Chemical Kinetics

1. 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 min at constant temperature will be:
(a) 136.25 mm Hg
(b) 106.25 mm Hg
(c) 175.0 mm Hg
(d) 116.25 mm Hg

2. At $518^{\circ}C$, 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) 0
(b) 2
(c) 3
(d) 1

3. If 50 % of a reaction occurs in 100 second and 75 % of the reaction occurs in 200 second, the order of this reaction is :
(a) 2
(b) 3
(c) Zero
(d) 1

4. The rate of a reaction A doubles on increasing the temperature from 300 to 310 K. By how much, the temperature of reaction B should be increased from 300 K, so that rate doubles if activation energy of the reaction B is twice to that of reaction A.
(a) 9.84 K
(b) 4.92 K
(c) 2.45 K
(d) 19.67 K

5. 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) $107.2\ kJ\ mol^{-1}$
(b) $53.6\ kJ\ mol^{-1}$
(c) $26.8\ kJ\ mol^{-1}$
(d) $214.4\ kJ\ mol^{-1}$

6. Two reactions, R_1 and R_2 have identical preexponential 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
(a) 12
(b) 6
(c) 4

(d) 8

7. Decomposition of H_2O_2 follows a first order reaction. In fifty minutes, the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be :
(a) 6.93×10^{-2} mol min $^{-1}$
(b) 6.93×10^{-4} mol min $^{-1}$
(c) 2.66 L min $^{-1}$ at STP
(d) 1.34×10^{-2} mol min $^{-1}$

8. 200 g water is heated from 40^0C to 60^0C. Ignoring the slight expansion of water, the change in its internal energy is close to (Given specific heat of water=4184 J/kg/K) :
(a) 8.4 kJ
(b) 4.2 kJ
(c) 16.7 kJ
(d) 167.4 kJ

9. The rate law for the reaction below
A + B ⟶ Product is given by the expression, k [A][B].
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) k
(b) k/3
(c) 3k
(d) 9k

10. Higher order (>3) reactions are rare due to
(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.

11. 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

12. A + 2B ⟶ C, the rate equation for this reaction is given as Rate = k [A][B]. If the concentration of A is kept the same but that of B is doubled, what will happen to the rate itself?
(a) halved
(b) the same
(c) doubled
(d) quadrupled

13. For the non-stoichiometric reaction, 2A + B ⟶C + D, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial Concentration (A)	Initial Concentration (B)	Initial rate of formation of C (mol $L^{-1}s^{-1}$)
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	2.4×10^{-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) $\frac{dC}{dt} = k[A]$

14. In the following sets of reactants which two sets best exhibit the amphoteric character of $Al_2O_3.xH_2O$?

Set-1: $Al_2O_3.xH_2O(s)$ and $OH^-(aq)$

Set-2: $Al_2O_3.xH_2O(s)$ and $H_2O(l)$

Set-3: $Al_2O_3.xH_2O(s)$ and $H^+(aq)$

Set-4: $Al_2O_3.xH_2O(s)$ and $NH_3(aq)$

(a) 1 and 2
(b) 2 and 4
(c) 1 and 3
(d) 3 and 4

15. Which of the following statements about Na_2O_2 is not correct?

(a) Na_2O_2 oxidises Cr^{3+} to CrO_4^{2-} in acid medium.
(b) It is diamagnetic in nature.
(c) It is the super oxide of sodium.
(d) It is a derivative of H_2O_2.

16. The standard enthalpy of formation $(\Delta_f H^\circ_{298})$ for methane, (CH_4) is – 74.9 kJ mol $^{-1}$. In order to calculate the average energy given out in the formation of a C-H bond from this it is necessary to know which one of the following is correct?

(a) the dissociation energy of the hydrogen molecule, H_2
(b) the dissociation energy of H_2 and enthalpy of sublimation of carbon (graphite)
(c) the first four ionisation energies of carbon and electron affinity of hydrogen

(d) the first four ionisation energies of carbon

17. Which type of ‘defect’ has the presence of cations in the interstitial sites ?
(a) Metal deficiency defect
(b) Schottky defect
(c) Vacancy defect
(d) Frenkel defect

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

$$\log k = \frac{2000}{T} + 6.0$$

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

(a) $1.0 \times 10^6\ s^{-1}$ and $9.2\ kJ\ mol^{-1}$
(b) $6.0\ s^{-1}$ and $16.6\ kJ\ mol^{-1}$
(c) $1.0 \times 10^6\ s^{-1}$ and $16.6\ kJ\ mol^{-1}$
(d) $1.0 \times 10^6\ s^{-1}$ and $38.3\ kJ \cdot mol^{-1}$

19. Under the same reaction conditions, initial concentration of 1.386 mol d^{-3} of a substance becomes half in 40 s and 20 s through first order and zero order kinetics respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constants for first order (k_1) and zero order (k_o) of the reaction is
(a) $0.5\ mol^{-1}\ dm^3$
(b) $1.0\ mol\ dm^{-3}$
(c) $1.5\ mol\ dm^{-3}$
(d) $2.0\ mol^{-1}\ dm^3$

20. 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
(a) 0
(b) 1
(c) 2
(d) 3

21. Which one of the following statement(s) is incorrect about order of reaction?
(a) Order of reaction is determined experimentally
(b) Order of reaction is equal to sum of the power of cementation terms in differential rate law
(c) It is not affected with stoichiometric coefficient of the reactants
(d) Order cannot be fractional

22. (*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.

(a) 3.47×10^{-4} M min^{-1} (b) 3.47×10^{-5} M min^{-1}

(c) 1.73×10^{-4} M min^{-1} (d) 1.73×10^{-5} M min^{-1}

23. In a first order reaction, the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2 x 10^4 s. The rate constant of reaction in s^{-1} is

(a) 2×10^4 (b) 3.45×10^{-5}

(c) 1.386×10^{-4} (d) 2×10^{-4}

24. Consider the chemical reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. 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 $= -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

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

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

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

25. If I is the intensity of absorbed light and C is the concentration of *AB* for a photochemical process, then AB + hv → AB*, the rate of formation of AB* is directly proportional to

(a) C

(b) I

(c) I^2

(d) C.I

26. The rate constant for the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ 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

(a) 1.4

(b) 1.2

(c) 0.04

(d) 0.8

27. The half-life period of a radioactive element is 140 days. After 650 days, one gram of the element will reduce to

(a) $\frac{1}{2}g$

(b) $\frac{1}{4}g$

(c) $\frac{1}{8}g$

(d) $\frac{1}{16}g$

28. A catalyst is a substance which

(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

29. The specific rate constant of a first order reaction depends on the

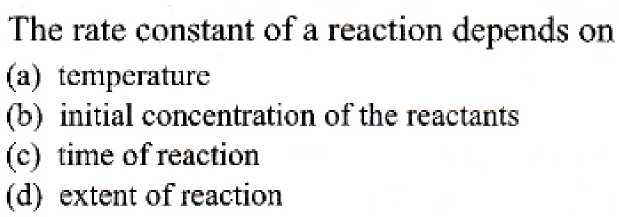
(a) concentration of the reactant

(b) concentration of the product

(c) time

(d) temperature

30.



The rate constant of a reaction depends on

(a) temperature

(b) initial concentration of the reactants

(c) time of reaction

(d) extent of reaction

31. For the first order reaction, $2N_2O_5(g) \rightarrow 4N_2(g) + O_2(g)$.

(a) the concentration of the reactant decreases exponentially with time

(b) the half-life of the reaction decreases with decreasing temperature

(c) the half-life of the reaction depends on the initial concentration of the reactant

(d) the reaction proceeds 98.6% completion in eight half-life duration

32. The following statement (s) is are correct

(a) A plot of log K_p vs $\frac{1}{T}$ is non-linear

(b) A plot of log [X] vs time is linear for a first order reaction, $x \rightarrow p$

(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 non-linear at constant temperature

33. For the first order reaction,

(a) the degree of dissociation is equal to $(1 — e^{-kt})$

(b) a plot of reciprocal concentration of the reactant vs time gives a non-straight line

(c) the time taken for the completion of 75% reaction is thrice the half-life of the reaction

(d) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}

34. A catalyst

(a) decreases 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

Passage Based Questions

Passage

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

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

^{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-I4 undergoes.

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

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

The decay constant (λ) can be calculated by using the following formula $\lambda = \dfrac{0.693}{t_{1/2}}$

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

35. Which of the following option is correct?

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

(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 ^{14}C in dead beings.

36. 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

37. 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

$$T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

(b) the age of fossil will decrease at the place where explosion has taken place and

$$T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

(c) the age of fossil will be determined to be the same

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

38. An organic compound undergoes first order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of

$$\frac{[t_{1/8}]}{[t_{1/10}]} \times 10 ? \ (\log_{10} 2 = 0.3)$$

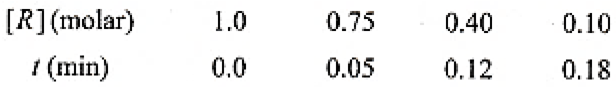
(a) 7

(b) 8

(c) 9

(d) 10

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



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

The order of the reaction is

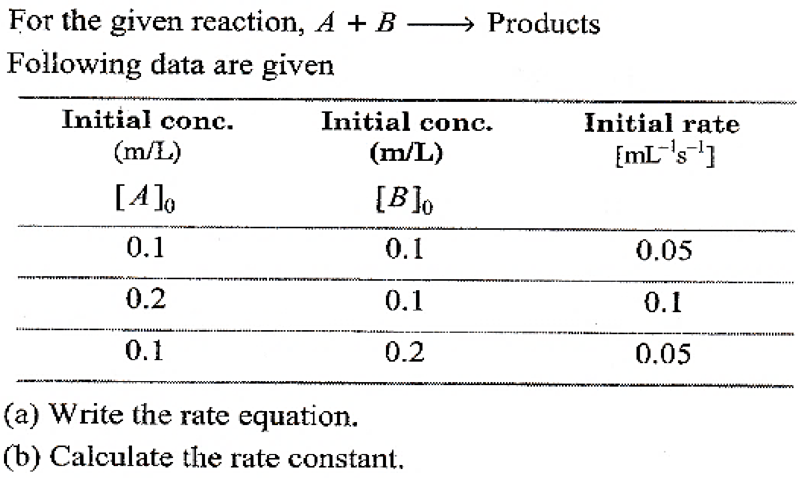
(a) 0

(b) 1

(c) 2

(d) 1.5

40.



For the given reaction, $A + B \longrightarrow$ Products

Following data are given

Initial conc. (m/L) $[A]_0$	**Initial conc.** (m/L) $[B]_0$	**Initial rate** $[\mathrm{mL^{-1}s^{-1}}]$
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.

(a) k[A] , 1 s^{-1}

(b) k[A] , 1.5 s^{-1}

(c) k[A] , 0 s^{-1}

(d) k[A] , 0.5 s^{-1}

41. ^{64}Cu (half-life = 12.8 h) decays by β emission (38%), β^{+} emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes.

(a) 30 h

(b) 29 h

(c) 29.76 h

(d) 28 h

42. The rate of first order reaction is 0.04 mol $L^{-1}s^{-1}$ at 10 min and 0.03 mol $L^{-1}s^{-1}$ at 20 min after initiation. Find the half-life of the reaction.

(a) 20 min

(b) 25 min

(c) 30 min

(d) 35 min

43. 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}.

(a) 10 kJ mol^{-1}

(b) 100 J mol^{-1}

(c) 100 kJ mol^{-1}

(d) 1 kJ mol^{-1}

44. The rate constant for an isomerisation reaction, $A \rightarrow B$ is 4.5×10^{-3} min. If the initial concentration of A is 1 M, calculate the rate of the reaction after I h.

(a) 3.42×10^{-3} mol L^{-1} min^{-1}

(b) 3.42×10^{-5} mol L^{-1} min^{-1}

(c) 3.42 mol L^{-1} min^{-1}

(d) 3.42×10^{-2} mol L^{-1} min^{-1}

45. 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.

(a) 6×10^{-7} g

(b) 6.9×10^{-7} g

(c) 5.6×10^{-7} g

(d) 6.1×10^{-7} g

Answer Key

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

Solution

1.

Solution:

$$\begin{array}{llll} & N_2O_5 \rightarrow & 2NO_2 + & \frac{1}{2}O_2 \\ t = 0 & 50 & 0 & 0 \\ t = 50\text{ min.} & 50 - p_1 & 2p_1 & \frac{p_1}{2} \\ & = 25 & & \\ t = 100\text{ min.} & 50 - p_2 & 2p_2 & \frac{p_2}{2} \\ & = 12.5 & & \end{array}$$

$$50 - p_1 + 2p_1 + \frac{p_1}{2} = 87.5$$

$$50 + \frac{3p_1}{2} = 87.5$$

$$\frac{3p_1}{2} = 37.5$$

$$p_1 = \frac{37.5 \times 2}{3} = 25$$

50 min is half-life period

For, 100 min is (2 x half-life)

$50 - p_1 = 12.5$

$p_2 = 37.5$ mm of Hg

Total pressure at 100 min

$$= 50 - p_2 + 2p_2 + \frac{p_2}{2}$$

$$50 + \frac{3p_2}{2} = 50 + \frac{3}{2} \times 37.5$$

$$= 50 + 56.25$$

$$= 106.25 \text{ mm of Hg}$$

2.

Solution:

$r = k(p)^m \, m = \text{order of reaction}$

$$1 = \text{k}\left[363 \times \frac{95}{100}^{m}\right] \text{.....(1)}$$

$$0.5 = k\left(362 \times \frac{67}{100}\right) \text{.....(2)}$$

Equation - 1 / Equation – 2, gives

$$\frac{1}{0.5} = \left[\frac{95}{67}\right]^m$$

$$2 = \left(\frac{95}{67}\right)^m$$

$$2 = (0.4)^m$$

$$\log 2 = m \log 1.4$$

$$\frac{0.3010}{\log 1.4} = m$$

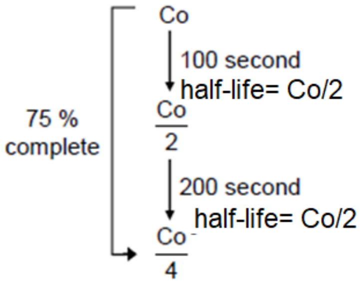
$$m \approx \frac{0.3010}{0.15}$$

$$m = 2$$

Hence, the answer is option (b).

3.

Solution:



For first order reaction, the half-life is constant.

4.
Solution:
For reaction A

By using Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{-E_a}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{.... (i)}$$

$$\therefore \frac{k_1}{k_2} = \frac{r_1}{r_2}$$

$$\Rightarrow \frac{k_1}{k_2} = \frac{r_1}{2r_1}$$

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

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

Given, T2 = 310; T1 = 300K

On putting values in Eq (i), we get

$$\log 2 = \frac{-E_a}{2.303 \times 8.314}\left(\frac{1}{310} - \frac{1}{300}\right)$$

$$\Rightarrow E_a = 53598.6\ \text{J/mol} = 53.6\ \text{kJ/mol}$$

For reaction B

$$\log \frac{k_2}{k_1} = \frac{-E_a}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{.... (i)}$$

(In this equation replace E_a by E_b.

$E_b=2E_a= 2\ (53.6)$

$T_1= 300\text{K}$

Putting the values in above equation and solving it for $T_{2,}$ we get $T_2 = 304.92$ K

The answer is (304.92 – 300) K= 4.92K.

5.
Solution:

$$\log\frac{K_1}{K_2}=\frac{-E_a}{2.303R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\frac{K_1}{K_2}=\frac{r_1}{r_2}=\frac{r_1}{4r_1}=\frac{1}{4}$$

$$\log\frac{1}{4}=\frac{-E_a}{2.303\times 8.314}\left(\frac{1}{310}-\frac{1}{300}\right)$$

$$E_a=214.4kJ/mol$$

6.
Solution:

$$k_1=Ae^{-E_{a_1}/RT}$$

$$k_2=Ae^{-E_{a_2}/RT}$$

$$\frac{k_2}{k_1}=e^{\frac{1}{RT}\left(E_{a_1}-E_{a_2}\right)}$$

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

$$=\frac{10\times 10^3}{8.314\times 300}\approx 4$$

7.
Solution:

$$t_{3/4}=2\times t_{1/2}=50\text{ min}$$

$$i.e., t_{1/2}=25\text{min}$$

$$k=\frac{0.693}{t_{1/2}}=\frac{0.693}{25}\text{min}^{-1}$$

Rate of H_2O_2 decomposition =

$$k[H_2O_2]=\frac{0.693}{25}\times 0.05=-\frac{d[H_2O_2]}{dt}$$

$$H_2O_2\to H_2O+\frac{1}{2}O_2$$

$$-\frac{d[H_2O_2]}{dt}=2\frac{d[O_2]}{dt}$$

$$\Rightarrow\frac{d[O_2]}{dt}=6.93\times 10^{-4}\text{mol min}^{-1}$$

8.
Solution:

9.

Solution:

A + B → Product

Rate = K[A][B]

$= K \times 0.1 \times 0.1 = 0.1K$

$\Rightarrow K = \frac{rate}{0.1}$

When [B] increased from 0.1 to 0.3 mol then,

$rate = K \times 0.1 \times 0.3$

$= 0.3k$

$K = \frac{rate}{0.3}$

$K = \frac{rate}{0.01 \times 3}$

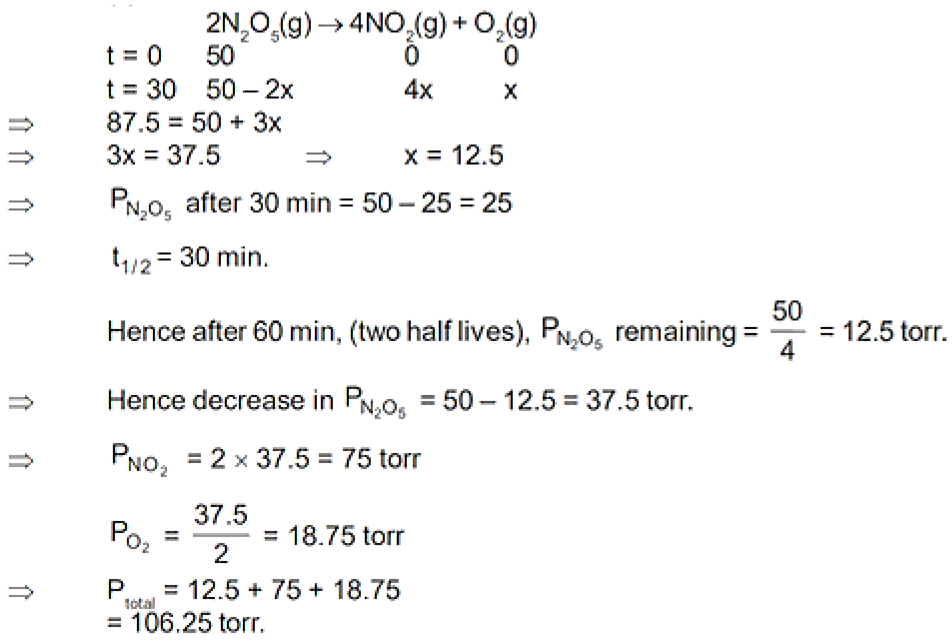
$K = \frac{1}{3}\left(\frac{rate}{0.01}\right)$

10.

Solution: Higher order (greater than 3) reaction is rare because there is low probability of simultaneous collision of all the reacting species.

11.

Solution:



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

t = 0   50   0   0

t = 30   50 – 2x   4x   x

$\Rightarrow$ 87.5 = 50 + 3x

$\Rightarrow$ 3x = 37.5 $\Rightarrow$ x = 12.5

$\Rightarrow$ $P_{N_2O_5}$ after 30 min = 50 – 25 = 25

$\Rightarrow$ $t_{1/2}$ = 30 min.

Hence after 60 min, (two half lives), $P_{N_2O_5}$ remaining = $\frac{50}{4}$ = 12.5 torr.

$\Rightarrow$ Hence decrease in $P_{N_2O_5}$ = 50 – 12.5 = 37.5 torr.

$\Rightarrow$ P_{NO_2} = 2 × 37.5 = 75 torr

$P_{O_2} = \frac{37.5}{2}$ = 18.75 torr

$\Rightarrow$ P_{total} = 12.5 + 75 + 18.75

= 106.25 torr.

12.

Solution:

Rate is first order with respect to B. So it doubles on doubling concentration of B, while keeping concentration of A as same.

13.

Solution: 2A + B ⟶C + D

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

$= \frac{d[C]}{dt} = \frac{d[D]}{dt}$

Let rate of Reaction $= k[A]^x[B]^y$

Or, $\frac{d[C]}{dt} = k[A]^x[B]^y$

Now from table,

$1.2\times10^{-3} = k[0.1]^x[0.1]^y \quad ...(i)$

$1.2\times10^{-3} = k[0.1]^x[0.2]^y \quad ...(ii)$

$2.4\times10^{-3} = k[0.2]^x[0.1]^y \quad ...(iii)$

Dividing equation (i) by (ii)

$\Rightarrow \frac{1.2\times10^{-3}}{1.2\times10^{-3}} = \frac{k[0.1]^x[0.1]^y}{k[0.1]^x[0.2]^y}$

$\Rightarrow 1 = \left[\frac{1}{2}\right]^y$

$\Rightarrow y = 0$

Now Dividing equation (i) by (iii)

$\Rightarrow \frac{1.2\times10^{-3}}{2.4\times10^{-3}} = \frac{k[0.1]^x[0.1]^y}{k[0.2]^x[0.1]^y}$

$\Rightarrow \left[\frac{1}{2}\right]^1 = \left[\frac{1}{2}\right]^x$

$\Rightarrow x = 1$

Hence, $\frac{d[C]}{dt} = k[A]^1[B]^0$.

14.

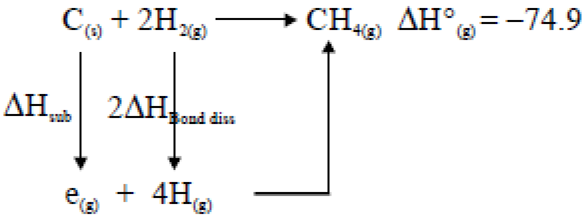
Solution: In set 1: $Al(OH)_4^-$ is formed

In set 2: Al^{+3} and H_2O is formed.

15.

Solution: Na_2O_2 is a peroxide (O_2^{2-}) which is occupied all paired electrons with $\pi*2px$ and $\pi*2py$.

16.
Solution:



To calculate average bond energy of (C-H) bond, both dissociation energy of H_2 and enthalpy of sublimation of carbon (graphite) are needed.

17.
Solution: Frankel defect has the presence of cation in interstitial site.
Hence the correct answer is option (d).

18.
Solution:
The logarithmic form of Arrhenius equation is

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

Given : $$\log k = 6 - \frac{2000}{T}$$

Comparing the above two equations :

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

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

$$\Rightarrow \quad E_a = 2000 \times 2.303 \times 8.314 \text{ J}$$
$$= 38.3 \text{ kJ} \quad \text{mol}^{-1}$$

19.
Solution:

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

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

$$\Rightarrow \quad \text{Eq. (ii)/(i)} \quad = \frac{1}{2} = \frac{[A]_0}{2k_0} \times \frac{k_1}{\ln 2}$$

$$\Rightarrow \quad \frac{k_1}{k_0} = \frac{\ln 2}{[A]_0} = \frac{0.693}{1.386} = 0.5$$

20.
Solution:

Rate $\propto [G]^m [H]^n$

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

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.

$$\Rightarrow \qquad R \propto [H]^2$$

$$\Rightarrow \qquad \text{Overall order} = m + n = 1 + 2 = 3$$

21.
Solution: Order of a reaction can take any real value, i.e., negative, integer, fraction etc.

22.
Solution:

For first order reaction,

$$k = \frac{2.303}{t} \log\frac{a}{a-x} = \frac{2.303}{40} \log\frac{0.1}{0.025} = 3.46\times10^{-2}$$

$$\text{Rate} = [k]\,A = 3.46\times10^{-2}\times0.01 = 3.46\times10^{-4}$$

23.

Solution:

For a first order reaction, $kt = \ln\dfrac{[A]_0}{[A]}$

$$\Rightarrow \qquad k = \frac{1}{t}\ln\frac{[A]_0}{[A]} = \frac{1}{2\times10^4}\ln\frac{800}{50} = \frac{4\ln 2}{2\times10^4}\ \text{s}^{-1}$$

$$= 1.386\times10^{-4}\ \text{s}^{-1}$$

24.

Solution: For any general reaction,

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt}$$

$$= \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

$\Rightarrow$ For $\quad N_2 + 3H_2 \longrightarrow 2NH_3$

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

25.

Solution: Rate will be directly proportional to both concentration and intensity, i.e., rate of formation of $AB^* \propto C.I$

26.

Solution: The unit of rate constant (t^{-1}) indicating that the decomposition reaction follows the first order kinetics.

$$\text{Rate} = k[N_2O_5]$$

$$[N_2O_5] = \frac{\text{Rate}}{k} = \frac{2.40 \times 10^{-5}}{3 \times 10^{-5}} = 0.8\,\text{M}$$

27.

Solution:

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

Amount of reactant remaining after n-half-lives

$$= \left(\frac{1}{2}\right)^n \times \text{initial amount}$$

$$= \left(\frac{1}{2}\right)^4 \times 1.0 \text{ g} = \frac{1}{16} \text{ g}$$

28.

Solution: A catalyst increases the rate of reaction but by the same factor to both forward and backward reactions. Hence, a catalyst shortens the time requires to reach the equilibrium.

29.

Solution: Specific rate constant of reaction depends on the temperature.

30.

Solution: The rate constant (k) of all chemical reactions depends on temperature.

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

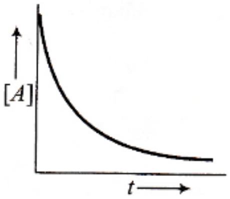
where, A = pre-exponential factor, E_a = activation energy.

Objective Questions II (One or more than one correct option)

31.

Solution:

(a) For a first order reaction, the concentration of reactant remaining after time t is given by $[A]=[A]_o e^{-kt}$ Therefore, concentration of reactant decreases exponentially with time.



32.

Solution:

Equilibrium constant is related to temperature

$$\log K_p = \text{constant} - \frac{\Delta H}{2.3\ RT}$$

⇒ Plot of $\log K_p$ vs $1/T$ will be a straight line.

For the first order reaction $X \rightarrow P$

$$\log \frac{[X]_0}{[X]} = \frac{kt}{2.3} \quad \Rightarrow \quad \log[X] = \log[X_0] - \frac{kt}{2.3},$$

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

Also at constant temperature, pV = constant

⇒ Plot of p vs $\frac{1}{V}$ will give a straight line.

33.

Solution:

For a first order reaction :

$$kt = \ln \frac{1}{1-\alpha} \qquad \text{where, } \alpha = \text{degree of dissociation.}$$

$$\Rightarrow \qquad 1-\alpha = e^{-kt} \Rightarrow \alpha = 1 - e^{-kt}$$

Also $\frac{1}{[A]} = \frac{e^{kt}}{[A]_0}$, i.e. plot of reciprocal of concentration of reactant *vs* time will be exponential.

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

The Arrhenius equation is :

$$\ln k = \ln A - \frac{E_a}{RT}$$

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

34

Solution: 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 avenge kinetic energies of reactants or the collision frequency.

Passage Based Questions

Passage

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

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

^{14}C is absorbed by living organisms during photosynthesis. The ^{14}C content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ^{14}C in the dead being, falls due to the decay which C-I4 undergoes.

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

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

The decay constant (λ) can be calculated by using the following formula $\lambda = \frac{0.693}{t_{1/2}}$

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

35.

Solution: 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.

36.

Solution: Fossil whose age is closest to half-life of C-14 (5770 yr) will yield the most accurate age by C-14 dating.

37

Solution:

$$\lambda T = \ln \frac{N_0}{N}$$

where N_o = 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 nearby area increases. This will increase N_0 because living plants are still taking C-l4 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, $$\lambda T_1 = \ln \frac{C_1}{C} \Rightarrow \lambda T_2 = \ln \frac{C_2}{C}$$

$$\Rightarrow \quad T_1 - T_2 = \frac{1}{\lambda} = \ln \frac{C_1}{C_2}$$

C = Concentration of C-14 in fossil.

Integer Answer Type Questions:

38.

Solution:

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

where, $[A]_0$ = initial concentration.

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

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

$$\text{and} \quad kt_{1/10} = \ln \frac{[A]_0}{[A]_0/10} = \ln 10 \qquad \ldots(ii)$$

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

$$\Rightarrow \quad \frac{t_{1/8}}{t_{1/10}} \times 10 = 0.9 \times 10 = 9$$

39.

Solution: Rate of reaction is constant with time.

0

From two data, (for zero order kinetics)

$$K_I = \frac{x}{t} = \frac{0.25}{0.05} = 5$$

$$K_{II} = \frac{x}{t} = \frac{0.60}{0.12} = 5$$

Subjective Questions:

40.

Solution:

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{0.05}{0.10} = \frac{1}{2} = \left(\frac{1}{2}\right)^a \Rightarrow a = 1; \quad \text{order w.r.t } A.$$

Order w.r.t $B = 0$

(a) Rate $= k\,[A]$

(b) $k = \frac{\text{Rate}}{[A]} = \frac{0.05}{0.10} = 0.5\ \text{s}^{-1}$

41.

Solution:

$$_{29}\mathrm{Cu}^{64} \xrightarrow[k_1]{38\%} {}_{-1}\beta^{0} + {}_{30}\mathrm{Zn}^{64}$$

$$_{29}\mathrm{Cu}^{64} \xrightarrow[k_2]{19\%} {}_{+1}\beta^{0} + {}_{28}\mathrm{Ni}^{64}$$

$$_{29}\mathrm{Cu}^{64} + {}_{-1}e^{0} \xrightarrow[k_3]{43\%} {}_{28}\mathrm{Ni}^{64}$$

Above are the parallel reactions occurring from Cu^{64}.

$$\frac{k_1}{k_2} = \frac{38}{19} = 2 = \frac{T_2}{T_1} \quad \text{and} \quad \frac{k_1}{k_3} = \frac{38}{43} = \frac{T_3}{T_1}$$

T_1, T_2 and T_3 are the corresponding partial half-lives.

Also $\qquad k = k_1 + k_2 + k_3$

$$\Rightarrow \qquad \frac{\ln 2}{T} = \frac{\ln 2}{T_1} + \frac{\ln 2}{T_2} + \frac{\ln 3}{T_3}$$

$$\Rightarrow \qquad \frac{1}{T} = \frac{1}{T_1} + \frac{1}{T_2} + \frac{1}{T_3} = \frac{1}{T_1} + \frac{1}{2T_1} + \frac{43}{38T_1}$$

$$= \frac{1}{T_1}\left(1 + \frac{1}{2} + \frac{43}{38}\right)$$

$$= \frac{1}{T_1}\left(\frac{38 + 19 + 43}{38}\right) = \frac{100}{38T_1}$$

$$\Rightarrow \qquad T_1 = \frac{100T}{38} = \frac{100}{38} \times 12.8 = 33.68 \text{ h}$$

$$T_2 = 2T_1 = 67.36 \text{ h}$$

$$T_3 = \frac{38T_1}{43} = \frac{38 \times 33.68}{43} = 29.76 \text{ h}$$

42.

Solution:

$$R = k\,[A]$$

$\Rightarrow$ $$R_1 = k\,[A]_1$$

and $$R_2 = k\,[A]_2$$

$\Rightarrow$ $$\frac{R_1}{R_2} = \frac{4}{3} = \frac{[A]_1}{[A]_2}$$

Also $$k\,(t_2 - t_1) = \ln \frac{[A]_1}{[A]_2} = \ln \frac{4}{3}$$

$\Rightarrow$ $$\frac{\ln 2}{t_{1/2}} \times 10 = \ln \frac{4}{3}$$

$\Rightarrow$ $$t_{1/2} = \frac{10 \log 3}{\log 4 - \log 3} = \frac{3}{0.6 - 0.48} = 25 \text{ min}$$

43.

Solution:

$$k_{500} = A\,e^{-E_1/RT_1}$$

$$k_{400} = A\,e^{-E_2/RT_2}$$

$\because$ $$k_{500} = k_{400}$$

$\Rightarrow$ $$\frac{E_1}{RT_1} = \frac{E_2}{RT_2}$$

$\Rightarrow$ $$\frac{E_2}{E_1} = \frac{T_2}{T_1} = \frac{400}{500} = \frac{4}{5}$$

Also $$E_1 = E_2 + 20000 \text{ J}$$

$\Rightarrow$ $$\frac{E_1 - 20{,}000}{E_1} = \frac{4}{5}$$

$\Rightarrow$ $$E_1 = 100{,}000 \text{ J} = 100 \text{ kJ mol}^{-1}$$

44.

Solution:

$$kt = \ln \frac{[A]_0}{[A]}$$

$$\Rightarrow \qquad 4.5 \times 10^{-3} \times 60 = \ln \frac{1}{[A]}$$

$$\Rightarrow \qquad [A] = 0.76 \text{ M}$$

$$\Rightarrow \qquad \text{Rate } = k\,[A] = 4.5 \times 10^{-3} \times 0.76$$

$$= 3.42 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

45.

Solution:

$$k_t = \ln \frac{w_0}{w}$$

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