18

CHEMICAL KINETICS

MCQs with One Correct Answer

1. The rate of the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ can be written in three ways :

$$\frac{-d[N_2O_5]}{dt} = k[N_2O_5]; \quad \frac{d[NO_2]}{dt} = k'\,[N_2O_5]$$

$$\frac{d[O_2]}{dt} = k''[N_2O_5]$$

The relationship between k and k' and between k and k'' are:

(a) $k' = 2k$; $k' = k$ (b) $k' = 2k$; $k'' = k/2$

(c) $k' = 2k$; $k'' = 2k$ (d) $k' = k$; $k'' = k$

2. A reaction proceeds by first order, 75% of this reaction was completed in 32 min. The time required for 50% completion is

(a) 8 min (b) 16 min

(c) 20 min (d) 24 min

3. Cyclopropane rearranges to form propene

$$\longrightarrow CH_3 - CH = CH_2$$

This follows first order kinetics. The rate constant is 2.714×10^{-3} sec^{-1}. The initial concentration of cyclopropane is 0.29 M. What will be the concentration of cyclopropane after 100 sec?

(a) 0.035 M (b) 0.22 M

(c) 0.145 M (d) 0.0018 M

4. The time taken for 90% of a first order reaction to complete is approximately

(a) 1.1 times that of half-life

(b) 2.2 times that of half-life

(c) 3.3 times that of half-life

(d) 4.4 times that of half-life

5. The initial rates of reaction

$3A + 2B + C \longrightarrow$ Products, at different initial concentrations are given below:

Initial rate, Ms^{-1}	**$[A]_0$, M**	**$[B]_0$, M**	**$[C]_0$, M**
5.0×10^{-3}	0.010	0.005	0.010
5.0×10^{-3}	0.010	0.005	0.015
1.0×10^{-2}	0.010	0.010	0.010
1.25×10^{-3}	0.005	0.005	0.010

The order with respect to the reactants, A, B and C are respectively

(a) 3, 2, 0 (b) 3, 2, 1

(c) 2, 2, 0 (d) 2, 1, 0

6. Consider the two hypothetical reactions given below :

I $aA \rightarrow$ Products, $k = x\ \text{mol}^{-1}\ \text{L}\ \text{min}^{-1}$

II $bB \rightarrow$ Products, $k = y\ \text{min}^{-1}$

The half-lives of both the reactions are the same, equal to 1 hr when molar concentration of the reactant is 1.0 M in each case. If these reactions are started at the same time taking 1M of the reactant in each case, the ratio $[A]/[B]$ after 3 hr will be :

(a) 0.5 (b) 4

(c) 1 (d) 2

7. For a homogeneous gaseous reaction $A \longrightarrow 3B$, if pressure after time t was P_t and after completion of reaction, pressure was P_∞ then select correct relation

(a) $k = \frac{1}{t}\ln\left(\frac{P_\infty}{3\left(P_\infty - P_t\right.}\right))$

(b) $k = \frac{1}{t}\ln\left(\frac{2P_\infty}{\left(P_\infty - P_t\right.}\right))$

(c) $k = \frac{1}{t}\ln\left(\frac{3P_\infty}{2P_\infty - P_t}\right)$

(d) $k = \frac{1}{t}\ln\left(\frac{2P_\infty}{3\left(P_\infty - P_t\right.}\right))$

8. For a first order homogeneous gaseous reaction, $A \longrightarrow 2B + C$ then initial pressure was P_i while total pressure after time 't' was P_t. The right expression for the rate constants k in terms of P_i, P_t and t is :

(a) $k = \frac{2.303}{t}\log\left(\frac{2P_i}{3P_i - P_t}\right)$

(b) $k = \frac{2.303}{t}\log\left(\frac{2P_i}{2P_t - P_i}\right)$

(c) $k = \frac{2.303}{t}\log\left(\frac{P_i}{P_i - P_t}\right)$

(d) None of these

9. The reaction $A(g) \longrightarrow B(g) + 2C(g)$ is a first order reaction with rate constant $2.772 \times 10^{-3}\ s^{-1}$. Starting with 0.1 mole of A in 2 litre vessel, find the concentration of A after 250 sec when the reaction is allowed to take place at constant pressure and at 300 K?

(a) 0.0125 M (b) 0.025 M

(c) 0.05 M (d) None of these

10. $A(aq) \longrightarrow B(aq) + C(aq)$ is a first order reaction.

Time	t	∞
mole of reagent	n_1	n_2

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

(a) $k = \frac{1}{t}\ln\left(\frac{n_2}{n_2 - n_1}\right)$

(b) $k = \frac{1}{t}\ln\left(\frac{2n_2}{n_2 - n_1}\right)$

(c) $k = \frac{1}{t}\ln\left(\frac{4n_2}{n_2 - n_1}\right)$

(d) $k = \frac{1}{t}\ln\left(\frac{4n_2}{5\,(n_2 - n_1)}\right)$

11. The gaseous decomposition reaction, $A(g) \rightarrow 2B(g) + C\ (g)$ is observed to first order over the excess of liquid water at 25°C. It is found that after 10 minutes the total pressure of system is 188 torr and after very long time it is 388 torr. The rate constant of the reaction (in hr^{-1}) is : [Given : vapour pressure of H_2O at 25° is 28 torr ($\ln 2 = 0.7$, $\ln 3 = 1.1$, $\ln 10 = 2.3$)]

(a) 0.02 (b) 1.2

(c) 0.2 (d) 0.5

12. The decomposition of N_2O_5 according to the equation :

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

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 and on complete decomposition, the total pressure is 584.5 mm of Hg. the rate constant of the reaction is:

(a) $5.2\ min^{-1}$ (b) $520 \times 10^{-3}\ min^{-1}$

(c) $5.2 \times 10^{-3}\ min^{-1}$ (d) $0.52 \times 10^{-3}\ min^{-1}$

13. The activation energy for a simple chemical reaction $A \rightarrow B$ is E_a in forward direction. The activation energy for reverse reaction

(a) is always double of E_a

(b) is negative of E_a

(c) is always less than E_a

(d) can be less than or more than E_a

14. The rate constant, the activation energy and the arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} s^{-1}$, 104.4 kJ mol^{-1} and $6.0 \times 10^{14} s^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is

(a) $2.0 \times 10^{18} s^{-1}$ (b) $6.0 \times 10^{14} s^{-1}$

(c) Infinity (d) $3.6 \times 10^{30} s^{-1}$

15. The activation energy for a reaction is 9.0 kcal/mol. The increase in the rate constant when its temperature is increased from 298K to 308K is

(a) 63% (b) 50%

(c) 100% (d) 10%

16. A reaction rate constant is given by

$k = 1.2 \times 10^{14} e^{-25000/RT} \text{sec}^{-1}$. It means

(a) log k versus log T will give a straight line with a slope as –25000

(b) log k versus T will give a straight line with slope as 25000

(c) log k versus log 1/T will give a straight line with slope as –25000

(d) log k versus 1/T will give a straight line

17. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C? ($R = 8.314 \text{ J mol}^{-1} K^{-1}$)

(a) 269 kJ mol^{-1} (b) 34.5 kJ mol^{-1}

(c) 15.1 kJ mol^{-1} (d) 342 kJ mol^{-1}

18. The rate of decomposition for methyl nitrite and ethyl nitrite can be given in terms of rate constant (in sec^{-1}) k_1 and k_2 respectively. The energy of activations for the two reactions are 152.30 kJ mol^{-1} and 157.7 kJ mol^{-1} as well as frequency factors are 10^{13} and 10^{14} respectively for the decomposition of methyl and ethyl nitrite. The temperature at which rate constant same for the two reactions will be:

(a) 285 K (b) 290 K

(c) 282 K (d) 275 K

19. A first order reaction $A \rightarrow B$ requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 minute, 25% decomposition took place. What will be the per cent decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature.

(a) 67.21 (b) 65.21

(c) 70.50 (d) 64.25

20. The activity of a radio nuclide (X^{100}) is 6.023 curie at a time t. If the disintegration constant is $3.7 \times 10^4 \text{ sec}^{-1}$, the mass of X after t seconds is–

(a) 10^{-3}g (b) 10^{-6}g

(c) 10^{-14}g (d) 10^{-15}g

Numeric Value Answer

21. The gas phase decomposition of dimethyl ether follows first order kinetics.

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

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

22. A compound A dissociates by two parallel first order paths at certain temperature

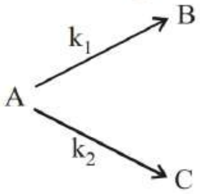
$$A(g) \xrightarrow{k_1(\text{min}^{-1})} 2B(g) \quad k_1 = 6.93 \times 10^{-3} \text{ min}^{-1}$$

$$A(g) \xrightarrow{k_2(\text{min}^{-1})} C(g) \quad k_2 = 6.93 \times 10^{-3} \text{ min}^{-1}$$

The reaction is started with 1 mole of pure 'A' in 1 litre closed container with initial pressure 2 atm. What is the pressure (in atm) developed in container after 50 minutes from start of experiment?

23. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is $3.56 \times 10^9 s^{-1}$, the rate constant (in kcal mol^{-1}) at 318 K is:

24. For first order parallel reactions k_1 and k_2 are 4 and 2 min^{-1} respectively at 300 K. If the activation energies for the formation of B and C are respectively 30,000 and 38,314 joule/mol respectively, the temperature (in K) at which B and C will be obtained in equimolar ratio is :



25. The rate constant of a reaction increases by 7% when its temperature is raised from 300 K to 310 K, while its equilibrium constant increases by 3%. The ratio of activation energy of the forward and reverse reactions is:

26. In the age of the earth is 4.5 billion years and the half-life of ^{40}K is 1.26 billion years, what percent of the earth's original amount of ^{40}K remains today ?

27. A reaction $A + B \rightarrow$ Products is first order w.r.t. each reactant, k being $5.052 \times 10^{-3}\ M^{-1}\ s^{-1}$. If start is made with initial concentration of A to be 0.1 M acid that of $B = 5.0$ M, calculate the concentration of A (in mM) remaining after 100 s.

28. Carbon monoxide reacts with O_2 to form CO_2: $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$. Informations about this reaction are given in the table below.

[CO] mol/L	**$[O_2]$ mol/L**	**Rate of reaction (mol/L min)**
0.02	0.02	4×10^{-5}
0.04	0.02	1.6×10^{-4}
0.02	0.04	8×10^{-5}

What is the value for the rate constant for the reaction in properly related unit ?

29. Two I order reactions having same reactant concentrations proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75°C.

30. For the reaction, $2NO + H_2 \rightarrow N_2O + H_2$, the value of $-\frac{dP}{dt}$ was found to be 1.5 Pa s^{-1} for a pressure of 359 Pa of NO and 0.25 Pa s^{-1} for a pressure of 152 Pa of NO. The pressure of H_2 being constant. If pressure of NO was kept constant, the value of $-\frac{dP}{dt}$ was found 1.60 Pa s^{-1} for a pressure of H_2 289 Pa and 0.79 Pa s^{-1} for a pressure of 147 Pa of H_2. Calculate the order of reaction.

ANSWER KEY

1	(b)	**4**	(c)	**7**	(d)	**10**	(d)	**13**	(d)	**16**	(c)	**19**	(a)	**22**	(2.5)	**25**	(1.8)	**28**	(5)
2	(b)	**5**	(d)	**8**	(a)	**11**	(b)	**14**	(b)	**17**	(b)	**20**	(d)	**23**	(18.39)	**26**	(8.42)	**29**	(8)
3	(b)	**6**	(d)	**9**	(a)	**12**	(c)	**15**	(a)	**18**	(c)	**21**	(0.75)	**24**	(378.74)	**27**	(8)	**30**	(3)

Hints & Solutions

CHAPTER 18

Chemical Kinetics

1. **(b)** Rate of disappearance of reactants = Rate of appearance of products

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt}=\frac{1}{4}\frac{d[NO_2]}{dt}=\frac{d[O_2]}{dt}$$

$$\frac{1}{2}k[N_2O_5]=\frac{1}{4}k'[N_2O_5]=k''[N_2O_5]$$

$$\frac{k}{2}=\frac{k'}{4}=k''$$

$$k'=2k,\quad k''=\frac{k}{2}$$

2. **(b)** Given: 75% reaction gets completed in 32 min

$$\text{Thus, } k=\frac{2.303}{t}\log\frac{a}{(a-x)}$$

$$=\frac{2.303}{32}\log\frac{100}{(100-75)}$$

$$=\frac{2.303}{32}\log 4 = 0.0433\ \text{min}^{-1}$$

Now we can use this value of k to get the value of time required for 50% completion of reaction

$$t=\frac{2.303}{k}\log\frac{a}{(a-x)}=\frac{2.303}{0.0433}\log\frac{100}{50}$$

$$=\frac{2.303}{0.0433}\log 2 = 16\ \text{min}$$

3. **(b)** $k=\frac{2.303}{t}\log\frac{a}{(a-x)}$

$(a-x)$ is the concentration left after 100 sec.

$$2.7\times10^{-3}=\frac{2.303}{100}\log\frac{0.29}{(a-x)}$$

$$\Rightarrow\frac{0.27}{2.303}=\log\frac{0.29}{(a-x)}\Rightarrow 0.117=\log\frac{0.29}{(a-x)}$$

$$\Rightarrow\quad(a-x)=0.22\ \text{M.}$$

4. **(c)** $t_{90\%}=\frac{2.303}{k}\log\frac{100}{100-90}$ (I)

$t_{50\%}=\frac{2.303}{k}\log\frac{100}{100-50}$ (II)

Dividing $\frac{t_{90\%}}{t_{50\%}}=\frac{\log 10}{\log 2}$

$\therefore t_{90\%}=3.3t_{50\%}$

5. **(d)** If rate $= k[A]^x[B]^y[C]^z$

$5.0\times10^{-3}=k[0.010]^x[0.005]^y[0.010]^z$ ...(i)

$5.0\times10^{-3}=k[0.010]^x[0.005]^y[0.015]^z$ ...(ii)

$1.0\times10^{-2}=k[0.010]^x[0.010]^y[0.010]^z$ ...(iii)

$1.25=k[0.005]^x[0.005]^y[0.010]^z$ ...(iv)

From 1st and 2nd sets of data - no change in rate is observed with the change in concentration of 'C'. So the order with respect to 'C' is zero.

From 1st and 4th sets of data

Dividing eq. (iv) by eq. (i)

$$\frac{1.25\times10^{-3}}{5.0\times10^{-3}}=\left[\frac{0.005}{0.010}\right]^x$$

or $0.25=(0.5)^x$ or $(0.5)^2=(0.5)^x$

$\therefore x=2$

The order with respect to 'A' is 2 from the 1st and 3rd sets of data Dividing eq. (i) by eq. (iii)

$$\frac{5.0\times10^{-3}}{1.0\times10^{-2}}=\left[\frac{0.005}{0.010}\right]^y$$

or $(0.5)^1=(0.5)^y\Rightarrow y=1$

The order with respect to 'B' is 1

So the order with respective the reactants A, B and C is 2, 1 and 0.

6. **(d)** Units of k indicate that reaction I is of second order and reaction II is first order.
For I reaction, $t_{1/2} \propto 1/a$,
first $t_{1/2=}$ 1 hr, second $t_{1/2}$ = 2 hr

$$[A] = 1\text{M} \xrightarrow{1\text{hr}} 0.5\text{M} \xrightarrow{2\text{hr}} 0.25\text{M}$$

$$[B] = 1\text{M} \xrightarrow{1\text{hr}} 0.5\text{M} \xrightarrow{1\text{hr}}$$

$$0.25\text{M} \xrightarrow{1\text{hr}} 0.125\text{M}$$

$$\frac{[A]}{[B]} = \frac{0.25\text{M}}{0.125\text{M}} = 2$$

7. **(d)** $\text{A} \longrightarrow 3\text{B}; \quad \text{P}_\text{T} = \text{P}_0 + 2\text{x}$
After time t, $\quad \text{P}_0 - \text{x} \quad 3\text{x}$

$$\text{x} = \frac{\text{P}_\text{T} - \text{P}_0}{2} \quad \text{k} = \frac{1}{\text{t}} \ln\left(\frac{\text{P}_0}{\text{P}_0 - \text{x}}\right)$$

After long time, $0 \quad 3\text{P}_0$

$$\text{x} = \frac{\text{P}_\text{T} - \frac{\text{P}_\infty}{3}}{2} \,\text{k} = \frac{1}{\text{t}} \ln\left(\frac{\frac{\text{P}_\infty}{3}}{\frac{\text{P}_\infty}{3} - \left(\frac{3\text{P}_\text{T} - \text{P}_\infty}{6}\right)}\right)$$

$$\text{P}_\infty = 3\text{P}_0 \quad \text{x} = \frac{3\text{P}_\text{T} - \text{P}_\infty}{6} \,\text{k} = \frac{1}{\text{t}} \ln\left(\frac{\text{P}_\infty / 3}{\frac{\text{P}_\infty}{2} - \frac{\text{P}_\text{T}}{2}}\right)$$

$$k = \frac{1}{t} \ln\left(\frac{2P_\infty}{3(P_\infty - P_T)}\right)$$

8. **(a)**

$$\begin{array}{llccc} & \text{A} & \longrightarrow & 2\text{B} & + \text{C} \\ \text{t} = 0 & \text{P}_\text{i} & & 0 & 0 \\ \text{t} = \text{t} & \text{P}_\text{i} - \text{y} & & 2\text{y} & \text{y} \end{array}$$

Total pressure $\text{P}_\text{t} = \text{P}_\text{i} - \text{y} + 2\text{y} + \text{y} = \text{P}_\text{i} + 2\text{y}$

$$\frac{\text{P}_\text{t} - \text{P}_\text{i}}{2} = \text{y}$$

$$\text{k} = \frac{2.303}{\text{t}} \log \frac{2\text{P}_\text{i}}{3\text{P}_\text{i} - \text{P}_\text{t}}$$

9. **(a)** $\text{t}_{1/2} = \dfrac{0.693}{\text{k}}$

$$= \frac{0.693}{2.772 \times 10^{-3}} = 250 \text{ sec}$$

Since volume is changing therefore half-life should be defined on the basis of moles, so moles of A remaining after 250 sec. Also final volume of the container

$$\text{V}_\text{f} = \frac{\text{n}_\text{f}}{\text{n}_\text{i}} \times \text{V}_\text{i} = \frac{0.05 + 0.15}{0.1} \times 2 = 4 \text{ litre}$$

$\therefore$ Final concentration of $\text{A} = \dfrac{0.05}{4} = 0.0125 \text{ M}$

10. **(d)** Let n is the moles of reagent 'R' when R is reacted with A at time t = 0

$$\begin{array}{lcccc} & \text{A} & \longrightarrow & \text{B} & + \quad \text{C} \\ \text{t} = 0 & \text{n} & & 0 & 0 \\ \text{at t} & \text{n} - \text{x} & & 2\text{x} & 3\text{x} \\ \text{at t} \to \infty & 0 & & 2\text{n} & 3\text{n} \end{array}$$

$$\therefore \quad 5\,\text{n} = \text{n}_2 \Rightarrow \text{n} = \frac{\text{n}_2}{5}$$

$$\text{n} + 4\text{x} = \text{n}_1 \Rightarrow \text{x} = \frac{\text{n}_1 - \text{n}}{4}$$

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

$$\text{so} \quad \text{k} = \frac{1}{\text{t}} \ln\left(\frac{4\text{n}_2}{5(\text{n}_2 - \text{n}_1}\right))$$

11. **(b)**

$$\begin{array}{lcccc} & \text{A(g)} & \longrightarrow & 2\text{B(g)} & + \text{C(g)} \\ \text{Let initial pressure} & \text{P}_0 & & 0 & 0 \\ \text{After 10 min.} & (\text{P}_0 - \text{x}) & & 2\text{x} & \text{x} \\ \text{After long time } (\text{t} \to \infty) & 0 & & 2\text{P}_0 & \text{P}_0 \end{array}$$

as per given $(\text{P}_0 - \text{x}) + 2\text{x} + \text{x} +$ vapour pressure of $\text{H}_2\text{O} = 188$
$\text{P}_0 + 2\text{x} = 160$ and $3\text{P}_0 + 28 = 388$
so, $\text{P}_0 = 120$ and x = 20 torr

$$\text{k} = \frac{1}{\text{t}} \ln\left(\frac{\text{P}_0}{\text{P}_0 - \text{x}}\right)$$

$$\Rightarrow \quad \frac{1}{10} \ln\left(\frac{120}{100}\right) = \frac{1}{10} \times (\ln 4 + \ln 3 - \ln 10)$$

$$= 0.02 \text{ min}^{-1} = 1.2 \text{ hr}^{-1}$$

12. **(c)** $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
2 mol of gaseous nitrogen pentoxide on complete decomposition gives 5 mol of gaseous products.

Therefore, initial pressure of $\text{N}_2\text{O}_5 = 584.5 \times \dfrac{2}{5}$

$= 233.8$ mm Hg.

Let x be the amount of N_2O_5 decomposed after 30 min.

∴ After 30 min.
Pressure due to $N_2O_5 = 233.8 - x$
Pressure due to $NO_2 = 2x$
and pressure due to $O_2 = \frac{x}{2}$
Total pressure after 30 min

$$= 284.5 \text{ mm Hg} = 233.8 - x + 2x + \frac{x}{2}$$

or $233.8 + \frac{3x}{2} = 284.5$
or $x = 33.8$ mm Hg
Hence pressure of N_2O_5 after 30 min.
$= 233.8 - 33.8 = 200$ mm Hg

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)} = \frac{2.303}{30}\log\frac{233.8}{200}$$

$$k = \frac{2.303}{30} \times 0.0679 = 5.2 \times 10^{-3}\ \text{min}^{-1}$$

13. **(d)** The activation energy of reverse reaction will depend upon whether the forward reaction is exothermic or endothermic.
As $\Delta H = E_a$ (forward reaction) $- E_a$ (backward reaction)
For exothermic reaction
$\Delta H = -\text{ve}$
∴ $-\Delta H = E_a(f) - E_a(b)$
or $E_a(f) = E_a(b) - \Delta H$
∴ $E_a(f) < E_a(b)$
for endothermic reaction
$\Delta H = +\text{ ve}$
∴ $\Delta H = E_a(f) - E_a(b)$ or $E_a(f) = \Delta H + E_a(b)$
∴ $E_a(f) > E_a(b)$.

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

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

$$\log\frac{k_2}{3\times10^{-4}} = \frac{104.4\times10^3 \text{ J mol}^{-1}}{2.303\times(8.314 \text{ J K}^{-1}\text{mol}^{-1})}\left[\frac{1}{298} - \frac{1}{\text{T}}\right]$$

As $T \to \infty, \frac{1}{T} \to 0$

$$\therefore \log\frac{k_2}{3\times10^{-4}} = \frac{104.4\times10^3 \text{ J mol}^{-1}}{2.303\times8.314\times298}$$

$$\log\frac{k_2}{3\times10^{-4}} = 18.297, \frac{k_2}{3\times10^{-4}} = 1.98\times10^{18}$$

$$k_2 = (1.98\times10^{18})\times(3\times10^{-4}) = 6\times10^{14}\text{s}^{-1}$$

15. **(a)** $$2.303\log\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{k_2}{k_1} = \frac{9.0\times10^3}{2.303\times2}\left[\frac{308-298}{308\times298}\right]$$

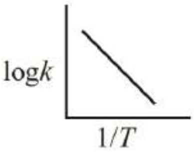
$$\frac{k_2}{k_1} = 1.63;\ k_2 = 1.63k_1;$$

$$\text{Increase in } k_1 = \frac{k_2 - k_1}{k_1}\times100$$

$$= \frac{1.63k_1 - k_1}{k_1}\times100 = 63.0\%$$

16. **(c)** $k = 1.2\times10^{14}e^{-25000/\text{RT}}\ \text{sec}^{-1}$ or

$$\log k = \log 1.2 \times 10^{14} - \frac{25000}{\text{R}}.\frac{1}{\text{T}}$$



Equation of straight line

$$\text{slope} = -\frac{2500}{R}$$

17. **(b)** $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log 2 = \frac{E_a}{2.303\times8.314}\left[\frac{1}{293} - \frac{1}{308}\right]$$

$$0.3 = \frac{E_a}{2.303\times8.314}\times\frac{15}{293\times308}$$

$$E_a = \frac{0.3\times2.303\times8.314\times293\times308}{15}.$$

$= 34558 \text{ J mol}^{-1} = 34.5 \text{ kJ mol}^{-1}$

18. **(c)** $k = Ae^{-E_a/RT}$

For methyl nitrite $k_1 = 10^{13} \times e^{[-152300/(8.314 \times T\,])}$

For ethyl nitrite$k_2 = 10^{14} \times e^{[-157700/(8.314 \times T\,])}$

if $k_1 = k_2$, then

$$10^{13} e^{[-152300/(8.314 \times T)]} = 10^{14} e^{[-155700/(8.314 \times T)]}$$

$$10 = e^{(+157700 - 152300)/(8.314 \times T)}$$

or $2.303 \log 10 = \dfrac{157700 - 152300}{8.314 \times T}$

$\therefore$ $T = 282\,K$

19. **(a)** Given, $A \longrightarrow B$

and 20% solution of A decomposes 25% in 20 minute at 25°C

$\therefore$ Initial amount, $a = 20$

$\therefore$ Amount left, $(a - x) = 20 \times \dfrac{75}{100} = 15$

$\therefore$ $k_{25} = \dfrac{2.303}{20} \log_{10} \dfrac{20}{15}$ $(\because t = 20 \text{ minute})$

$= 0.0144 \text{ minute}^{-1}$

Now, $2.303 \log_{10} \dfrac{k_{40}}{k_{25}} = \dfrac{E_a}{R} \dfrac{[T_2 - T_1]}{T_1 T_2}$

$\therefore$ $2.303 \log_{10} \dfrac{k_{40}}{k_{25}} = \dfrac{70 \times 10^3}{8.314} \left[\dfrac{313 - 298}{313 \times 298}\right]$

$$\frac{k_{40}}{k_{25}} = 3.872$$

$\therefore$ $k_{40} = 0.05575 \text{ min}^{-1}$ $(\because k_{25} = 0.0144)$

Now suppose amount 'm' is left in 30% solution in 20 minute at 40°C.

$$k_{40} = \frac{2.303}{t} \log_{10} \frac{a}{(a - x\ )}$$

$$0.05575 = \frac{2.303}{20} \log_{10} \frac{30}{m}$$

$\therefore$ $m = 9.838$

$\therefore$ % decomposition

$$= \frac{(a - m)}{a} \times 100 = \frac{30 - 9.838}{30} \times 100 = 67.21\%$$

20. **(d)** An activity of 6.023 curie means $6.023 \times 3.7 \times 10^{10}$ dps.

Activity $= \lambda \times N$

$\therefore$ $6.023 \times 3.7 \times 10^{10} = 3.7 \times 10^4 \times N$

or $N = \dfrac{6.023 \times 3.7 \times 10^{10}}{3.7 \times 10^4}$

$\therefore$ Mass of X^{100}

$$= \left[\frac{6.023 \times 3.7 \times 10^{10}}{3.7 \times 10^4}\right] \times \frac{1}{6.023 \times 10^{23}} \times 100$$

$$= 10^{-15}\,g$$

21. **(0.75)** $CH_3.O.CH_3 \rightarrow CH_4 + CO + H_2$

	$CH_3.O.CH_3$	CH_4	CO	H_2	Total conc.
Initial state	a	0	0	0	a
After 12 mts.	$a - x$	x	x	x	$a + 2x$

Calculation of initial concentration (a) of CH_3OCH_3

$PV = nRT$

or $\dfrac{n}{V} = \dfrac{P}{RT}$

$a = \dfrac{P}{RT} = \dfrac{0.4}{0.082 \times 773} = 6.31 \times 10^{-3}$ moles L^{-1}

Calculation of k

$k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{14.5} = 4.78 \times 10^{-2} \text{ min}^{-1}$

Substituting the values in the first order equation.

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

$$4.78 \times 10^{-2} = \frac{2.303}{12} \log \frac{a}{a - x}$$

$$\frac{a}{a - x} = 1.77446$$

$a - x = \dfrac{6.31 \times 10^{-3}}{1.77446}$ moles $L^{-1} = 3.556 \times 10^{-3}$ moles L^{-1}

$\therefore$ $x = (6.310 - 3.556) \times 10^{-3}$ moles/l

$= 2.754 \times 10^{-3}$ moles L

$\therefore$ After 12 min.

Total no. of moles L^{-1}

$= a + 2x = 6.31 \times 10^{-3} + 2 \times 2.754 \times 10^{-3}$

$= 11.818 \times 10^{-3}$

$\therefore \quad P = \dfrac{n}{V}RT = 11.818 \times 10^{-3} \times 0.082 \times 773$

$= 0.75 \text{ atm}$

22. **(2.5)** $\underset{a_0-x-y}{A} \xrightarrow{k_1} \underset{2x}{2B}; \qquad \underset{a_0-x-y}{A} \xrightarrow{k_2} \underset{y}{C}$

$$\frac{d[A]}{dt} = (k_1 + k_2)[A]; \quad \frac{[B]}{[C]} = \frac{2k_1}{k_2} = \frac{2x}{y}$$

$$= \frac{k_1}{k_2} = \frac{x}{y}$$

$\because \quad k_1 = k_2 = x = y$

$$(k_1 + k_2\ t) = \ln\left[\frac{A_0}{A_t}\right]$$

$$2 \times 6.93 \times 10^{-3} \times 50 = \ln\left[\frac{A_0}{A_t}\right]$$

$$= [A]_t = \frac{[A_0]}{2} = a_0 - x - y = a_0/2 \quad (\because x = y \quad)$$

$\therefore \quad x = a_0/4$. Total moles in container

$a_0 - x - y + 2x + y = a_0 + x = 1.25\, a_0$

% increase in moles $\Rightarrow$ 25, So final pressure

$= 2 \times 1.25 = 2.5$ atm

23. **(18.39)** Let the initial concentration $(A) = 100$
Final concentration at 298 K $= 100 - 10 = 90$
Final concentration at 308 K $= 100 - 25 = 75$
Substituting the values in the 1st order rate reaction

$$t = \frac{2.303}{k_{298}} \log\frac{100}{90} \qquad \text{...(i)}$$

$$t = \frac{2.303}{k_{308}} \log\frac{100}{75} \qquad \text{...(ii)}$$

From (i) and (ii) $\dfrac{k_{308}}{k_{208}} = 2.73$

Substituting the value in the following relation

$$E_a = \frac{2.303\, R \times T_1 \times T_2}{T_2 - T_1} \log\frac{k_2}{k_1}$$

$$= \frac{2.303 \times 8.314 \times 298 \times 308}{308 - 298} \log 2.73$$

$E_a = 76.62 \text{ kJ mol}^{-1} = 18.39 \text{ kcal mol}^{-1}$

24. **(378.74)** $\ln\dfrac{k_1'}{k_1} = \dfrac{E_1}{R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right] \qquad \text{...(i)}$

$$\ln\frac{k_2'}{k_2} = \frac{E_2}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \text{...(ii)}$$

Solving we get (ii)–(i),

$$\ln\frac{k_2'}{k_2} - \ln\frac{k_1'}{k_1} = \left(\frac{E_2 - E_1}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(for equimolar formation of B and C, $k_2' = k_1'$)

$$\ln\left(\frac{k_1}{k_2}\right) = \left(\frac{8314}{8.314}\right)\frac{(T_2 - 300)}{300 \times T_2}$$

$$\ln 2 = (1000)\left(\frac{T_2 - 300}{300 \times T_2}\right)$$

$$T_2 = 378.74\text{K}$$

25. **(1.8)** Rate constant at 300 K $= k$

$\therefore$ Rate constant at

$$310\text{ K} = k + \left[k \times \frac{7}{100}\right] = 1.07\, k$$

Thus, $2.303 \log\dfrac{k_2}{k_1} = \dfrac{E_a(f)}{R}\dfrac{[T_2 - T_1]}{T_2 T_1}$

$$2.303 \log\frac{1.07k}{k} = \frac{E_a(f)}{2}\left[\frac{310 - 300}{310 \times 300}\right]$$

$\therefore \quad E_a(f) = 1258.68$ cal

Now, equilibrium constant at 300 K $= K'$
Equilibrium constant at 310 K

$$= K' + \frac{3}{100} \times K' = 1.03\, K'$$

Using $2.303 \log\dfrac{K_2}{K_1} = \dfrac{\Delta H}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$$2.303 \log\frac{1.03K'}{K'} = \frac{\Delta H}{2}\left[\frac{310 - 300}{310 \times 300}\right]$$

$\therefore \quad \Delta H = 549.89$ cal

Since, $\Delta H = E_a(f) - E_a(b)$

$\therefore \quad 549.89 = 1258.68 - E_a(b)$

$\therefore \quad E_a(b) = 708.79 \text{ cal} \quad \dfrac{E_a(f)}{E_a(b)} = 1.8$

26. **(8.42)** $t = 4.5$ billion years and $T_{1/2}$ of ^{40}K $= 1.26$ billion years.

Then, percentage of ^{40}K remaining $\left[\frac{a-x}{a}\right]\times 100$

$$t = \frac{2.303}{\lambda}\log\frac{a}{a-x}$$

$$\lambda = 0.693/T_{1/2} = 0.693/1.26 = 0.55$$

$$\frac{a}{a-x} = 11.86 \quad \therefore \frac{a-x}{a} = \frac{1}{11.86} = 0.0843$$

$$\therefore \frac{a-x}{a}\times 100 = 0.0843\times 100 = 8.42\%$$

27. **(8)** Since $[B] >>> [A]$, $[B]$ remains practically constant and the rate is dependent only on $[A]$. The reaction is pseudo first order w.r.t. A.
Rate $= k[A][B] = k[A]\times 5 = 5k[A] = k'[A]$

$$k' = \frac{2.303}{t}\log\frac{C_o}{C_t} = \frac{2.303}{100}\log\frac{C_o}{C_t}$$

$$\log\frac{C_o}{C_t} = \frac{100\ k'}{2.303} = \frac{100\times 5k}{2.303}$$

$$= \frac{100\times 5\times 5.052\times 10^{-3}}{2.303} = 1.0968$$

$$\frac{C_o}{C_t} = 12.5\ ,\ C_t = \frac{C_o}{12.5} = \frac{0.1}{12.5} = 0.008M$$

Hence, concentration of the reactant A remaining after 100 s = 0.008 M = 8 mM

28. **(5)** Rate of reaction $= k[CO]^x[O_2]^y$

$4\times 10^{-5} = k\,(0.02)^x(0.02)^y$ ...(i)

$1.6\times 10^{-4} = k\,(0.04)^x(0.02)^y$ ...(ii)

$8\times 10^{-5} = k\,(0.02)^x(0.04)^y$ ...(iii)

$$\frac{\text{(i)}}{\text{(ii)}}\ \frac{1}{4} = \left(\frac{1}{2}\right)^x$$

$x = 2$

$$\frac{\text{(i)}}{\text{(iii)}}\ \frac{1}{2} = \left(\frac{1}{2}\right)^y$$

$y = 1$

From eq. (1)

$4\times 10^{-5} = k\,(0.02)^2\,(0.02)^1$

$$k = \frac{4\times 10^{-5}}{4\times 10^{-4}\times 2\times 10^{-2}} = \frac{10}{2} = 5$$

29. **(8)** For I order reaction $r_1 = k[C]^1$

$$\therefore \quad \frac{R_1}{R_2} = k_1/k_2 = \text{temperature coefficient}$$

Let temperature coefficient be a $\frac{r_{35}}{r_{25}} = \frac{k_{35}}{k_{25}} = a$

$$\frac{r_{45}}{r_{35}} = \frac{k_{45}}{k_{35}} = a \quad \therefore \quad \frac{r_{45}}{r_{25}} = a\times a = a^2$$

Similarly, $\frac{r_{75}}{r_{25}} = a^5$

For I reaction $(r_{75})_I = 2^5\times(r_{25})_I$
For II reaction $(r_{75})_{II} = 3^5\times(r_{25})_{II}$

$$\therefore \frac{(r_{75})_{II}}{(r_{75})_I} = \frac{3^5}{2^5} = 7.594 \approx 8 \quad [\because (r_{25})_I = (r_{25})_{II}]$$

30. **(3)** Rate of reaction $= -\frac{1}{2}\frac{dP_{NO}}{dt} = -\frac{dP_{H_2}}{dt}$

For P_{H_2} constant :

$$-\frac{1}{2}\frac{dP_{NO}}{dt} = 1.5 = k(359)^m(P_{H_2})^n$$

$$-\frac{1}{2}\frac{dP_{NO}}{dt} = 0.25 = k(152)^m(P_{H_2})^n$$

$$\therefore \quad \frac{1.5}{0.25} = \left(\frac{359}{152}\right)^m \quad \therefore \quad m = 2$$

For P_{NO} constant : $-\frac{dP_{H_2}}{dt} = 1.60 = (P_{NO})^m(289)^n$

$$-\frac{dP_{H_2}}{dt} = 0.79 = (P_{NO})^m(147)^n$$

$$\therefore \quad \frac{1.60}{0.79} = \left(\frac{289}{147}\right)^n \quad \therefore \quad n = 1$$

$\therefore$ Rate $= k[P_{NO}{}^{2}][P_{H_2}]^1$

$\therefore$ Order of reaction $= 2 + 1 = 3$