

DPP - Daily Practice Problems

Chapter-wise Sheets

Date : Start Time : End Time :

CHEMISTRY (CC18)

SYLLABUS : Chemical Kinetics

Max. Marks : 180

Marking Scheme : + 4 for correct & (-1) for incorrect

Time : 60 min.

INSTRUCTIONS : This Daily Practice Problem Sheet contains 45 MCQ's. For each question only one option is correct. Darken the correct circle/ bubble in the Response Grid provided on each page.

1. The decomposition of a substance follows first order kinetics. Its concentration is reduced to 1/8th of its initial value in 24 minutes. The rate constant of the decomposition process is

- (a) $1/24 \text{ min}^{-1}$ (b) $\frac{0.692}{24} \text{ min}^{-1}$
 (c) $\frac{2.303}{24} \log \left(\frac{1}{8} \right) \text{ min}^{-1}$ (d) $\frac{2.303}{24} \log \left(\frac{8}{1} \right) \text{ min}^{-1}$

2. 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) $\text{L mol}^{-1} \text{s}^{-1}$
 (c) no unit (d) $\text{mol L}^{-1} \text{s}^{-1}$

3. A reaction involving two different reactants can never be

- (a) bimolecular reaction (b) second order reaction
 (c) first order reaction (d) unimolecular reaction

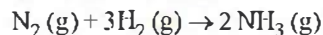
4. Select the rate law that corresponds to the data shown for the following reaction $A + B \rightarrow C$

Expt. No.	(A)	(B)	Initial Rate
1	0.012	0.035	0.10

2	0.024	0.070	0.80
3	0.024	0.035	0.10
4	0.012	0.070	0.80

- (a) $\text{Rate} = k[\text{B}]^3$ (b) $\text{Rate} = k[\text{B}]^4$
 (c) $\text{Rate} = k[\text{A}][\text{B}]^3$ (d) $\text{Rate} = k[\text{A}]^2[\text{B}]^2$

5. Consider the reaction



The equality relationship between $\frac{d[\text{NH}_3]}{dt}$ and $-\frac{d[\text{H}_2]}{dt}$ is

- (a) $+\frac{d[\text{NH}_3]}{dt} = -\frac{2}{3} \frac{d[\text{H}_2]}{dt}$ (b) $+\frac{d[\text{NH}_3]}{dt} = -\frac{3}{2} \frac{d[\text{H}_2]}{dt}$

- (c) $\frac{d[\text{NH}_3]}{dt} = -\frac{d[\text{H}_2]}{dt}$ (d) $\frac{d[\text{NH}_3]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$

6. Diazonium salt decomposes as



At 0°C , the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is

- (a) a first order reaction
 (b) a second order reaction
 (c) independent of the initial concentration of the salt
 (d) a zero order reaction

RESPONSE
GRID

1. (a) (b) (c) (d) 2. (a) (b) (c) (d) 3. (a) (b) (c) (d) 4. (a) (b) (c) (d) 5. (a) (b) (c) (d)
 6. (a) (b) (c) (d)

Space for Rough Work

7. $\text{CHCl}_3 + \text{Cl}_2 \longrightarrow \text{CCl}_4 + \text{HCl}$
Rate law for above reaction will be
Rate = $k[\text{CHCl}_3][\text{Cl}_2]^2$
On the basis of information provided which of the following option will be correct ?
(a) Rate law for any chemical reaction can be predicted accurately by looking at balanced chemical equation.
(b) Rate law for a chemical reaction has to determine experimentally.
(c) Either determined experimentally or obtained from balanced chemical reaction, rate law will be same.
(d) None of the above is correct.
8. Which of the following statements is incorrect?
(a) Activation energy for the forward reaction equals to activation energy for the reverse reaction
(b) For a reversible reaction, an increase in temperature increases the reaction rate for both the forward and the backward reaction
(c) The larger the initial reactant concentration for a second order reaction, the shorter is its half-life.
(d) When Δt is infinitesimally small, the average rate equals the instantaneous rate
9. In a reaction $A \rightarrow \text{Products}$, when start is made from $8.0 \times 10^{-2} \text{ M}$ of A , half-life is found to be 120 min etc. For the initial concentration $4.0 \times 10^{-2} \text{ M}$, the half-life of the reaction becomes 240 minute. The order of the reaction is :
(a) zero (b) one (c) two (d) 0.5
10. During decomposition of an activated complex.
(i) energy is always released
(ii) energy is always absorbed
(iii) energy does not change
(iv) reactants may be formed
(a) (i), (ii) and (iii) (b) (i) and (iv)
(c) (ii) and (iii) (d) (ii), (iii) and (iv)
11. Which of the following statements is incorrect ?
(a) Energy is always released when activated complex decomposes to form products.
(b) Peak of the energy distribution curve corresponds to the most probable potential energy.
(c) Peak of the energy distribution curve corresponds to the most probable kinetic energy.
(d) When the temperature is raised maximum of energy distribution curve moves to higher energy value and broadens out.
12. A catalyst increases rate of reaction by
(a) decreasing enthalpy
(b) decreasing internal energy
(c) decreasing activation energy
(d) increasing activation energy
13. Consider a reaction $aG + bH \rightarrow \text{Products}$. 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
(a) 0 (b) 1 (c) 2 (d) 3
14. For a first order reaction $(A) \rightarrow \text{products}$ 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) $1.73 \times 10^{-5} \text{ M/min}$ (b) $3.47 \times 10^{-4} \text{ M/min}$
(c) $3.47 \times 10^{-5} \text{ M/min}$ (d) $1.73 \times 10^{-4} \text{ M/min}$
15. The given reaction
 $2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$
is an example of
(a) first order reaction (b) second order reaction
(c) third order reaction (d) None of these
16. In a first-order reaction $A \rightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M, then the half-life is
(a) $\frac{\log 2}{k}$ (b) $\frac{\log 2}{k\sqrt{0.5}}$
(c) $\frac{\ln 2}{k}$ (d) $\frac{0.693}{0.5k}$
17. The integrated rate equations can be determined for
(a) zero order reactions (b) first order reactions
(c) second order reactions (d) Both (a) and (b)
18. The rate constant, the activation energy and the arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is
(a) $2.0 \times 10^{18} \text{ s}^{-1}$ (b) $6.0 \times 10^{14} \text{ s}^{-1}$
(c) Infinity (d) $3.6 \times 10^{30} \text{ s}^{-1}$
19. According to the adsorption theory of catalysis, the speed of the reaction increases because
(a) in the process of adsorption, the activation energy of the molecules becomes large
(b) adsorption produces heat which increases the speed of the reaction
(c) adsorption lowers the activation energy of the reaction
(d) the concentration of product molecules at the active centres of the catalyst becomes high due to adsorption.
20. Consider a general chemical change $2A + 3B \rightarrow \text{products}$. The rate with respect to A is r_1 and that with respect to B is r_2 . The rates r_1 and r_2 are related as
(a) $3r_1 = 2r_2$ (b) $r_1 = r_2$
(c) $2r_1 = 3r_2$ (d) $r_1^2 = 2r_2^2$
21. 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) 7.5 minutes (b) 15 minutes
(c) 30 minutes (d) 60 minutes

RESPONSE
GRID

- | | | | | |
|------------------|------------------|------------------|------------------|------------------|
| 7. (a)(b)(c)(d) | 8. (a)(b)(c)(d) | 9. (a)(b)(c)(d) | 10. (a)(b)(c)(d) | 11. (a)(b)(c)(d) |
| 12. (a)(b)(c)(d) | 13. (a)(b)(c)(d) | 14. (a)(b)(c)(d) | 15. (a)(b)(c)(d) | 16. (a)(b)(c)(d) |
| 17. (a)(b)(c)(d) | 18. (a)(b)(c)(d) | 19. (a)(b)(c)(d) | 20. (a)(b)(c)(d) | 21. (a)(b)(c)(d) |

Space for Rough Work

22. Activation energy (E_a) and rate constants (k_1 and k_2) of a chemical reaction at two different temperatures (T_1 and T_2) are related by :

- (a) $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$
- (b) $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$
- (c) $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$
- (d) $\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

23. $t_{\frac{1}{4}}$ can be taken as the time taken for the concentration of a reactant to drop to $\frac{3}{4}$ of its initial value. If the rate constant for a first order reaction is k , the $t_{\frac{1}{4}}$ can be written as

- (a) $0.75/k$ (b) $0.69/k$ (c) $0.29/k$ (d) $0.10/k$

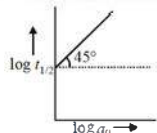
24. The decomposition of ammonia on tungsten surface at 500 K follows zero order kinetics. The half-life period of this reaction is 45 minutes when the initial pressure is 4 bar. The half-life period (minutes) of the reaction when the initial pressure is 16 bar at the same temperature is

- (a) 120 (b) 60 (c) 240 (d) 180

25. In a 1st order reaction, reactant concentration C varies with time t as:

- (a) $\frac{1}{C}$ increases linearly with t
- (b) $\log C$ decreases linearly with t
- (c) C decreases with $\frac{1}{t}$
- (d) $\log C$ decreases with $\frac{1}{t}$

26. For a reaction $A \rightarrow \text{Product}$, a plot of $\log t_{1/2}$ versus $\log a_0$ is shown in the figure. If the initial concentration of A is represented by a_0 , the order of the reaction is



- (a) one (b) zero (c) two (d) three

27. 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 :

- (a) 10 times (b) 24 times (c) 32 times (d) 64 times

28. For a first order reaction $t_{0.75}$ is 1368 seconds, therefore, the specific rate constant in sec^{-1} is

- (a) 10^{-3} (b) 10^{-2} (c) 10^{-9} (d) 10^{-5}

29. The integrated rate equation is $Rt = \log C_0 - \log C_t$

The straight line graph is obtained by plotting

- (a) time Vs $\log C_t$ (b) $\frac{1}{\text{time}} \text{ Vs } C_t$
- (c) time Vs C_t (d) $\frac{1}{\text{time}} \text{ Vs } \frac{1}{C_t}$

30. 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

31. The half-life period of a first order reaction is 15 minutes. The amount of substance left after one hour will be:

- (a) $\frac{1}{4}$ of the original amount
- (b) $\frac{1}{8}$ of the original amount
- (c) $\frac{1}{16}$ of the original amount
- (d) $\frac{1}{32}$ of the original amount

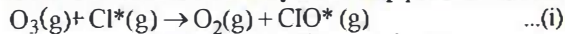
32. Reaction rate between two substance A and B is expressed as following:

$$\text{rate} = k[A]^m[B]^n$$

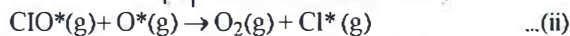
If the concentration of A is doubled and concentration of B is made half of initial concentration, the ratio of the new rate to the earlier rate will be:

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

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



$$[\text{K}_1 = 5.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}]$$



$$[\text{K}_2 = 2.6 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}]$$

The closest rate constant for the overall reaction $\text{O}_3(\text{g}) + \text{O}^*(\text{g}) \rightarrow 2\text{O}_2(\text{g})$ is :

- (a) $1.4 \times 10^9 \text{ s}^{-1}$ (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) $2.6 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$

34. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation,

$k = A \cdot e^{-E_a/R}$ Activation energy (E_a) of the reaction can be calculated by plotting

- (a) k vs. $\frac{1}{\log T}$ (b) $\log k$ vs. $\frac{1}{T}$
- (c) $\log k$ vs. $\frac{1}{\log T}$ (d) k vs. T

RESPONSE GRID

22. (a) (b) (c) (d)	23. (a) (b) (c) (d)	24. (a) (b) (c) (d)	25. (a) (b) (c) (d)	26. (a) (b) (c) (d)
27. (a) (b) (c) (d)	28. (a) (b) (c) (d)	29. (a) (b) (c) (d)	30. (a) (b) (c) (d)	31. (a) (b) (c) (d)
32. (a) (b) (c) (d)	33. (a) (b) (c) (d)	34. (a) (b) (c) (d)		

Space for Rough Work

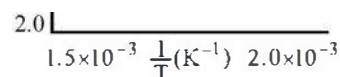
35. For the reaction system :
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO , the rate of reaction will
 (a) diminish to one-eighth of its initial value
 (b) increase to eight times of its initial value
 (c) increase to four times of its initial value
 (d) diminish to one-fourth of its initial value
36. In the reaction of formation of sulphur trioxide by contact process $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ the rate of reaction was measured as $\frac{d[\text{O}_2]}{dt} = -2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. The rate of reaction in terms of $[\text{SO}_2]$ in $\text{mol L}^{-1} \text{ s}^{-1}$ will be:
 (a) -1.25×10^{-4} (b) -2.50×10^{-4}
 (c) -3.75×10^{-4} (d) -5.00×10^{-4}
37. A reactant (A) forms two products :
 $\text{A} \xrightarrow{k_1} \text{B}$, Activation Energy Ea_1
 $\text{A} \xrightarrow{k_2} \text{C}$, Activation Energy Ea_2
 If $Ea_2 = 2 Ea_1$, then k_1 and k_2 are related as :
 (a) $k_2 = k_1 e^{Ea_1/RT}$ (b) $k_2 = k_1 e^{Ea_2/RT}$
 (c) $k_1 = Ak_2 e^{Ea_1/RT}$ (d) $k_1 = 2k_2 e^{Ea_2/RT}$
38. Consider an endothermic reaction $\text{X} \rightarrow \text{Y}$ with the activation energies E_b and E_f for the backward and forward reactions, respectively. In general
 (a) there is no definite relation between E_b and E_f
 (b) $E_b = E_f$
 (c) $E_b > E_f$
 (d) $E_b < E_f$
39. Which of the following influences the rate of a chemical reaction performed in solution?
 (a) Temperature
 (b) Activation energy
 (c) Presence of a catalyst
 (d) All of the above influence the rate
40. The rate of a reaction quadruples when the temperature changes from 300 to 310 K. The activation energy of this reaction is : (Assume activation energy and pre-exponential factor are independent of temperature; $\ln 2 = 0.693$; $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
 (a) $107.2 \text{ kJ mol}^{-1}$ (b) 53.6 kJ mol^{-1}
 (c) 26.8 kJ mol^{-1} (d) $214.4 \text{ kJ mol}^{-1}$
41. Consider the reaction :
 $\text{Cl}_2(\text{aq}) + \text{H}_2\text{S}(\text{aq}) \rightarrow \text{S}(\text{s}) + 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq})$
 The rate equation for this reaction is

$$\text{rate} = k[\text{Cl}_2][\text{H}_2\text{S}]$$

Which of these mechanisms is/are consistent with this rate equation?

- A. $\text{Cl}_2 + \text{H}_2\text{S} \rightarrow \text{H}^+ + \text{Cl}^- + \text{Cl}^+ + \text{HS}^-$ (slow)
 $\text{Cl}^+ + \text{HS}^- \rightarrow \text{H}^+ + \text{Cl}^- + \text{S}$ (fast)
- B. $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$ (fast equilibrium)
 $\text{Cl}_2 + \text{HS}^- \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{S}$ (Slow)
- (a) B only (b) Both A and B
 (c) Neither A nor B (d) A only
42. The slope in Arrhenius plot, is equal to:
 (a) $\frac{E_a}{2.303R}$ (b) $\frac{E_a}{R}$
 (c) $\frac{R}{2.303E_a}$ (d) None of these
43. A schematic plot of $\ln K_{\text{eq}}$ versus inverse of temperature for a reaction is shown below

6.0



The reaction must be

- (a) highly spontaneous at ordinary temperature
 (b) one with negligible enthalpy change
 (c) endothermic
 (d) exothermic
44. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is
-
45. The reaction $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ 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 mmHg (b) 150 mmHg
 (c) 125 mmHg (d) 116.25 mmHg

RESPONSE
GRID

35. (a) (b) (c) (d) 36. (a) (b) (c) (d) 37. (a) (b) (c) (d) 38. (a) (b) (c) (d) 39. (a) (b) (c) (d)
 40. (a) (b) (c) (d) 41. (a) (b) (c) (d) 42. (a) (b) (c) (d) 43. (a) (b) (c) (d) 44. (a) (b) (c) (d)
 45. (a) (b) (c) (d)

Space for Rough Work

DAILY PRACTICE PROBLEMS

CHEMISTRY SOLUTIONS

1. (d) $k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{24} \log \frac{1}{1} = \frac{2.303}{24} \log 8$
2. (b) Since doubling the concentration of B does not change half-life, the reaction is of 1st order w.r.t. B.
Order of reaction with respect to A = 1 because rate of reaction doubles when concentration of A is doubled keeping concentration of B constant.
 \therefore Order of reaction = 1 + 1 = 2 and units of second order reaction are $\text{L mol}^{-1} \text{sec}^{-1}$.
3. (d) The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction. Thus the reaction involving two different reactant can never be unimolecular.
4. (a) Let the rate law be $r = k[A]^x[B]^y$
Divide (3) by (1) $\frac{0.10}{0.10} = \frac{[0.024]^x [0.035]^y}{[0.012]^x [0.035]^y}$
 $\therefore 1 = [2]^x, x = 0$
Divide (2) by (3) $\frac{0.80}{0.10} = \frac{[0.024]^x [0.070]^y}{[0.024]^x [0.035]^y}$
 $\therefore 8 = (2)^y, y = 3$
Hence rate equation, $R = k[A]^0[B]^3 = k[B]^3$
5. (a) If we write rate of reaction in terms of concentration of NH_3 and H_2 , then
Rate of reaction = $\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$
So, $\frac{d[\text{NH}_3]}{dt} = -\frac{2}{3} \frac{d[\text{H}_2]}{dt}$
6. (a) As doubling the initial conc. doubles the rate of reaction, order = 1
7. (b) Rate law has to be determined experimentally as Cl_2 is raised to power $\frac{1}{2}$ in rate law whereas its stoichiometric coefficient in balanced chemical equation is 1.
8. (a)
- 9.
10. (b)
11. (b)
12. (c) Activation energy is lowered in presence of +ve catalyst.
13. (d) Overall order = sum of orders w.r.t each reactant.
Let the order be x and y for G and H respectively

Exp.No.	[G]molc litre ⁻¹	[H]molc litre ⁻¹	rate(molc litre ⁻¹ time ⁻¹)
1	a	b	r
2	2a	2b	8r
3	2a	b	2r

\therefore For (1) and (3), the rate is doubled when conc. of G is doubled keeping that of H constant i.e.,

$$\text{rate} \propto [\text{G}] \therefore x = 1$$

From (2) and (3), $y = 2$

\therefore Overall order is 3.

14. (b) For a first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{40} \log \frac{0.1}{0.025}$$

$$= \frac{2.303}{40} \log 4 = \frac{2.303 \times 0.6020}{40}$$

$$= 3.47 \times 10^{-2} \text{ min}^{-1}$$

$$\text{Rate} = k[\text{A}] = 3.47 \times 10^{-2} \times 0.01$$

$$= 3.47 \times 10^{-4} \text{ M/min}$$

15. (c) Third order

16. (c) For a first order reaction

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

when $t = t_{1/2}$

$$k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{a-a/2}$$

$$\text{or } t_{1/2} = \frac{2.303}{k} \cdot \frac{\ln 2}{k}$$

17. (d) The integrated rate equations are different for the reactions of different reaction orders. We shall determine these equations only for zero and first order chemical reactions.

18. (b) $T_2 = T(\text{say}), T_1 = 25^\circ\text{C} = 298\text{K}$,
 $E_a = 104.4 \text{ kJ mol}^{-1} = 104.4 \times 10^3 \text{ J mol}^{-1}$
 $k_1 = 3 \times 10^{-4}, k_2 = ?$,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3 \text{ J mol}^{-1}}{2.303 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \left[\frac{1}{298} - \frac{1}{T} \right]$$

$$\text{As } T \rightarrow \infty, \frac{1}{T} \rightarrow 0$$

$$\therefore \log \frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \times 298}$$

$$\log \frac{k_2}{3 \times 10^{-4}} = 18.297, \quad \frac{k_2}{3 \times 10^{-4}} = 1.98 \times 10^{18}$$

$$k_2 = (1.98 \times 10^{18}) \times (3 \times 10^{-4}) = 6 \times 10^{14} \text{ s}^{-1}$$

19. (c) Adsorption lowers the activation energy.

20. (a) For the change $2A + 3B \rightarrow \text{products}$

$$-\frac{1}{2} \frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt}, \quad \frac{1}{2} r_1 = \frac{1}{3} r_2; \quad 3r_1 = 2r_2$$

21. (c) The $t_{1/2}$ is 15 minutes. To fall the concentration from 0.1 to 0.025 we need two half lives i.e., 30 minutes.

22. (b) According to Arrhenius equation

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

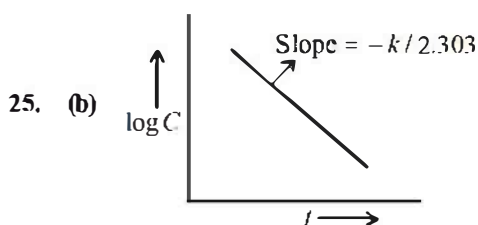
$$\ln \frac{k_1}{k_2} = -\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\begin{aligned} 23. \text{ (c)} \quad t_{1/4} &= \frac{2.303}{k} \log \frac{1}{3/4} = \frac{2.303}{k} \log \frac{4}{3} \\ &= \frac{2.303}{k} (\log 4 - \log 3) = \frac{2.303}{k} (2 \log 2 - \log 3) \\ &= \frac{2.303}{k} (2 \times 0.301 - 0.4771) = \frac{0.29}{k} \end{aligned}$$

24. (d) For a zero order reaction,
 $t_{1/2} \propto a_0$ (initial concentration or initial pressure)
 $(t_{1/2})_1 \propto P_1$
 $(t_{1/2})_2 \propto P_2$

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{P_2}{P_1}, \quad \frac{(t_{1/2})_2}{45} = \frac{16}{4}$$

$$(t_{1/2})_2 = \frac{16}{4} \times 45 = 180 \text{ min}$$



26. (b) Plot given is for zero order reaction.

27. (c) Since for every 10°C rise in temperature rate doubles for 50°C rise in temperature increase in reaction rate $= 2^5 = 32$ times

28. (a) $k = \frac{2.303}{1386} \log \frac{100}{100-75}$ On solving we get $k = 10^{-3}$

29. (a)

30. (a) Presence of catalyst does not affect enthalpy change of reaction $\Delta H_R = E_f - E_b = 180 - 200 = -20 \text{ kJ/mol}$

31. (c) Given $t_{1/2} = 15$ minutes
 Total time (T) = 1 hr = 60 min
 From $T = n \times t_{1/2}$

$$n = \frac{60}{15} = 4$$

Now from the formula $\frac{N}{N_0} = \left(\frac{1}{2}\right)^n$

Where N_0 = initial amount
 N = amount left after time t

hence the amount of substance left after 1 hour will

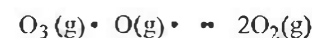
be $\frac{1}{16}$

32. (d) Rate₁ = $k[A]^n [B]^m$

$$\text{Rate}_2 = k[2A]^n \left[\frac{1}{2}B\right]^m$$

$$\begin{aligned} \therefore \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{k[2A]^n \left[\frac{1}{2}B\right]^m}{k[A]^n [B]^m} = (2)^n \left(\frac{1}{2}\right)^m \\ &= 2^n \cdot (2)^{-m} = 2^{n-m} \end{aligned}$$

33. (a) On adding eq. (i) and eq. (ii) we get



Hence overall rate constant = $K_i \times K_{ii}$
 $= 5.2 \times 10^9 \times 2.6 \times 10^{10} = 1.4 \times 10^{20} \text{ mol}^{-1} \text{ L s}^{-1}$

34. (b) $k = A e^{-E_a/RT}$ $\log k = \log A - \frac{E_a}{2.303R} \cdot \frac{1}{T}$

Plot of $\log k$ Vs. $\frac{1}{T}$

Straight line Slope = $-\frac{E_a}{2.303R}$

35. (b) $r = k [\text{O}_2][\text{NO}]^2$. When the volume is reduced to $1/2$, the conc. will double

$$\therefore \text{New rate} = k [2\text{O}_2][2\text{NO}]^2 = 8k [\text{O}_2][\text{NO}]^2$$

The new rate increases to eight times of its initial.

36. (d) From rate law

$$-\frac{1}{2} \frac{dSO_2}{dt} = -\frac{dO_2}{dt} = \frac{1}{2} \frac{dSO_3}{dt}$$

$$\therefore -\frac{dSO_2}{dt} = -2 \times \frac{dO_2}{dt}$$

$$= -2 \times 2.5 \times 10^{-4}$$

$$= -5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

37. (c) $k_1 = A_1 e^{-E_{a1}/RT}$ (i)

$k_2 = A_2 e^{-E_{a2}/RT}$ (ii)

On dividing eqn (i) from eqn. (ii)

$$\frac{k_1}{k_2} = \frac{A_1}{A_2} (E_{a2} - E_{a1}) / RT$$
(iii)

Given $E_{a2} = 2E_{a1}$

On substituting this value in eqn. (iii)

$$k_1 = k_2 A \times e^{E_{a1}/RT}$$

38. (d) Enthalpy of reaction (ΔH) = $E_{a(i)} - E_{a(b)}$
 for an endothermic reaction $\Delta H = +ve$ hence for ΔH to be positive
 $E_{a(b)} < E_{a(i)}$

39. (d)

$$\ln 4 = \frac{E_a}{8.314} \left(\frac{310 - 300}{310 \times 300} \right)$$

$$2 \ln 2 = \frac{E_a}{8.314} \left(\frac{310 - 300}{310 \times 300} \right)$$

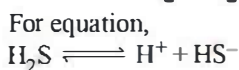
$$E_a = \frac{0.693 \times 2 \times 8.314 \times 300 \times 310}{10} = 107.2 \text{ kJ/mol}$$

41. (d) Since the slow step is the rate determining step hence if we consider option (A) we find

$$\text{Rate} = k[\text{Cl}_2][\text{H}_2\text{S}]$$

Now if we consider option (B) we find

$$\text{Rate} = k[\text{Cl}_2][\text{HS}^-]$$
(i)



$$K = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

or $[\text{HS}^-] =$

Substituting this value in equation (i) we find

$$\text{Rate} = k[\text{Cl}_2] K \frac{[\text{H}_2\text{S}]}{[\text{H}^+]} = k' \frac{[\text{H}_2\text{S}]}{[\text{H}^+]}$$

Thus slow step should involve 1 molecule of Cl_2 and 1 molecule of H_2S .

hence only, mechanism (A) is consistent with the given rate equation.

42. (a) Arrhenius equation is given by

$$k = A e^{-E_a/(2.303RT)}$$

Taking log on both sides, we get

$$\log k = \log A - \frac{E_a}{2.303RT}$$

Arrhenius plot a graph between $\log k$ and $\frac{1}{T}$ whose

slope is $-E_a$.

43. (d) The graph show that reaction is exothermic.

$$\log k = \frac{-\Delta H}{RT} + \log A$$

For exothermic reaction $\Delta H < 0$

$\therefore \log k$ Vs $\frac{1}{T}$ would be negative straight line with positive slope.

44. (a) As per Arrhenius equation ($k = A e^{-E_a/RT}$), the rate constant increases exponentially with temperature.

45. (a) Rate law for first order reaction = $k[\text{N}_2\text{O}_5]$

t = 0 min	50	0	0
(Pressure in mm Hg)			
t = 30 min	50 - 2p	4p	p
(Pressure in mm Hg)			

Total pressure $50 - 2p + 4p + p = 50 + 3p$
 $= 87.5 \text{ mmHg}$

$\therefore P = 12.5 \text{ mmHg}$
 $\therefore P_{\bullet} = 50 \text{ \& } P (t=30 \text{ min})$
 $= 25 \text{ for } \text{N}_2\text{O}_5 \text{ reactant}$

$$\therefore k = \frac{2.303}{30 \text{ min}} \times \log \left(\frac{50}{25} \right) = \frac{2.303}{60 \text{ min}} \times \log \left(\frac{50}{x} \right)$$

On solving $x = 12.5 \text{ mm Hg} = 50 - 2p$

$\therefore P = 18.75 \text{ mmHg}$

$\therefore \text{Total pressure} = 50 + 3P = 106.25 \text{ mm Hg}$