CHEMICAL KINETICS

1. Consider the following data for the given reaction

$2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

	1	2	3
HI (mol L^{-1})	0.005	0.01	0.02
Rate (mol $L^{-1}s^{-1}$)	7.5×10^{-4}	3.0×10^{-3}	1.2×10^{-2}

The order of the reaction is_____.

2. Time required for completion of 99.9% of a First order reaction is _____times of half life ($t_{1/2}$) of the reaction.

3. For a reaction taking place in three steps at same temperature, overall rate constant $K = \frac{K_1K_2}{K_3}$.

If Ea_1, Ea_2 and Ea_3 are 40, 50 and 60 kJ/mol respectively, the overall Ea is _____ kJ/mol.

4. The half-life of radioisotopic bromine - 82 is 36 hours. The fraction which remains after one day is _____ $\times 10^{-2}$.

(Given antilog 0.2006 = 1.587)

5. The rate of first order reaction is 0.04 mol L^{-1} s^{-1} at 10 minutes and 0.03 mol L^{-1} s^{-1} at 20 minutes after initiation. Half life of the reaction is _____minutes.

(Given: log2 = 0.3010, log3 = 0.4771)

6. NO_2 required for a reaction is produced by decomposition of N_2O_5 in CCl_4 as by equation

$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$

The initial concentration of N_2O_5 is 3 mol L^{-1} and it is 2.75 mol L^{-1} after 30 minutes.

The rate of formation of NO_2 is

$x \times 10^{-3}$ mol L^{-1} min^{-1}, value of x is _____.

7. Integrated rate law equation for a first order gas phase reaction is given by (where P_i is initial pressure and P_t is total pressure at time t)

(1) $k = \frac{2.303}{t} \cdot \log\frac{P_i}{(2P_i - P_t)}$

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

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

(4) $k = \frac{2.303}{t} \cdot \frac{P_i}{(2P_i - P_t)}$

8. r = k [A] for a reaction, 50% of A is decomposed in 120 minutes. The time taken for 90% decomposition of A is _____minutes.

9. The ratio of $\frac{^{14}C}{^{12}C}$ in a piece of wood is $\frac{1}{8}$ part that of atmosphere. If half life of ^{14}C is 5730 years, the age of wood sample is _____years.

10. The following data were obtained during the first order thermal decomposition of a gas A at constant volume:

$A(g) \rightarrow 2B(g) + C(g)$

S.No	Time/s	Total pressure/(atm)
1.	0	0.1
2.	115	0.28

The rate constant of the reaction is___$\times 10^{-2}$ s^{-1} (nearest integer)

11. Consider the following transformation involving first order elementary reaction in each step at constant temperature as shown below.

$A + B \xrightarrow{\text{Step 1}} C \xrightarrow{\text{Step 2}} P$

Some details of the above reaction are listed below.

Step	Rate constant (sec^{-1})	Activation energy (kJ mol^{-1})
1	k_1	300
2	k_2	200
3	k_3	Ea_3

If the overall rate constant of the above transformation (k) is given as $k = \frac{k_1 k_2}{k_3}$ and the overall activation energy (E_a) is 400 kJ mol^{-1}, then the value of Ea_3 is _____kJ mol^{-1}.

(nearest integer)

12. Consider the following reaction, the rate expression of which is given below

A + B → C

rate = k $[A]^{1/2}$ $[B]^{1/2}$

The reaction is initiated by taking 1M concentration A and B each. If the rate constant (k) is 4.6 × 10^{-2} s^{-1}, then the time taken for A to become 0.1 M is_____sec. (nearest integer)

13. During Kinetic study of reaction

2A + B → C + D, the following results were obtained :

	A[M]	B[M]	Initial rate of formation of D
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Based on above data, overall order of the reaction is_____.

14. Consider the following single step reaction in gas phase at constant temperature.

$2A_{(g)} + B_{(g)} \rightarrow C_{(g)}$

The initial rate of the reaction is recorded as r_1 when the reaction starts with 1.5 atm pressure of A and 0.7 atm pressure of B. After some time, the rate r_2 is recorded when the pressure of C becomes 0.5 atm. The ratio $r_1 : r_2$ is_____× 10^{-1}.

(Nearest integer)

15. Time required for 99.9% completion of a first order reaction is _____ time the time required for completion of 90% reaction.

(Nearest integer)

16. Consider the following reaction

A + B → C

The time taken for A to become $1/4^{th}$ of its initial concentration is twice the time taken to become 1/2 of the same. Also, when the change of concentration of B is plotted against time, the resulting graph gives a straight line with a negative slope and a positive intercept on the concentration axis.

The overall order of the reaction is _____.

17. For a reaction $A \xrightarrow{K_1} B \xrightarrow{K_2} C$

If the rate of formation of B is set to be zero then the concentration of B is given by :

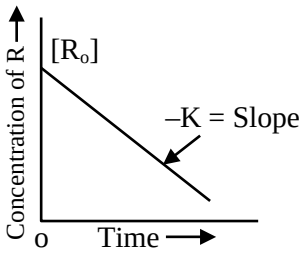
(1) $K_1K_2[A]$ (2) $(K_1 - K_2)[A]$

(3) $(K_1 + K_2)[A]$ (4) $(K_1/K_2)[A]$

18. Given below are two statements :

Statement I : The rate law for the reaction A + B → C is rate (r) = $k[A^2][B]$. When the concentration of both A and B is doubled, the reaction rate is increased "x" times.

Statement II :



The figure is showing "the variation in concentration against time plot" for a "y" order reaction. The value of x + y is _____.

19. Consider the following first order gas phase reaction at constant temperature

A(g) → 2B(g) + C(g)

If the total pressure of the gases is found to be 200 torr after 23 sec. and 300 torr upon the complete decomposition of A after a very long time, then the rate constant of the given reaction is____ × 10^{-2} s^{-1} (nearest integer)

[Given : $\log_{10}(2) = 0.301$]

SOLUTIONS

1. Ans. (2)

Sol. Let, $R = k[HI]^n$

using any two of given data,

$$\frac{3\cdot 10^{-3}}{7.5\cdot 10^{-4}} = \left(\frac{0.01}{0.005}\right)^n$$

$n = 2$

2. Ans. (10)

Sol. $$\frac{t_{99.9\%}}{t_{1/2}} = \frac{\frac{2.303}{k}\left(\frac{a}{a-x}\right)}{\frac{2.303}{k}\log 2} = \frac{\log\left(\frac{100}{100-99.9}\right)}{\log 2}$$

$$= \frac{\log 10^3}{\log 2} = \frac{3}{0.3} = 10$$

3. Ans. (30)

Sol. $$K = \frac{K_1K_2}{K_3} = \frac{A_1A_2}{A_3}\cdot e^{-\frac{\left(E_{a_1}+E_{a_2}-E_{a_3}\right)}{RT}}$$

$$A\, e^{-E_a/RT} = \frac{A_1A_2}{A_3}\cdot e^{-\frac{\left(E_{a_1}+E_{a_2}-E_{a_3}\right)}{RT}}$$

$$E_a = E_{a_1} + E_{a_2} - E_{a_3} = 40 + 50 - 60$$

$= 30$ kJ / mole.

4. Ans. (63)

Sol. Half life of bromine – 82 = 36 hours

$$t_{1/2} = \frac{0.693}{K}$$

$$K = \frac{0.693}{36} = 0.01925\ hr^{-1}$$

1st order rxn kinetic equation

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

$$\log\frac{a}{a-x} = \frac{t\cdot K}{2.303} \quad (t = 1day = 24hr)$$

$$\log\frac{a}{a-x} = \frac{24hr\cdot 0.01925\ hr^{-1}}{2.303}$$

$$\log\frac{a}{a-x} = 0.2006$$

$$\frac{a}{a-x} = \text{anti}\log(0.2006)$$

$$\frac{a}{a-x} = 1.587$$

If a = 1

$$\frac{1}{1-x} = 1.587 \Rightarrow 1 - x$$

= 0.6301 = Fraction remain after one day

5. Ans. (24)

Sol. $0.04 = k[A]_0e^{-k\times 10\times 60}$ …(1)

$0.03 = k[A]_0e^{-k\times 20\times 60}$ …(2)

(1)/(2)

$$\frac{4}{3} = e^{600\,k(2-1)}$$

$$\frac{4}{3} = e^{600k}$$

$$\ln\frac{4}{3} = 600k$$

$$\ln\frac{4}{3} = 600\cdot\frac{\ln 2}{t_{1/2}}$$

$$t_{1/2} = 600\frac{\ln 2}{\ln\frac{4}{3}}\text{sec}$$

$$t_{1/2} = 600\cdot\frac{\log 2}{\log 4 - \log 3}\ \text{sec.}$$

$$= 10\cdot\frac{0.3010}{0.6020-0.477}\ \text{min.}$$

$t_{1/2}$ = 24.08 min

Ans. 24

6. Ans. (17)

Sol. Rate of reaction (ROR)

$$= -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

ROR

$$= -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = -\frac{1}{2}\frac{(2.75-3)}{30}\text{mol L}^{-1}\text{min}^{-1}$$

$$\text{ROR} = -\frac{1}{2}\frac{(-0.25)}{30}\text{mol L}^{-1}\text{min}^{-1}$$

$$\text{ROR} = \frac{1}{240}\text{mol L}^{-1}\text{min}^{-1}$$

$$\text{Rate of formation of } NO_2 = \frac{\Delta[NO_2]}{\Delta t} = 4\cdot\text{ ROR}$$

$$= \frac{4}{240} = 16.66\cdot 10^{-3}\text{molL}^{-1}\text{min}^{-1} - 17\cdot 10^{-3}.$$

7. Ans. (1)

Sol. A → B + C

P_i 0 0

$P_i - x$ x x

$P_t = P_i + x$

$P_i - x = P_i - P_t + P_i$

$= 2P_i - P_t$

$$K = \frac{2.303}{t}\log\frac{P_i}{2P_i - P_t}$$

8. Ans. (399)

Sol:- r = k [A]

So, order of reaction = 1

$t_{1/2}$ = 120 min

For 90% completion of reaction

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

$$\Rightarrow \frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\frac{100}{10}$$

$\therefore t =$ 399 min.

9. Ans. (17190)

Sol. $$\lambda t = \ln\frac{(^{14}C/^{12}C)_{atmosphere}}{(^{14}C/^{12}C)_{wood\ sample}}$$

As per the question,

$$\frac{(^{14}C/^{12}C)_{wood}}{(^{14}C/^{12}C)_{atmosphere}} = \frac{1}{8}$$

So, $\lambda t = \ln 8$

$$\frac{\ln 2}{t_{1/2}}t = \ln 8$$

$t = 3 \times t_{1/2}$ = 17190 years

10. Ans. (2)

Sol.

	A(g) →	2B(g) +	C(g)
t = 0	0.1		
t = 115 sec.	0.1 – x	2x	x

0.1 + 2x = 0.28

2x = 0.18

x = 0.09

$$K = \frac{1}{115}\ln\frac{0.1}{0.1-0.09}$$

$= 0.0200\ sec^{-1}$

$= 2 \times 10^{-2}\ sec^{-1}$

11. Ans. (100)

Sol. $$K = \frac{K_1K_2}{K_3}$$

$$Ae^{\frac{-E_a}{RT}} = \frac{A_1e^{\frac{-E_{a_1}}{RT}}A_2e^{\frac{-E_{a_2}}{RT}}}{A_3e^{\frac{-E_{a_3}}{RT}}}$$

$$Ae^{\frac{-E_a}{RT}} = \frac{A_1A_2}{A_3}e^{\frac{-(E_{a_1}+E_{a_2}-E_{a_3})}{RT}}$$

$$E_a = E_{a_1} + E_{a_2} - E_{a_3}$$

$400 = 300 + 200 - E_{a_3}$

E_{a_3} = 100 kJ/mole

12. Ans. (50)

Sol. $$K = \frac{2.303}{t}\log\frac{1}{0.1}$$

$$4.6 \times 10^{-2} = \frac{2.303}{t}$$

t = 50 sec.

13. Ans. (3)

Sol. $r = K[A]^x[B]^y$

(I) $6 \times 10^{-3} = K[0.1]^x[0.1]^y$

(IV) $2.4 \times 10^{-2} = K[0.4]^x[0.1]^y$

(IV)/(I)

$4 = (4)^x$

x = 1

$r = K[A]^x[B]^y$

(III) $2.88 \times 10^{-1} = K[0.3]^x[0.4]^y$

(II) $7.2 \times 10^{-2} = K[0.3]^x[0.2]^y$

(III)/(II)

$4 = 2^y$

y = 2

Overall order = x + y = 1 + 2 = 3

14. Ans. (315)

Sol. $2A(g) + B(g) \rightarrow C(g)$

r_1 1.5 atm 0.7 atm

r_2 0.5 atm 0.2 atm 0.5 atm

$\because r = K[P_A]^2[P_B]$

$r_1 = K[1.5]^2[0.7]$

$r_2 = K[0.5]^2[0.2]$

$$\frac{r_1}{r_2} = 9 \cdot \frac{7}{2} = 31.5 = 315 \cdot 10^{-1}$$

Ans. 315

15. Ans. (3)

Sol. $$K = \frac{1}{t_{99.9\%}} \text{ln}\left(\frac{100}{0.1}\right) = \frac{1}{t_{90\%}} \text{ln}\left(\frac{100}{10}\right)$$

$$t_{99.9\%} = t_{90\%} \frac{\text{ln}(10^3)}{\text{ln}10}$$

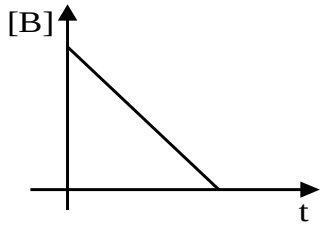
$t_{99.9\%} = t_{90\%} \times 3$

16. Ans. (1)

Sol. For 1st order reaction

75% life = 2 × 50% life

So order with respect to A will be first order.



So order with respect to B will be zero.

Overall order of reaction = 1 + 0 = 1

17. Ans. (4)

Sol. Rate of formation of B is

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$0 = k_1[A] - k_2[B]$

$$\left(\frac{k_1}{k_2}\right)[A] = [B]$$

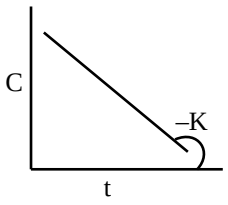
18. Ans. (8)

Sol. $r = K[A]^2|B|$

if conc. are doubled

$r' = K[2A]^2[2B]^1$

$r' = 8r \Rightarrow x = 8$



$\Rightarrow$ Zero order, y = 0

x + y = 8

19. Ans. (3)

Sol. $A(g) \rightarrow 2B(g) + C(g)$

$P_{23} = P_0 + 2x = 200$

$P_\infty = 3P_0 = 300$

$P_0 = 100$

$$K = \frac{1}{t} \ln \frac{P_\infty - P_0}{P_\infty - P_t}$$

$$K = \frac{2.3}{23} \log \frac{300 - 100}{300 - 200}$$

$$= \frac{2.3 \cdot 0.301}{23} = 0.0301 = 3.01 \cdot 10^{-2} \text{sec}^{-1}$$