBr_{2(g)}$ $NOBr_{2(g)} + NO_{(g)} \rightarrow 2NOBr_{(g)}$ [rate determining step] Rate of the reaction (r) = K [NOBr₂] [NO] where [NOBr₂] = K_C [NO][Br₂] $r = K \cdot K_C \cdot$ [NO][Br₂][NO] r = K' [NO]² [Br₂] The order of the reaction with respect to $NO_{(g)} = 2$

25. (b) :
$$k = Ae^{-E/RT}$$

where E = activation energy, *i.e.* the minimum amount of energy required by reactant molecules to participate in a reaction.

26. (c): Given
$$r_1 = \frac{dx}{dt} = k[CO]^2$$
; $r_2 = k[2CO]^2 = 4k[CO]^2$

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

27. (b):
$$t_{1/4} = \frac{2.303}{k} \log \frac{4}{3} = \frac{0.29}{k}$$

28. (a) : 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.

But a reaction involving two different reactants can a first order reaction. For example, for the following reaction

 $RCl + H_2O \rightarrow ROH + HCl$

Expected rate law : Rate = $k[RC1][H_2O]$, expected order = 1 + 1 = 2 But actual rate law : Rate = k'[RC1], actual order = 1

Here water is taken in excess, hence its concentration may be taken constant.

Here the molecularity of the reaction = 2 and the order of the reaction = 1.

29. (d) : $2A + B \rightarrow C$ 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. For a second order reaction, unit of rate constant, k is L mol⁻¹ sec⁻¹ for

a second order reaction, $t_{1/2} = \frac{1}{ka}$

i.e. $t_{1/2}$ is inversely proportional to initial concentration.

$$2A + B \to C$$

$$1 d[A] \quad d[B] \quad d[C]$$

Rate
$$=-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

i.e. rate of formation of C is half the rate of disappearance of B.

30. (a) : 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 M in two half lives. *i.e.* $2t_{1/2} = 2 \times 15 = 30$ minutes.

31. (c) : In Arrhenius equation, $k = Ae^{-E_a/RT}$

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.

32. (c) : Rate₁ = k [NO]² [O₂] When volume is reduced to 1/2, concentration becomes two times. Rate₂ = k [2NO]² [2O₂]

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\text{NO}]^2 [\text{O}_2]}{k[2\text{NO}]^2 [2\text{O}_2]} = \frac{1}{8} \implies \text{Rate}_2 = 8 \text{ Rate}_1$$

33. (d) : Rate₁ = $k [A]^n [B]^m$ On doubling the concentration of A and halving the concentration of B

Rate₂ =
$$k [2A]^n [B/2]^m$$

Ratio between new and earlier rate =
$$\frac{k[2A]^n [B/2]^n}{k[A]^n [B]^m}$$

$$=2^n \times \left(\frac{1}{2}\right)^m = 2^{n - m}$$

34. (a)

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

Thus the rate may be expressed as

$$\frac{-d[\mathrm{H}_{2}]}{dt} = \frac{-d[\mathrm{I}_{2}]}{dt} = \frac{1}{2}\frac{d[\mathrm{HI}]}{dt}$$

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

36. (a) : Order is the sum of the power of the concentrations terms in rate law expression. $R = [A] \cdot [B]^2$

Thus, order of reaction = 1 + 2 = 3

37. (a) : Unit of $K = (\text{mol } L^{-1})^{1-n} s^{-1}$,

where n =order of reaction

 $n = 0 \Rightarrow$ zero order reaction

 $n = 1 \Rightarrow$ first order reaction

