

## CHEMICAL KINETICS & NUCLEAR CHEMISTRY

### Rate of Appearance or Disappearance of Substance C

(i) Average  $\left(\pm \frac{\Delta[c]}{\Delta t}\right)$

(ii) Instantaneous  $\left(\pm \frac{d[c]}{dt}\right)$

❖ **Expressions of the rate:**

For a general reaction:  $aA + bB \longrightarrow cC + dD$ ,

Rate of disappearance of A =  $-\frac{d[A]}{dt}$ ; Rate of disappearance of B =  $-\frac{d[B]}{dt}$

Rate of appearance of C =  $\frac{d[C]}{dt}$  & Rate of appearance of D =  $\frac{d[D]}{dt}$

The positive sign shows that concentrations of C and D increases with time and the negative sign is indicating that concentrations of A and B decrease with time.

Instantaneous rate of reaction :  $-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$

Average rate of reaction:  $-\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$

Rate of reaction (ROR) =  $\frac{\text{Rate of disappearance of reactant}}{\text{Stoichiometry coefficient of reactant}}$   
 $= \frac{\text{Rate of appearance of product}}{\text{Stoichiometry coefficient of product}}$

❖ **Units of Rate of Reaction:** =  $\text{mol L}^{-1}\text{s}^{-1}$  or  $\text{mol L}^{-1} \text{min}^{-1}$  (concentration time<sup>-1</sup>).

## Rate Law and Rate Constant

$$\text{Rate} \propto [A]^a \cdot [B]^b \text{ or Rate} = k[A]^a[B]^b$$

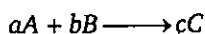
The constant of proportionality,  $k$  is known as the rate constant (specific reaction rate) and may be defined as the rate at unit concentrations of the reactants.

- ❖  $k$  depends on the temperature and is independent of the concentration of the reactants.
- ❖ At a fixed temperature,  $k$  is a constant and is a characteristic of the reaction. Larger value of  $k$  indicates fast reaction and small  $k$  indicates slow reactions.

## Molecularity

It is always a whole number (not zero) and never a fraction. Its value does not exceed 3 & it has no meaning for a complex reaction.

## Order of Reaction



$$\text{Rate of reaction} = k[A]^m[B]^n$$

Order of reaction =  $m + n$  & the order w.r.t.  $A, B$  are  $m, n$  respectively.

- ❖ The order of reaction is obtained from the experimentally determined rate and may be zero, integral or a fraction. In a multi-step complex reaction, the order of the reaction can be determined with the help of slowest step, which is called rate determining step.
- ❖ In elementary reaction stoichiometric coefficient of reactants is equal to order of reaction :  $m + n = a + b$ .

Order	Differential rate law	Integrated rate law	Straight line plot	Half life	Units of $k$	Example
0	$-d[R]/dt = k$	$kt = [R]_0 - [R]$	$[R]_0$ vs $t$	$[R]_0 / 2k$	conc time <sup>-1</sup> or mole L <sup>-1</sup> s <sup>-1</sup>	$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$ $2HI(g) \xrightarrow[\text{surface}]{Au} H_2(g) + I_2(g)$
1	$-d[R]/dt = k[R]$	$[R] = [R]_0 e^{-kt}$ $kt = \ln\{[R]_0/[R]\}$	$\ln [R]$ vs $t$	$(\ln 2)/k$ or $\frac{0.693}{k}$	time <sup>-1</sup> or s <sup>-1</sup>	Decomposition of $H_2O_2$ in aqueous solution Radioactive disintegration
2	$-d[R]/dt = k[R]^2$	$kt = \frac{1}{[R]} - \frac{1}{[R]_0}$	$\frac{1}{[R]}$ vs $t$	$\frac{1}{k[R]_0}$	mol <sup>-1</sup> L s <sup>-1</sup>	$CH_3COOC_2H_5 + NaOH$ ↓ $CH_3COONa + C_2H_5OH$ $C_2H_4 + H_2 \xrightarrow{100^\circ C} C_2H_6$

Important Graphical Representation		

where  $a_0$  = Initial Concentration of reactant,  $r$  = rate of reaction

- Some useful relationships between times for different fractions of reaction of first order to complete

$$\begin{aligned}
 t_{3/4} \text{ or } t_{75\%} &= 2t_{1/2} \\
 t_{87.5\%} &= 3t_{1/2} \\
 t_{99.9\%} &\approx 10t_{1/2}
 \end{aligned}$$

- Amount of the substance left after  $n$  half-lives =  $\frac{A_0}{2^n}$

## $n^{\text{th}}$ Order Reaction

$A \rightarrow \text{Product}$

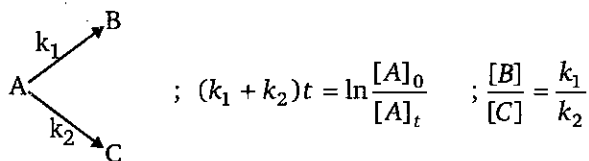
$$k \cdot t = \frac{1}{n-1} \left\{ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right\} \quad [n \neq 1, n = \text{order}]$$

$$t_{1/2} = \frac{1}{k(n-1)} \left[ \frac{2^{n-1} - 1}{a^{n-1}} \right]$$

- Reversible reaction  $A \xrightleftharpoons[k_b]{k_f} B$

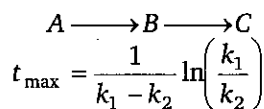
$$(k_f + k_b) = \frac{1}{t} \ln \left( \frac{x_{eq}}{x_{eq} - x} \right) ; \text{ At equilibrium } k_{eq} = \frac{k_f}{k_b} = \frac{[B]}{[A]} = \frac{x_{eq}}{a - x_{eq}}$$

### Parallel/Side Reaction



$$\% \text{ Yield of B} = \frac{k_1}{k_1 + k_2} \times 100 \quad \text{and} \quad \% \text{ Yield of C} = \frac{k_2}{k_1 + k_2} \times 100$$

### Series/Consecutive Reaction



$$\text{Temperature coefficient } (\mu) = \frac{k_{T+10}}{k_T}$$

- For general chemical reactions with rise in temperature by 10°C, the rate constant is nearly doubled.

### Arrhenius Equation

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

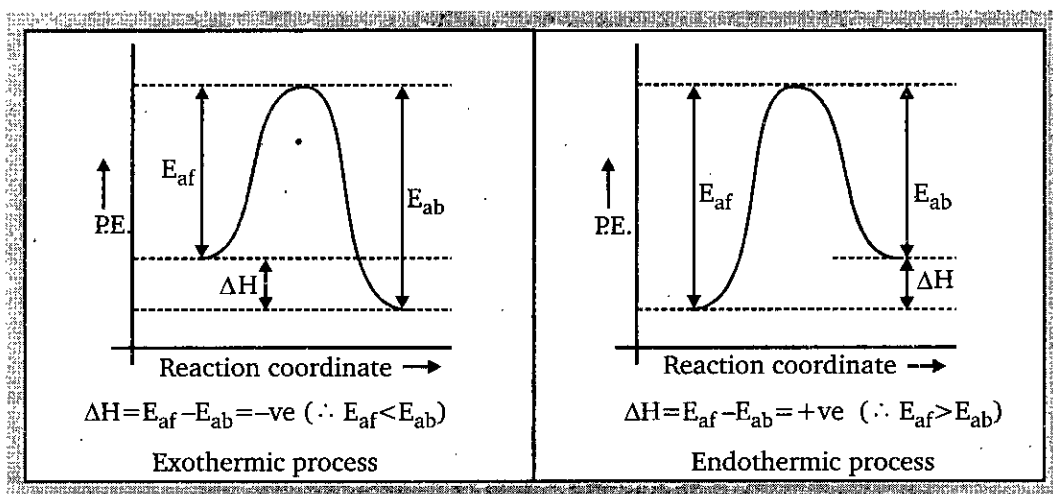
where  $k$  = Rate constant,  $A$  = Pre-exponential factor,  $T$  = Temperature in kelvin,

$E_a$  = Activation Energy

- The factor  $e^{-E_a/RT}$  represents fraction of molecules that have kinetic energy greater than  $E_a$
- Logarithmic expression**

$$\log_{10} \left( \frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

- Energy profile for exothermic process & endothermic process:

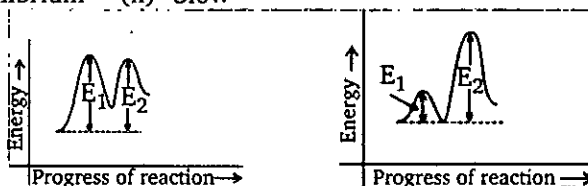


- Threshold Energy = Activation Energy + Energy possessed by reactant molecules.

❖ **Activation energy diagram for two step endothermic reaction:**

(A) (i) I<sup>st</sup> step-Slow (ii) II<sup>nd</sup> step-Fast

(B) (i) Rapid equilibrium (ii) Slow



**Factors affecting reaction rates :** Concentration of reactants and Reaction temperature. Besides these, presence of catalyst and surface area (if a reactant or a catalyst is a solid) exposure to radiation also affect the reaction rates.

## Nuclear Chemistry

Nuclear chemistry is the study of the properties and reactions of atomic nuclei. In nuclear reaction only the nuclides (nuclide : the nucleus of a specific isotope) participates and overall (mass + energy) remains conserved.

## Radioactivity

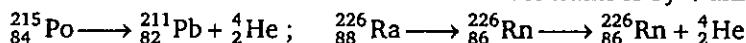
The property of a nucleus emitting radiations-like  $\alpha$ ,  $\beta$  and  $\gamma$  is known as radioactivity and the substance possessing the property is called a radioactive substance. The emission of these particles takes place because of the instability of the nucleus. Radioactivity is a property of nucleus.

Properties of  $\alpha$ ,  $\beta$ -particles and  $\gamma$ -rays.

Properties	Alpha	Beta	Gamma
Nature	Fast moving He nuclei ( $\text{He}^{2+}$ )	Fast moving electrons	High energy electromagnetic
Representation	${}^4_2\text{He}$ or $\alpha$	${}^0_{-1}e$ or ${}^0_{-1}\beta$	$\gamma$ or ${}^0_0\gamma$
Charge	2 unit (+ve)	1 unit (-ve)	No charge
Mass	$6.65 \times 10^{-24}$ g/particle	$9.11 \times 10^{-28}$ g/particle	0
Velocity	1/10 of light (min.)	nearly velocity of light	Same as light waves (max.)
Relative penetrating power	1	$\approx 100$	$\approx 10000$
Relative ionising power	$\approx 10000$	$\approx 100$	1
Effect of electromagnetic field	Deflected toward -ve electrode	Deflected toward +ve electrode	No effect
Kinetic energy	High	Low	-
Effect on ZnS Screen	Maximum effect	Little effect	-

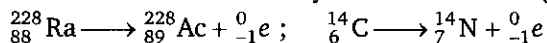
## Types of Radioactive Decay

1.  $\alpha$ -decay causes decrease of atomic number of 2 units and mass number by 4 units, e. g.,

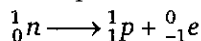


All nucleides with atomic number greater than 83 are beyond the band of stability are radioactive.

2.  $\beta$ -decay causes increase of atomic number by 1 unit and no change in mass number, e. g.,

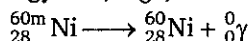


A neutron is converted to proton in this process.



Such emission occurs for the nuclei lying above the stability belt.

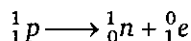
3.  $\gamma$ -ray emission ( ${}_0^0\gamma$ ) causes no change in atomic number and mass number, since it represents the energy lost, e. g.,



4. **Positron Emission** : Causes decrease the atomic number by 1 unit, e. g.,



A proton is converted to neutron and positron in this process.

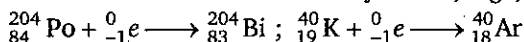


Such emission occurs for the nuclei lying below the stability belt:

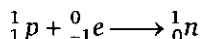
- ❖ Position ( ${}_{+1}^0e$ ) is a particle having the same mass as an electron, but positively charged.

5. **Electron-capture** :

Causes decrease the atomic number by 1 unit, e. g.,



A proton is converted to neutron in this process.



Electron capture occurs with the nuclei lying below the stability belt, in which an electron from the K-shell is captured by the nucleus.

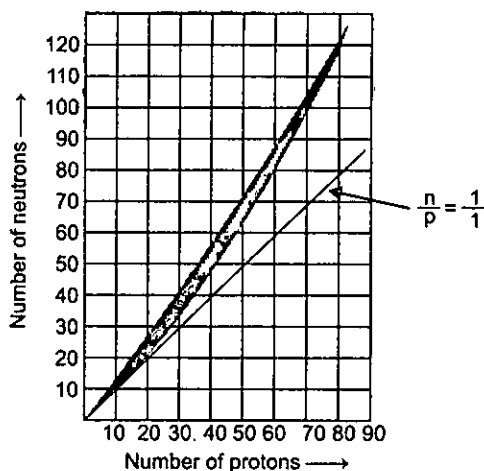
### Group Displacement Law (Soddy-Fajans)

In an  $\alpha$ -particle emission, the resulting element has a mass number less by four units and atomic number less by two units and so lies two places to the left in the periodic table.

In a  $\beta$ -particle emission the resulting element has the same mass number but has an atomic number greater by one unit and so lies one place to the right in the periodic table.

### Neutron/proton ratio and stability zone

- ❖ For atomic number < 20, most stable nuclei have  $n : p$  ratio nearly 1 : 1 (except H & Ar)
- ❖ For  $n/p$  ratio > 1.5, nucleus is unstable. Largest stable nucleus is  ${}^{209}_{83}\text{Bi}$  for which  $n/p$  ratio is 1.52.
- ❖ For atomic number > 83, there are no stable nuclei.



### Magic numbers and nuclear stability

Nuclei with 2, 8, 20, 28, 50, 82 or 126 protons or neutrons are unusually stable and have a larger number of stable isotopes than neighboring nuclei in the periodic table. These numbers are called magic numbers. They are supposed to represent completely filled nuclear shells of energy levels.

- ❖ Nuclei with magic number of protons as well as neutrons have notably high stabilities.

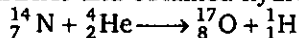
[e.g.,  ${}^4_2\text{He}$ ,  ${}^{16}_8\text{O}$ ,  ${}^{40}_{20}\text{Ca}$  and  ${}^{208}_{82}\text{Pb}$ ].

### Even Odd Theory

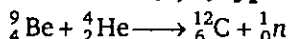
Most naturally occurring nuclides have even numbers of neutrons and even numbers of protons. 165 such stable nuclei are known. There exist 55 known nuclei with even number of protons and odd number of neutrons, and 50 known stable nuclei with odd number of protons and even number of neutrons. On the other hand, the number of known stable nuclei having odd numbers of both neutrons and protons is only 5.

### Artificial nuclear reactions

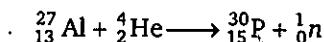
The first artificial transmutation was carried out by Rutherford in 1919 who bombarded nitrogen gas with alpha particles and obtained hydrogen and oxygen.



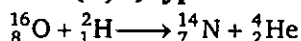
#### 1. Alpha particle induced or ( $\alpha, n$ ) type reactions :



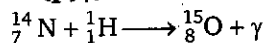
Since  $\alpha$ -particle is used and a neutron is produced, the reaction may be termed as ( $\alpha, n$ ) reaction. In another  $\alpha$ -bombardment nuclear reaction, the isotope ( ${}^{30}_{15}\text{P}$ ) produced is itself radioactive.



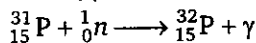
#### 2. Deuteron-induced or ( $D, \alpha$ ) type reaction :



**3. Proton-induced or (p, γ) reaction :**



**4. Neutron-induced or (n, γ) reaction :**



**Radioactive decay**

❖ Radioactive decay is a first order process. The rate of nuclear decay is determined from measurements of the activity (A) of a sample.

Hence 
$$-\frac{dN}{dt} = \lambda N \quad \text{or} \quad N = N_0 e^{-\lambda t}$$

where N = number of radioactive nuclei at any time t ; N<sub>0</sub> = number of radioactive nuclei at t = 0 ; λ = decay constant.

**S.I. units :** The SI unit is becquerel (Bq).

1 disintegration per second (dps) = 1 Bq.

**Other units :** 1 curie (Ci) = 3.7 × 10<sup>10</sup> dps, 1 Rutherford (Rd) = 10<sup>6</sup> dps.

❖ **Specific activity :** Activity per unit mass of radioactive sample (dps/g)

❖ **Half life (t<sub>1/2</sub>) :** The time taken by half the nuclei (originally present) to decay.  
t<sub>1/2</sub> = 0.693/λ

**Note :** After n half-lives have passed, activity is reduced to  $\frac{1}{2^n}$  of its initial value.

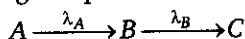
❖ Average life (t<sub>av</sub>): t<sub>av</sub> = 1/λ = 1.44t<sub>1/2</sub>

**Radioactive equilibrium**

Among the members of a decay chain, the state which prevails when the ratios between the activities of successive members remain constant. (This is not an equilibrium in the strict sense since radioactive decay is an irreversible process).

**Secular equilibrium**

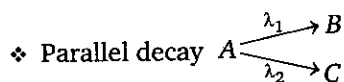
Radioactive equilibrium where the half life of the intermediate isotope is so long that the change of its activity can be ignored during the period of interest and all activities remain constant.



Number of nuclei of B is max. at t<sub>max</sub> ; 
$$t_{\max} = \frac{1}{(\lambda_1 - \lambda_2)} \ln \left( \frac{\lambda_1}{\lambda_2} \right)$$

$$\frac{dN_B}{dt} = \lambda_A N_A - \lambda_B N_B$$

Secular equilibrium occurs when  $\frac{dN_B}{dt} = 0$  or  $\frac{N_B}{N_A} = \frac{\lambda_A}{\lambda_B}$



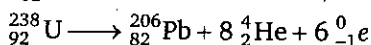
$$\% \text{ of } B = \left( \frac{\lambda_1}{\lambda_1 + \lambda_2} \right) \times 100$$

$$\% \text{ of } C = \left( \frac{\lambda_2}{\lambda_1 + \lambda_2} \right) \times 100$$



### Applications of Radioactivity :

- ❖ **Age of Minerals and Rocks :** We can determine the age of the rock by measuring the ratio of  ${}_{92}^{238}\text{U}$  and  ${}_{82}^{206}\text{Pb}$ .



At time  $t$        $w$  gram       $y$  gram

Age of Rock,       $t = \frac{1}{\lambda} \ln \left( \frac{w_0}{w} \right)$  where  $w_0 = w + x$ ,

$w_0$  = Initial wt. of  ${}_{92}^{238}\text{U}$ ;       $x$  = wt. of  ${}_{92}^{238}\text{U}$  disintegrated.  $x = \frac{238}{206} \times y$

- ❖ **Radiocarbon Dating :**  ${}^6_{14}\text{C}$  is used to date historical artifacts.

Age of wood artifacts,  $t = \frac{1}{\lambda} \ln \left( \frac{A_0}{A} \right)$  (where  $t_{1/2}$  of  ${}^6_{14}\text{C} = 5770$  years)

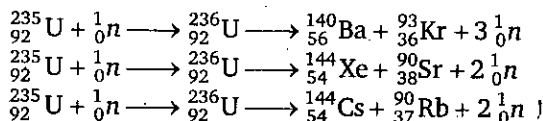
$A_0$  = Activity of fresh wood of plant/tree. ;       $A$  = Activity of old wood.

- ❖ Uses in Medicines and other Areas

### Nuclear Fission

In a nuclear fission reaction, a heavy nucleus splits up into two main fragments of lighter nuclei and several neutrons.

Of the three natural isotopes of uranium ( ${}_{92}^{238}\text{U}$ ,  ${}_{92}^{235}\text{U}$  and  ${}_{92}^{234}\text{U}$ , the  ${}_{92}^{235}\text{U}$ ) nucleus undergoes nuclear fission when bombarded with slow neutrons. The  ${}_{92}^{236}\text{U}$  formed breaks up in several different ways, for example :



- ❖ The key to the liberation of energy in the nuclear fission reaction is the production of two or more neutrons per reaction initiated by one neutron.
- ❖ Atom bomb is based on Nuclear fission.

A nuclear fission chain reaction has three general steps :

**1. Initiation :** The reaction of a single atom is needed to start the chain. Fission of  ${}_{92}^{235}\text{U}$  is initiated by the absorption of a neutron.

**2. Propagation :** This part of the process repeats itself over and over, with each step yielding more product. The fission of  ${}_{92}^{236}\text{U}$  releases neutrons that initiate the fission of other uranium atoms.

**3. Termination :** Eventually, the chain will end. Termination could occur if the reactant ( ${}_{92}^{235}\text{U}$ ) is used up, or if the neutrons that continue the chain escape from the sample without being captured by  ${}_{92}^{235}\text{U}$ .

### Nuclear Fusion

Just as the fission of heavy nuclei is accompanied by mass losses resulting into the liberation of large amounts of energy, the fusion of light nuclei is accompanied by mass losses and the evolution of large quantities of energy. Some such reactions and energy release in each process are shown below,

Fusion reaction	Mass loss	Energy released (kJ mol <sup>-1</sup> )
${}^2_1\text{H} + {}^2_1\text{H} \longrightarrow {}^4_2\text{He}$	0.026	$2.3 \times 10^9$
${}^2_1\text{H} + {}^3_1\text{H} \longrightarrow {}^4_2\text{He} + {}^1_0\text{n}$	0.018	$1.79 \times 10^9$

Compared with fission reactions, fusion reactions have the advantage that large amounts of highly radioactive nuclides are not obtained as by-products which may pose problem of safe storage.

- ❖ At the very high temperatures needed for a fusion reaction.
- ❖ Hydrogen bomb is based on nuclear fusion.
- ❖ **Einstein's mass-energy equation** : Energy changes in nuclear reactions can be determined by using Einstein's mass-energy equation  $E = mc^2$

Where  $E$  is the energy equivalent of mass  $m$  and  $c$  is the velocity of light.

For a change of 1 amu (atomic mass unit), the corresponding energy change,  $E \approx 931 \times 10^6 \text{ eV} \approx 931 \text{ MeV}$ , i.e., a mass of 1 amu is equivalent to 931 MeV of energy.

### Mass Defect

It has invariably been found that the actual mass of an isotope of an element is less than the sum of masses of the protons, neutrons and electrons present in it. This difference, is called mass defect. The mass defect is nothing, but the loss of mass during the formation of the nucleus of the isotope.

- ❖ **Mass defect in nuclear reaction** :

$\Delta m = \text{mass of nuclei of reactants} - \text{mass of nuclei of products.}$

Energy liberated in nuclear reaction :  $\Delta E = \Delta m \cdot c^2$ .

- ❖ **Mass defect in an isotope formation** :

Let  $m_p$ ,  $m_n$  and  $m_e$  are the respective masses of proton, neutron and electron. Then, the calculated mass of this isotope,

$$M' = Z m_p + Z m_e + (A - Z) m_n = Z m_{\text{H}} + (A - Z) m_n$$

( $\because m_p + m_e = \text{Mass of hydrogen atom} = m_{\text{H}}$ )

Let  $M = \text{Actual atomic mass as determined experimentally.}$

then,  $\Delta m = \text{Mass defect} = M' - M$

### Binding Energy

Loss of mass during the formation of the nucleus from nucleons is converted into energy. The release of energy imparts stability to the nucleus. The energy released when constituent nucleons combine to form a nucleus, is called binding energy of the nucleus. In other words, energy equal to binding energy will be needed to break up the nucleus into its constituent nucleons. Consequently, the greater the binding energy, the more stable is the nucleus.

### Binding Energy and Nuclear Stability

$$\text{B.E. per nucleon} = \frac{\text{B. E.}}{\text{No. of nucleons}}$$

Binding energy per nucleon is a direct indicator of its nuclear stability. Higher the binding energy per nucleon of an isotope, greater is its nuclear stability.

# Level 1

1. The differential rate law equation for the elementary reaction  $A + 2B \xrightarrow{k} 3C$ , is :

(a)  $-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A][B]^2$

(b)  $-\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = k[A]^2[B]$

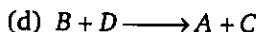
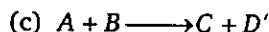
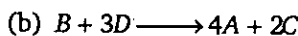
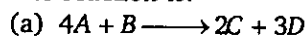
(c)  $-\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = k[A][B]^2$

(d) None of these

2. The rate of reaction is expressed in different ways as follows:

$$+\frac{1}{2} \frac{d[C]}{dt} = -\frac{1}{3} \frac{d[D]}{dt} = +\frac{1}{4} \frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is:



3. In the reaction,  $A + 2B \longrightarrow 6C + 2D$ , if the initial rate  $-\frac{d[A]}{dt}$  at  $t = 0$  is  $2.6 \times 10^{-2} \text{ M sec}^{-1}$ ,

what will be the value of  $-\frac{d[B]}{dt}$  at  $t = 0$  ?

(a)  $8.5 \times 10^{-2} \text{ M sec}^{-1}$

(b)  $2.5 \times 10^{-2} \text{ M sec}^{-1}$

(c)  $5.2 \times 10^{-2} \text{ M sec}^{-1}$

(d)  $7.5 \times 10^{-2} \text{ M sec}^{-1}$

4. For the reaction  $2A \longrightarrow B + 3C$ ; if  $-\frac{d[A]}{dt} = k_1[A]^2$ ;  $\frac{d[B]}{dt} = k_2[A]^2$ ;  $\frac{d[C]}{dt} = k_3[A]^2$

the correct relation between  $k_1$ ,  $k_2$  and  $k_3$  is :

(a)  $k_1 = k_2 = k_3$

(b)  $2k_1 = k_2 = 3k_3$

(c)  $4k_1 = k_2 = 3k_3$

(d)  $\frac{k_1}{2} = k_2 = \frac{k_3}{3}$

5. The rate constant of  $n^{\text{th}}$  order has units :

(a)  $\text{litre}^{1-n} \text{ mol}^{1-n} \text{ sec}^{-1}$

(b)  $\text{Mol}^{1-n} \text{ litre}^{1-n} \text{ sec}$

(c)  $\text{Mol}^{1-n^2} \text{ litre}^{n^2} \text{ sec}^{-1}$

(d)  $\text{Mole}^{1-n} \text{ litre}^{n-1} \text{ sec}^{-1}$

6. Which of the following statement is incorrect?

(a) Unit of rate of disappearance is  $\text{Ms}^{-1}$

(b) Unit of rate of reaction is  $\text{Ms}^{-1}$

(c) Unit of rate constant  $k$  depends upon order

(d) Unit of  $k$  for first order reaction is  $\text{Ms}^{-1}$

7. Which of the following relation is correct for  $k_f$  and  $k_b$  in an equilibrium process that contains equal moles of reactants and products.

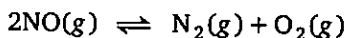
(a)  $k_f = k_b$

(b)  $k_f > k_b$

(c)  $k_f < k_b$

(d) we cannot predict

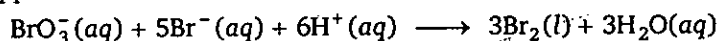
8. Listed in the table are forward and reverse rate constants for the reaction



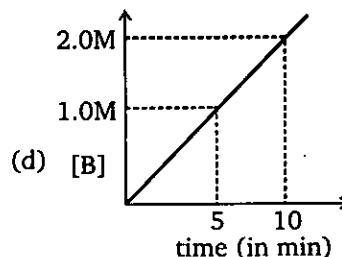
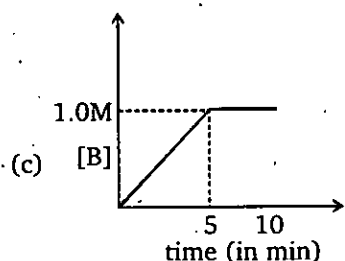
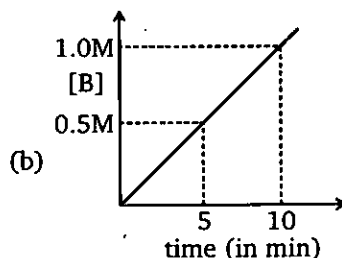
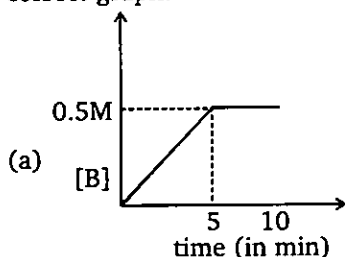
Temperature (K)	$k_f$ ( $M^{-1}S^{-1}$ )	$k_b$ ( $M^{-1}S^{-1}$ )
1400	0.29	$1.1 \times 10^{-6}$
1500	1.3	$1.4 \times 10^{-5}$

Select the correct statement :

- (a) Reaction is exothermic and value of equilibrium constant ( $K_{eq}$ ) at 1400 K is  $3.79 \times 10^{-6}$   
 (b) Reaction is endothermic and value of  $K_{eq}$  at 1400 K is  $2.63 \times 10^5$   
 (c) Reaction is exothermic and value of  $K_{eq}$  at 1400 K is  $2.63 \times 10^5$   
 (d) Reaction is endothermic and value of  $K_{eq}$  at 1500 K is  $9.28 \times 10^4$
9. The rate constant of a reaction depends on  
 (a) temperature  
 (b) pressure  
 (c) extent of reaction  
 (d) initial concentration of the reactant
10. In the following reaction, how is the rate of appearance of the underlined product related to the rate of disappearance of the underlined reactant



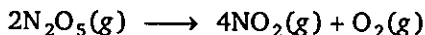
- (a)  $-\frac{d[BrO_3^-]}{dt} = \frac{d[Br_2]}{dt}$                       (b)  $-\frac{1}{3} \frac{d[BrO_3^-]}{dt} = \frac{d[Br_2]}{dt}$   
 (c)  $-\frac{d[BrO_3^-]}{dt} = \frac{1}{3} \frac{d[Br_2]}{dt}$                       (d) None of these
11. Consider a reaction  $A(g) \xrightarrow{k=0.1M\text{min}^{-1}} 2B(g)$ . If initial concentration of A is 0.5M then select correct graph.



12. Which of the following statements is incorrect?

- (a) A second order reaction must be a bimolecular elementary reaction
- (b) A bimolecular elementary reaction must be a second order reaction
- (c) Zero order reaction must be a complex reaction
- (d) First order reaction may be complex or elementary reaction

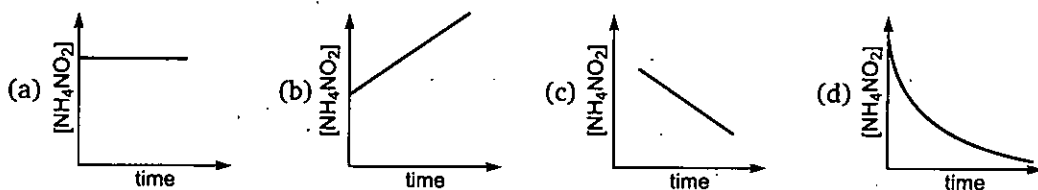
13. The molecularity of a complex reaction given below is :



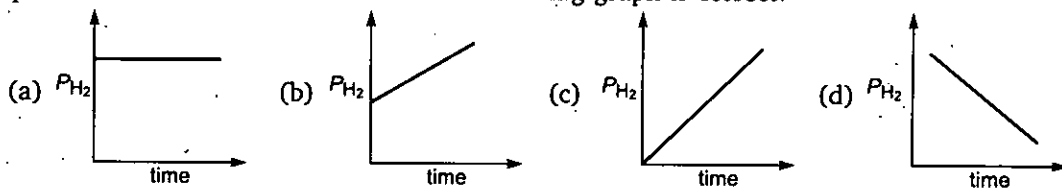
- (a) 1
- (b) 2
- (c) 3
- (d) has no meaning

14. Decomposition of  $\text{NH}_4\text{NO}_2(\text{aq})$  into  $\text{N}_2(\text{g})$  and  $2\text{H}_2\text{O}(\text{l})$  is first order reaction.

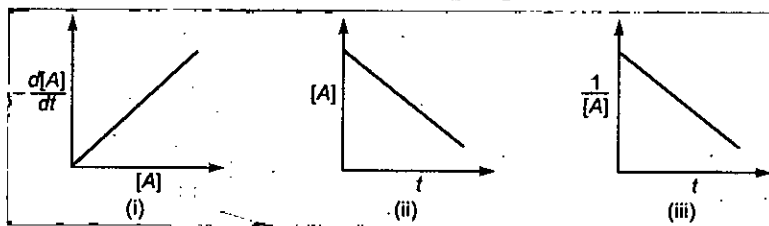
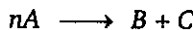
Which of the following graph is correct?



15. Decomposition of  $\text{HI}(\text{g})$  on Gold surface is zero order reaction. Initially few moles of  $\text{H}_2$  are present in container then which of the following graph is correct?



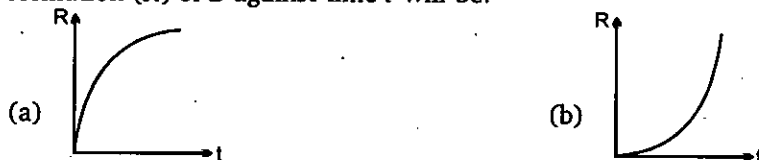
16. Consider the plots for the types of reaction

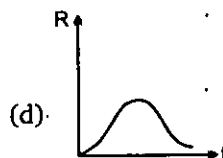
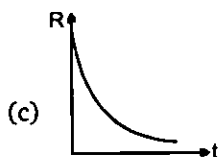


These plots respectively correspond to the reaction orders :

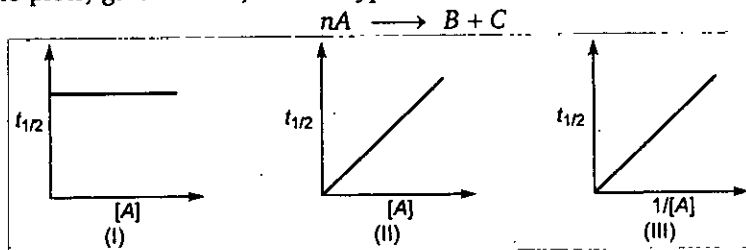
- (a) 0, 2, 1
- (b) 0, 1, 2
- (c) 1, 1, 2
- (d) 1, 0, 2

17. If decomposition reaction  $\text{A}(\text{g}) \longrightarrow \text{B}(\text{g})$  follows first order kinetics then the graph of rate of formation ( $R$ ) of  $B$  against time  $t$  will be:





18. Consider the plots, given below, for the types of reaction



These plots respectively correspond to the reaction orders :

- (a) 0, 1, 2                      (b) 1, 2, 0                      (c) 1, 0, 2                      (d) None of these

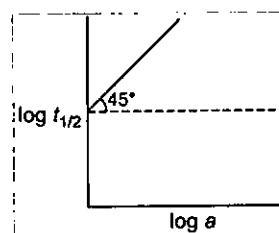
19. For a zero order reaction, the plot of conc.  $(a - x)$  vs time is linear with

- (a) +ve slope and zero intercept                      (b) -ve slope and zero intercept  
(c) +ve slope and non-zero intercept                      (d) -ve slope and non-zero intercept

20. What will be the order of reaction for a chemical change having  $\log t_{1/2}$  vs  $\log a$ ? (where  $a$  = initial concentration of reactant;

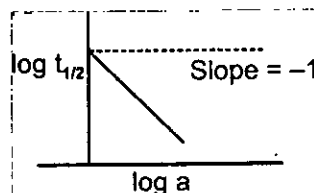
$t_{1/2}$  = half-life)

- (a) Zero order  
(b) First order  
(c) Second order  
(d) None of these

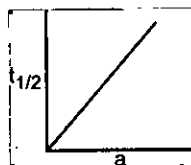


21. A graph between  $\log t_{1/2}$  and  $\log a$  (abscissa),  $a$  being the initial concentration of A in the reaction For reaction  $A \longrightarrow$  Product, the rate law is :

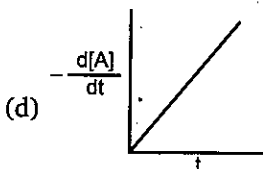
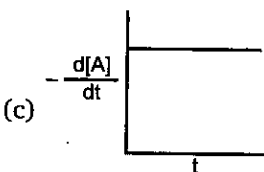
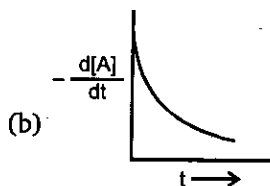
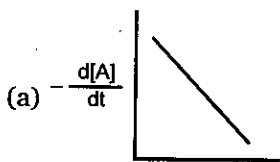
- (a)  $\frac{-d[A]}{dt} = K$                       (b)  $\frac{-d[A]}{dt} = K[A]$   
(c)  $\frac{-d[A]}{dt} = K[A]^2$                       (d)  $\frac{-d[A]}{dt} = K[A]^3$



22. Consider the reaction  $A \longrightarrow B$ , graph between half life ( $t_{1/2}$ ) and initial concentration ( $a$ ) of the reactant is



Hence graph between  $-\frac{d[A]}{dt}$  and time will be:



23. For the ideal gaseous reaction, the rate is generally expressed in terms of  $\frac{dP}{dt}$  instead of  $\frac{dC}{dt}$  or  $\frac{dn}{dt}$  (where  $C = \frac{n}{V}$  is concentration and  $n$  the no. of moles). What is the reaction among these

three expressions if  $T$  and  $V$  are constant?

(a)  $\frac{dC}{dt} = \frac{dn}{dt} = \frac{dP}{dt}$

(b)  $\frac{dC}{dt} = \frac{1}{V} \frac{dn}{dt} = \frac{1}{RT} \left( \frac{dP}{dt} \right)$

(c)  $RT \frac{dC}{dt} = \frac{dn}{dt} = \frac{dP}{dt}$

(d) None of these

24.  $A_2 + B_2 \longrightarrow 2AB$ ; R.O.R. =  $k[A]^a [B]^b$

Initial $[A_2]$	Initial $[B_2]$	R.O.R. ( $r$ ) $M s^{-1}$
0.2	0.2	0.04
0.1	0.4	0.04
0.2	0.4	0.08

Order of reaction with respect to  $A_2$  and  $B_2$  are respectively :

- (a)  $a = 1, b = 1$       (b)  $a = 2, b = 0$       (c)  $a = 2, b = 1$       (d) None

25. For a reaction the initial rate is given as:  $R_0 = k[A]_0^2[B]_0$  by what factor, the initial rate of reaction will increase if initial concentration of  $A$  is taken 1.5 times and of  $B$  is tripled?

- (a) 4.5      (b) 2.25      (c) 6.75      (d) None of these

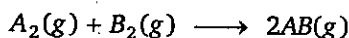
26. For  $A_{(s)} + B_{(s)} \longrightarrow C_{(s)}$ ; rate =  $k[A]^{1/2}[B]^2$ , if initial concentration of  $A$  and  $B$  are increased by factors 4 and 2 respectively, then the initial rate is changed by the factor:

- (a) 4      (b) 6      (c) 8      (d) None of these

27. Reaction  $A \rightarrow B$  follows second order kinetics. Doubling the concentration of  $A$  will increase the rate of formation of  $B$  by a factor of :

- (a) 1/4      (b) 1/2      (c) 2      (d) 4

- 28,29. The reaction of  $A_2$  and  $B_2$  follows the equation



The following data were observed

$[A_2]_0$	$[B_2]_0$	Initial rate of appearance of $AB(g)$ (in $M s^{-1}$ )
0.10	0.10	$2.5 \times 10^{-4}$
0.20	0.10	$5 \times 10^{-4}$
0.20	0.20	$10 \times 10^{-4}$

28. The value of rate constant for the written reaction is:  
 (a)  $2.5 \times 10^{-4}$  (b)  $2.5 \times 10^{-2}$  (c)  $1.25 \times 10^{-2}$  (d) None of these
29. Above given question, the value of rate constant for appearance of  $AB(g)$  is :  
 (a)  $2.5 \times 10^{-4}$  (b)  $2.5 \times 10^{-2}$  (c)  $1.25 \times 10^{-2}$  (d) None of these
30. The following data pertain to reaction between A and B

S. No	[A] mol. L <sup>-1</sup>	[B] mol. L <sup>-1</sup>	Rate mol.L <sup>-1</sup> sec <sup>-1</sup>
I	$1 \times 10^{-2}$	$2 \times 10^{-2}$	$2 \times 10^{-4}$
II	$2 \times 10^{-2}$	$2 \times 10^{-2}$	$4 \times 10^{-4}$
III	$2 \times 10^{-2}$	$4 \times 10^{-2}$	$8 \times 10^{-4}$

Which of the following inference(s) can be drawn from the above data

- (a) Rate constant of the reaction  $10^{-4}$   
 (b) Rate law of the reaction is  $k[A][B]$   
 (c) Rate of reaction increases four times on doubling the concentration of both the reactant,  
 Select the correct answer

codes

- (a) a, b and c (b) a and b (c) b and c (d) c alone

31. The unit of rate constant of elementary reaction depends upon the :  
 (a) temperature of the reaction (b) concentration of reactant  
 (c) activation energy of the reaction (d) molecularity of the reaction

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

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

33. An elementary reaction between A and B is a second order reaction. Which of the following rate equations must be correct?

- (a)  $r = k[A]^2[B]^0$  (b)  $r = k[A]^{3/2}[B]^{1/2}$  (c)  $r = k[A]^0[B]^2$  (d)  $r = k[A][B]$

34. If 'a' is the initial concentration of the reactant, the half-life period of the reaction of  $n^{\text{th}}$  order is inversely proportional to :

- (a)  $a^{n-1}$  (b)  $a^n$  (c)  $a^{1-n}$  (d)  $a^{n+1}$



35. Which of the following expressions is correct for zero order and first order respectively [where  $a$  is initial concentration]?
- (a)  $t_{1/2} \propto a$ ;  $t_{1/2} \propto \frac{1}{a}$  (b)  $t_{1/2} \propto a$ ;  $t_{1/2} \propto a^0$   
 (c)  $t_{1/2} \propto a^0$ ;  $t_{1/2} \propto a$  (d)  $t_{1/2} \propto a$ ;  $t_{1/2} \propto \frac{1}{a^2}$
36. The unit of rate constant of zero order and first order chemical reactions are respectively :
- (a)  $\text{mol L}^{-1} \text{s}^{-1}$ ,  $\text{mol L}^{-1} \text{s}^{-1}$  (b)  $\text{s}^{-1}$ ,  $\text{mol L}^{-1} \text{s}^{-1}$   
 (c)  $\text{mol L}^{-1} \text{s}^{-1}$ ,  $\text{s}^{-1}$  (d) None of these
37. The units of rate of reaction and rate constant are same for a :
- (a) zero order reaction (b) first order reaction  
 (c) second order reaction (d) third order reaction
38.  $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{H}_2\text{O}(\text{l}) \xrightarrow{\text{H}^+(\text{aq})} \text{CH}_3\text{COOH}(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{aq})$ . What type of reaction is this?
- (a) Unimolecular elementary (b) Pseudo first order  
 (c) Zero order (d) Second order
39. When ethyl acetate was hydrolysed in presence of  $0.1 \text{ M HCl}$ , the rate constant was found to be  $5.4 \times 10^{-5} \text{ s}^{-1}$ . But in presence of  $0.1 \text{ M H}_2\text{SO}_4$  the rate constant was found to be  $6.25 \times 10^{-5} \text{ s}^{-1}$ . Thus it may be concluded that :
- (a)  $\text{H}_2\text{SO}_4$  furnishes more  $\text{H}^+$  than  $\text{HCl}$   
 (b)  $\text{H}_2\text{SO}_4$  furnishes less  $\text{H}^+$  than  $\text{HCl}$   
 (c) both have the same strength  
 (d) will depend on concentration of ethyl acetate
40. For an elementary reaction  $2\text{A} + \text{B} \longrightarrow \text{A}_2\text{B}$  if the volume of vessel is quickly reduced to half of it's original volume then rate of reaction will
- (a) unchange  
 (b) increase four times  
 (c) increase eight times  
 (d) decrease eight times
41. In the following reaction  $\text{A} \rightarrow \text{B} + \text{C}$ , rate constant is  $0.001 \text{ Ms}^{-1}$ . If we start with  $1 \text{ M}$  of  $\text{A}$  then conc. of  $\text{A}$  and  $\text{B}$  after 10 minutes are respectively :
- (a)  $0.5 \text{ M}$ ,  $0.5 \text{ M}$  (b)  $0.6 \text{ M}$ ,  $0.4 \text{ M}$  (c)  $0.4 \text{ M}$ ,  $0.6 \text{ M}$  (d) none of these
42. For a reaction  $\text{A} \xrightarrow{k_r=0.6 \text{ M min}^{-1}} 2\text{B}$  starting with  $1 \text{ M}$  of 'A' only, concentration of  $\text{B}$  (in  $\text{M}$ ) after 100 sec. and 200 sec. is respectively ?
- (a) 2 and 4 (b) 1 and 2 (c) 2 and 3 (d) None of these
43. Half-life ( $t_{1/2}$ ) and completion time ( $T$ ) of the above reaction ( $\text{A} \longrightarrow \text{B} + \text{C}$ ) are :
- (a) 500 min, 750 min (b) 500 sec, 750 sec (c) 500 sec, 1000 sec (d) None of these

44. Column I

P Zero order reaction

Q First order reaction

R Second order reactions

S Pseudo unimolecular reaction

Column II

1.  $t_{1/2} \propto \frac{1}{[A]_0}$

2.  $t_{100\%} = [A]_0 / k$

3. Involves at least two reactants

4.  $[A] = [A]_0 e^{-kt}$

Code:

	P	Q	R	S
(a)	2	1	4	2
(b)	2	4	1	3
(c)	2	1	3	4
(d)	3	2	1	4

45. For the zero order reaction  $A \rightarrow B + C$ ; initial concentration of A is 0.1 M. If  $A = 0.08 M$  after 10 minutes, then its half-life and completion time are respectively :

(a) 10 min; 20 min

(b)  $2 \times 10^{-3}$  min;  $4 \times 10^{-3}$  min

(c) 25 min, 50 min

(d) 250 min, 500 min

46. For an elementary reaction,  $X(g) \rightarrow Y(g) + Z(g)$

the half life period is 10 min. In what period of time would the concentration of X be reduced to 10% of original concentration ?

(a) 20 Min.

(b) 33 Min

(c) 15 Min

(d) 25 Min

47. In the presence of an acid, the initial concentration of cane sugar was reduced from 0.20 to 0.10 molar in 5 hours and from 0.2 to 0.05 molar in 10 hours. The reaction is of-

(a) Zero order

(b) First order

(c) Second order

(d) Third order

48. A first order reaction is 75% completed in 100 minutes. How long time will it take for its 87.5% completion?

(a) 125 min

(b) 150 min

(c) 175 min

(d) 200 min

49. The rate constant for a first order reaction whose half life is 480 sec.

(a)  $1.44 \times 10^{-3} \text{ sec}^{-1}$

(b)  $1.44 \times \text{sec}^{-1}$

(c)  $0.72 \times 10^{-3} \text{ sec}^{-3}$

(d)  $2.88 \times 10^{-3} \text{ sec}^{-3}$

50. Rate constant  $k = 2.303 \text{ min}^{-1}$  for a particular reaction. The initial concentration of the reaction is 1 mol/litre then rate of reaction after 1 minute is :

(a)  $2.303 M \text{ min}^{-1}$

(b)  $0.2303 M \text{ min}^{-1}$

(c)  $0.1 M \text{ min}^{-1}$

(d) none of these

51. For the reaction  $3A(g) \xrightarrow{k} B(g) + C(g)$ ,  $k$  is  $10^{-14} \text{ L/mol.min}$ .

if  $[A] = 0.5M$  then the value of  $-\frac{d[A]}{dt}$  (in  $M\text{s}^{-1}$ ) is:

(a)  $7.5 \times 10^{-5}$

(b)  $3 \times 10^{-4}$

(c)  $2.5 \times 10^{-5}$

(d) none of these

52. 99% of a first order reaction was completed in 32 minutes when 99.9% of the reaction will complete :

(a) 50 min

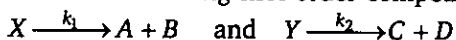
(b) 46 min

(c) 48 min

(d) 49 min

53. Which of the following represents the expression for  $\frac{3}{4}$ th life of first order reaction
- (a)  $\frac{k}{2.303} \log 4/3$       (b)  $\frac{2.303}{k} \log 3/4$       (c)  $\frac{2.303}{k} \log 4$       (d)  $\frac{2.303}{k} \log 3$

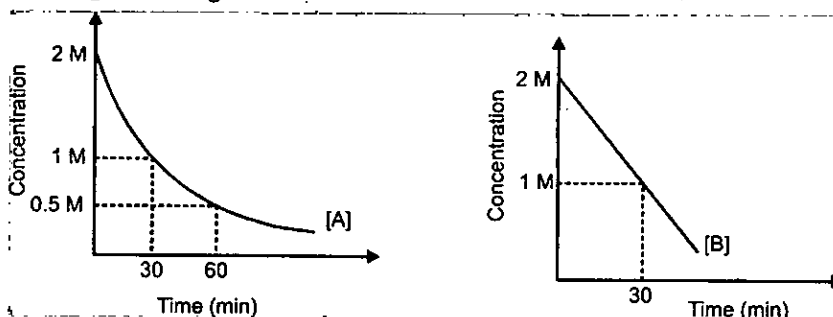
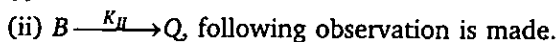
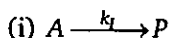
54. Consider the following first order competing reactions:



if 50% of the reaction of X was completed when 96% of the reaction of Y was completed, the ratio of their rate constants ( $k_2 / k_1$ ) is:

- (a) 4.06      (b) 0.215      (c) 1.1      (d) 4.65

55. For the reactions



Calculate  $\frac{k_I}{K_{II}}$ , where  $k_I$  and  $k_{II}$  and rate constant for the respective reaction.

- (a) 2.303      (b) 1      (c) 0.36      (d) 0.693
56. The decomposition of  $N_2O_5$  in chloroform was followed by measuring the volume of  $O_2$  gas evolved :  $2N_2O_5 (CCl_4) \longrightarrow 2N_2O_4 (CCl_4) + O_2(g)$ . The maximum volume of  $O_2$  gas obtained was  $100 \text{ cm}^3$ . In 500 minutes,  $90 \text{ cm}^3$  of  $O_2$  were evolved. The first order rate constant (in  $\text{min}^{-1}$ ) for the disappearance of  $N_2O_5$  is :
- (a)  $\frac{2.303}{500}$       (b)  $\frac{2.303}{500} \log \frac{100}{90}$       (c)  $\frac{2.303}{500} \log \frac{90}{100}$       (d)  $\frac{100}{10 \times 500}$

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

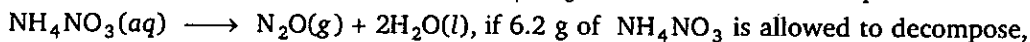
(a)  $k = \frac{1}{t} \ln \left( \frac{P_\infty}{3(P_\infty - P_t)} \right)$

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

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

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

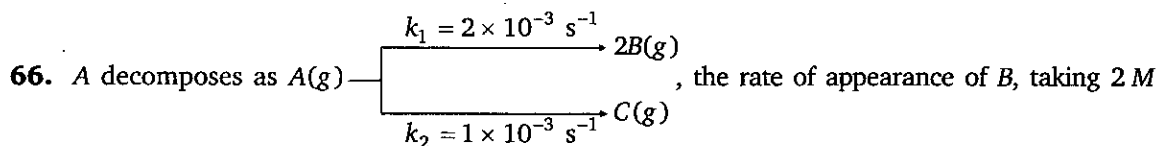
58. The half-life of first order decomposition of  $NH_4NO_3$  is 2.10 hr at 288 K temperature



if 6.2 g of  $NH_4NO_3$  is allowed to decompose, The time required for  $NH_4NO_3$  to decompose 90% and the volume of dry  $N_2O$  produced at this point measured at STP are respectively:

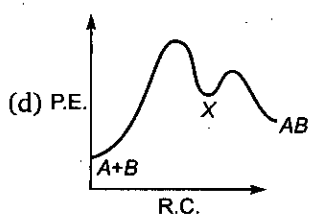
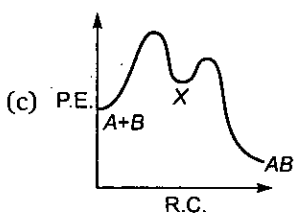
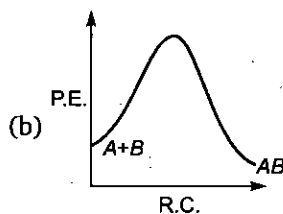
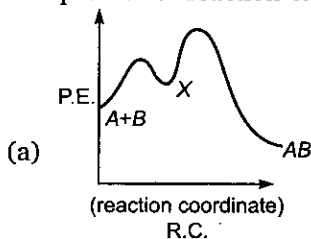
- (a) 6.978 hr, 2.016 L      (b) 0.319 hr, 2.12 L      (c) 0.319 hr, 2.016 L      (d) None of these

59. 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
60. The decomposition of azo methane, at certain temperature according to the equation  
 $(\text{CH}_3)_2\text{N}_2 \longrightarrow \text{C}_2\text{H}_6 + \text{N}_2$  is a first order reaction.  
After 40 minutes from the start, the total pressure developed is found to be 350 mm Hg in place of initial pressure 200 mm Hg of azo methane. The value of rate constant  $k$  is :
- (a)  $2.88 \times 10^{-4} \text{ sec}^{-1}$  (b)  $1.25 \times 10^{-4} \text{ sec}^{-1}$  (c)  $5.77 \times 10^{-4} \text{ sec}^{-1}$  (d) None of these
61. The hydrolysis of sucrose was studied with the help of polarimeter and following data were collected
- |                             |      |      |          |
|-----------------------------|------|------|----------|
| time (min.)                 | : 0  | 70   | $\infty$ |
| observed rotation (degrees) | : 44 | 16.5 | -11      |
- when the reaction mixture will be optically inactive ? (Given:  $\ln 2=0.7$ ,  $\ln 3=1.1$ ,  $\ln 5=1.6$ )  
(a) 16 min. (b) 69.47 min. (c) 160 min. (d) none of these
62. For a particular reaction with initial conc. of the reactants as  $a_1$  and  $a_2$ , the half-life period are  $t_1$  and  $t_2$  respectively. The order of the reaction ( $n$ ) is given by :
- (a)  $n = 1 + \frac{\log (t_2/t_1)}{\log (a_2/a_1)}$  (b)  $n = \frac{\log (t_1/t_2)}{\log (a_2/a_1)}$   
(c)  $n = 1 + \log \frac{(t_1/t_2)}{\log (a_2/a_1)}$  (d) none of these
63. The value of  $\frac{t_{0.875}}{t_{0.50}}$  for  $n^{\text{th}}$  order reaction is
- (a)  $2^{(2n-2)}$  (b)  $2^{(2n-2)-1}$  (c)  $\frac{8^{n-1} - 1}{2^{n-1} - 1}$  (d) None of these
64.  $A \longrightarrow B$  first order reaction  $A$  is optical active and  $B$  is optically inactive, a series of experiment were conducted on a solution of  $A$
- |                  |            |            |           |
|------------------|------------|------------|-----------|
| Time             | 0          | 60 min     | $\infty$  |
| optical rotation | $82^\circ$ | $77^\circ$ | $2^\circ$ |
- Assume some impurity present calculate the optical rotation after 5 hours.  
(Given in  $1.066 = 0.064$ ,  $e^{0.16} = 1.17$ )  
(a) 60 (b) 30 (c) 20 (d) 120
65. At 300 K the half-life of a sample of a gaseous compound initially at 1 atm is 100 sec. When the pressure is 0.5 atm the half-life is 50 sec. The order of reaction is :
- (a) 0 (b) 1 (c) 2 (d) 3

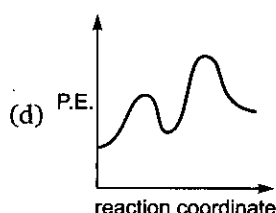
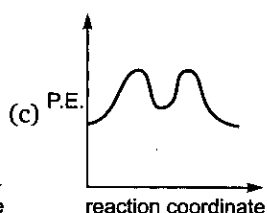
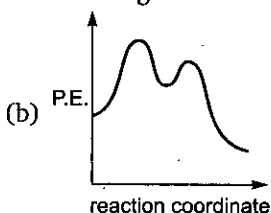
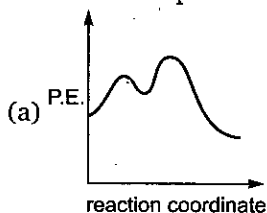


concentration of A, is equal to :

- (a)  $2 \times 10^{-3} \text{ M s}^{-1}$  (b)  $4 \times 10^{-3} \text{ M s}^{-1}$  (c)  $8 \times 10^{-3} \text{ M s}^{-1}$  (d) None of these
67. For an endothermic reaction where  $\Delta H$  represents the enthalpy of reaction in kJ/mol, the minimum value for the energy of activation will be :  
 (a) less than  $\Delta H$  (b) more than  $\Delta H$  (c) equal to  $\Delta H$  (d) zero
68. The activation energy of the reaction,  $A + B \rightarrow C + D + 38 \text{ kcal}$  is 20 kcal, What would be the activation energy of the reaction,  $C + D \rightarrow A + B$   
 (a) 20 kcal (b) -20 kcal (c) 18 kcal (d) 58 kcal
69. When the activation energies of the forward and backward reactions are equal, then:  
 (a)  $\Delta E = 0, \Delta S = 0$  (b)  $\Delta E = 0, \Delta G = 0$  (c)  $\Delta S = 0, \Delta G = 0$  (d) only  $\Delta E = 0$
70. For an exothermic chemical process occurring in two steps as follows  
 (i)  $A + B \rightarrow X$  (slow) (ii)  $X \rightarrow AB$  (fast)  
 The process of reaction can be best describe by:



71. Select the correct diagram for an endothermic reaction that proceeds through two steps, with the second step is rate determining :



72.  $\frac{k_{35^\circ}}{k_{34^\circ}} > 1$ , this means that

- (a) Rate increases with the rise in temperature  
 (b) Rate decreases with rise in temperature  
 (c) rate does not change with rise in temperature  
 (d) None of the above

73. The plot of  $\ln k$  versus  $1/T$  is linear with slope of:

- (a)  $-E_a/R$  (b)  $E_a/R$  (c)  $E_a/2.303 R$  (d)  $-E_a/2.303 R$

74. Rate constant for a chemical reaction takes place at 500K is expressed as  $k = A \cdot e^{-1000}$

The activation energy of the reaction is:

- (a) 100 cal/mol (b) 1000 kcal/mol (c)  $10^4$  kcal/mol (d)  $10^6$  kcal/mol

75. For a complex reaction  $A \xrightarrow{k} \text{products}$

$$E_{a_1} = 180 \text{ kJ/mol}; E_{a_2} = 80 \text{ kJ/mol}; E_{a_3} = 50 \text{ kJ/mol}$$

Overall rate constant  $k$  is related to individual rate constant by the equation  $k = \left( \frac{k_1 \cdot k_2}{k_3} \right)^{2/3}$

Activation energy (kJ/mol) for the overall reaction is :

- (a) 100 (b) 43.44 (c) 150 (d) 140

76. For reaction  $A \longrightarrow B$ , the rate constant  $k_1 = A_1 (e^{-E_{a_1}/RT})$  and for the reaction  $X \longrightarrow Y$ , the rate constant  $k_2 = A_2 (e^{-E_{a_2}/RT})$ . If  $A_1 = 10^9$ ,  $A_2 = 10^{10}$  and  $E_{a_1} = 1200$  cal/mol, then the temperature at which  $k_1 = k_2$  is: (Given;  $R = 2$  cal/K-mol)

- (a) 300K (b)  $300 \times 2.303K$  (c)  $\frac{300}{2.303} K$  (d) None of these

77. The activation energies of the forward and backward reactions in the case of a chemical reaction are 30.5 and 45.4 kJ/mol respectively. The reaction is :

- (a) Exothermic (b) Endothermic  
 (c) Neither exothermic nor endothermic (d) Independent of temperature

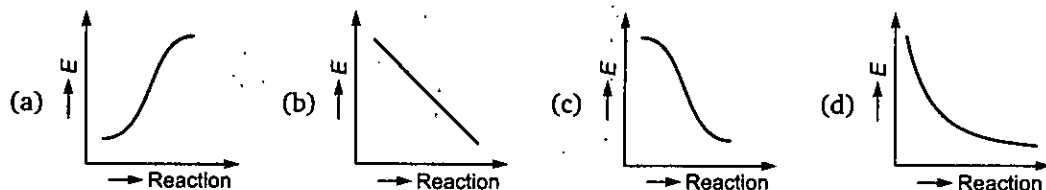
78. A reaction rate constant is given by :  $k = 1.2 \times 10^{14} e^{\frac{-25000}{RT}} \text{ sec}^{-1}$ . It means

- (a)  $\log k$  versus  $\log T$  will give a straight line with a slope as 25000  
 (b)  $\log k$  versus  $\log T$  will give a straight line with a slope as -25000  
 (c)  $\log k$  versus  $T$  will give a straight line with a slope as -25000  
 (d)  $\log k$  versus  $1/T$  will give a straight line

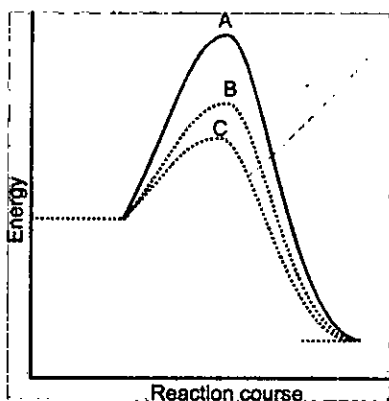
79. The temperature coefficient of a reaction is :

- (a) The rate constant  
 (b) The rate constant at a fixed temperature  
 (c) The ratio of rate constant at two temperature  
 (d) The ratio of rate constant differing by  $10^\circ\text{C}$  preferably  $k_{308}/k_{298}$

80. Which graph shows zero activation energy?



81. A homogeneous catalytic reaction takes place through the three alternative plots A, B and C shown in the given figure which one of the following indicates the relative ease with which the reaction can take place ?



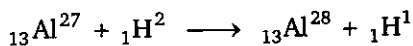
- (a)  $A > B > C$       (b)  $C > B > A$       (c)  $A > C > B$       (d)  $A = B = C$
82. A first order reaction is 50% completed in 20 minutes at  $27^\circ\text{C}$  and in 5 minutes at  $47^\circ\text{C}$ . The energy of activation of the reaction is :
- (a) 43.85 kJ/mol      (b) 55.14 kJ/mol      (c) 11.97 kJ/mol      (d) 6.65 kJ/mol
83. The rate of a reaction gets double when temp changes from  $7^\circ\text{C}$ . By what factor will it change for the temp range  $17^\circ\text{C}$  to  $27^\circ\text{C}$ .
- (a) 1.81      (b) 1.71      (c) 1.91      (d) 1.76
84. Which of the following explains the increase of the reaction rate by catalyst:
- (a) Catalyst decreases the rate of backward reaction so that the rate of forward reaction increases
- (b) Catalyst provides extra energy to reacting molecules so that they may reduce effective collisions
- (c) Catalyst provides an alternative path of lower activation energy to the reactants
- (d) Catalyst increases the number of collisions between the reacting molecules.
85. Collision theory is satisfactory for:
- (a) First order reactions      (b) Zero order reactions
- (c) Bimolecular reactions      (d) Any order reactions
86. For the first order reaction  $A \longrightarrow B + C$ , carried out at  $27^\circ\text{C}$  if  $3.8 \times 10^{-16}\%$  of the reactant molecules exists in the activated state, the  $E_a$  (activation energy) of the reaction is
- (a) 12 kJ/mole      (b) 831.4 kJ/mole      (c) 100 kJ/mole      (d) 88.57 kJ/mole
87. A catalyst lowers the activation energy for a certain reaction from  $83.314$  to  $75 \text{ kJ mol}^{-1}$  at  $500 \text{ K}$ . What will be the rate of reaction as compare to uncatalysed reaction? Assume other things being equal.

- (a) Double                      (b) 28 times                      (c) 7.38 times                      (d)  $7.38 \times 10^3$  times
- 88.** A following mechanism has been proposed for a reaction  
 $2A + B \rightarrow D + E$   
 $A + B \rightarrow C + D$  (slow)  
 $A + C \rightarrow E$  (fast)  
 The rate law expression for the reaction is:  
 (a)  $r = k[A]^2[B]$                       (b)  $r = k[A][B]$                       (c)  $r = k[A]^2$                       (d)  $r = k[A][C]$
- 89.** A hypothetical reaction  $A_2 + B_2 \rightarrow 2AB$  follows the mechanism as given below  
 $A_2 \rightleftharpoons A + A$  (fast)  
 $A + B_2 \rightarrow AB + B$  (slow)  
 $A + B \rightarrow AB$  (fast)  
 The order of the over all reaction is  
 (a) 2                      (b) 1                      (c)  $\frac{3}{2}$                       (d) 0
- 90.** Chemical reaction occurs as a result of collisions between reacting molecules. Therefore, the reaction rate is given by  
 (a) Total number of collisions occurring in a unit volume per second  
 (b) Fraction of molecules which possess energy less than the threshold energy  
 (c) Total number of effective collisions which have enough activation energy  
 (d) none of the above
- 91.** Radioactivity is affected by :  
 (a) temperature                      (b) pressure  
 (c) electric and magnetic field                      (d) none of these
- 92.** The radiation from naturally occurring radioactive substance as seen after deflection by a magnetic field in one direction are :  
 (a)  $\alpha$ -rays                      (b)  $\beta$ -rays  
 (c) both  $\alpha$  and  $\beta$  rays                      (d) either  $\alpha$  or  $\beta$ -rays
- 93.** In the radioactive decay  
 ${}_Z X^A \rightarrow {}_{Z+1} Y^A \xrightarrow{\text{high energy}} {}_{Z-1} Z^{A-4} \xrightarrow{\text{low energy}} {}_{Z-1} Z^{A-4}$  the sequence of the radiation emitted is :  
 (a)  $\alpha, \beta, \gamma$                       (b)  $\gamma, \alpha, \beta$   
 (c)  $\beta, \gamma, \alpha$                       (d)  $\beta, \alpha, \gamma$
- 94.** A radioactive nuclide emits  $\gamma$ -rays due to the :  
 (a) emission of an electron from its orbital  
 (b) nuclear energy transition from a higher state to a lower state  
 (c) presence of less neutrons than protons  
 (d) presence of more neutrons than protons
- 95.** Consider the following decay  ${}_Z X^A \rightarrow {}_{Z+1} Y^A + {}_{-1} e^0$ , X is unstable because :  
 (a) its nucleus has excess energy                      (b)  $\frac{n}{p}$  ratio is high  
 (c)  $\frac{n}{p}$  ratio is low                      (d) none of these



96. Consider the following decay  ${}_Z X^A \rightarrow {}_{Z-1} Y^A + {}_{+1} e^0 (\beta^+)$  X is unstable because :
- (a) it's nucleus has excess energy (b)  $\frac{n}{p}$  ratio is high  
 (c)  $\frac{n}{p}$  ratio is low (d) none of these
97. During  $\alpha$ -decay :
- (a)  $\frac{n}{p}$  ratio decreases (b)  $\frac{n}{p}$  ratio increases  
 (c)  $\frac{n}{p}$  remains constant (d) may increase or decrease
98. Which of the following processes causes the emission of X-ray?
- (a)  $\alpha$ -emission (b)  $\beta$ -emission  
 (c)  $\beta^+$  (Positron emission) (d) electron capture
99. Which of the following processes result in an increase in the atomic number of a nuclide?
- (a)  $\alpha$ -emission (b) electron capture (c)  $\gamma$ -emission (d)  $\beta$ -(Beta)emission
100. .... is produced when a positron and an electron collide.
- (a) X-ray (b) Neutron (c)  $\gamma$ -radiation (d) Neutrino
101.  ${}_{67} \text{Ho}^{165}$  is stable isotope.  ${}_{67} \text{Ho}^{150}$  is expected to disintegrated by:
- (a)  $\alpha$ -emission (b)  $\beta$ -emission (c) positron emission (d)  $\gamma$ -emission
102.  ${}_1 \text{H}^1$  is a stable isotope.  ${}_1 \text{H}^3$  is expected to disintegrated by :
- (a)  $\alpha$ -emission (b)  $\beta$ -emission (c) positron emission (d) proton emission
103. Loss in  $\beta$ -particle is equivalent to :
- (a) increase of one proton only (b) decrease of one neutron only  
 (c) both (a) and (b) (d) none of these
104. Atoms  ${}_7 X^A$ ,  ${}_8 Y^B$  and  ${}_9 Z^{17}$  are such that  ${}_8 Y$  is an isobar of  ${}_7 X$  and atom  ${}_9 Z^{17}$  is isotone of  ${}_8 Y$ . Mass no. of X and no. of neutrons in Y are respectively :
- (a) 8, 8 (b) 17, 7 (c) 9, 8 (d) 16, 8
105.  ${}_{90} \text{Th}^{234}$  disintegrate to give  ${}_{82} \text{Pb}^{206}$  as the final product. Total no. of  $\alpha$  and  $\beta$  particles emitted out during this process are :
- (a) 6 (b) 7 (c) 8 (d) 13
106. An isotone of  ${}_{32} \text{Ge}^{76}$  is :
- (a)  ${}_{32} \text{Ge}^{77}$  (b)  ${}_{33} \text{As}^{77}$  (c)  ${}_{34} \text{Se}^{77}$  (d)  ${}_{36} \text{Se}^{77}$
107. Pair of isobar is :
- (a)  ${}_{6} \text{C}^{13}$ ,  ${}_{7} \text{N}^{13}$  (b)  ${}_{6} \text{C}^{13}$ ,  ${}_{7} \text{N}^{14}$  (c)  ${}_{6} \text{C}^{14}$ ;  ${}_{8} \text{N}^{15}$  (d) none of these
108. Isodiaphers are atoms having:
- (a)  $n/p$  constant (b)  $p/n$  constant (c)  $(n-p)$  constant (d)  $(n-p)$  different
109. The 'Group displacement law' was given by:
- (a) Bacqueral (b) Rutherford (c) Madam Curie (d) Soddy and Fajan
110.  ${}_3 \text{Li}^7 + {}_1 p^1 \rightarrow X$ ; Identify X if reaction is  $(p, \alpha)$  type.
- (a)  ${}_4 \text{Be}^8$  (b)  ${}_2 \text{He}^4$  (c)  ${}_0 \gamma^0$  (d) none of these

111. Identify reaction type:



- (a) (d, p)                      (b) (p, p)                      (c) (p, d)                      (d) none of these
112.  ${}_{13}\text{Al}^{27} + {}_1\text{P}^1 \longrightarrow X + {}_0\gamma^0$ ; Identify X if reaction is (p,  $\gamma$ ) type artificial radioactive reaction.  
 (a)  ${}_{13}\text{Al}^{28}$                       (b)  ${}_{14}\text{Si}^{27}$                       (c)  ${}_{14}\text{Si}^{28}$                       (d) none of these
113. The number of neutrons accompanying in the formation of  ${}_{54}\text{X}^{139}$  and  ${}_{38}\text{Sr}^{194}$  from the absorption of slow neutron by  ${}_{92}\text{U}^{235}$  followed by nuclear fission is :  
 (a) 0                      (b) 1                      (c) 2                      (d) 3
114. What will be the product of reaction  ${}_{101}\text{Md}^{255}$  ( $\alpha$ , 2n) ?  
 (a)  ${}_{103}\text{Lr}^{256}$                       (b)  ${}_{102}\text{No}^{257}$                       (c)  ${}_{103}\text{Lr}^{257}$                       (d)  ${}_{82}\text{Pb}^{205}$
115. Complete the following nuclear equation by supplying the symbol for the other product of the fission :  
 ${}_{92}\text{U}^{235} + {}_0n^1 \longrightarrow {}_{38}\text{Sr}^{94} + \dots\dots\dots + 2{}_0n^1$   
 (a)  ${}_{54}\text{Xe}^{139}$                       (b)  ${}_{54}\text{Xe}^{140}$                       (c)  ${}_{64}\text{Gd}^{104}$                       (d) none of these
116.  ${}_{92}\text{U}^{235} + {}_0n^1 \longrightarrow {}_{56}\text{Ba}^{139} + {}_{36}\text{Kr}^{94} + 3{}_0n^1 + 200\text{MeV}$   
 Total energy released (in MeV) after 5<sup>th</sup> stage of fission is  
 (a) 48600                      (b) 16200                      (c) 24200                      (d) None of these
117. Proton bombardment of  $\text{Th}^{230}$  followed by emission of two alpha particles produce :  
 (a)  $\text{Rn}^{232}$                       (b)  $\text{Ra}^{233}$                       (c)  $\text{Fr}^{223}$                       (d)  $\text{Fr}^{222}$
118.  ${}_{84}\text{Po}^{210} \longrightarrow {}_{82}\text{Pb}^{206} + {}_2\text{He}^4$ . In this reaction predict the position of group of Po when Pb is in the IV B group :  
 (a) II B                      (b) IV B                      (c) VI A                      (d) VI B
119.  ${}_{90}\text{Th}$  is a member of III group on losing  $\alpha$ -particle forms a new elements belonging to :  
 (a) I group                      (b) II group                      (c) III group                      (d) IV group
120. Alpha decay of  ${}_{92}\text{U}^{238}$  forms  ${}_{90}\text{Th}^{234}$ . What kind of decay from  ${}_{90}\text{Th}^{234}$  produces  ${}_{89}\text{Ac}^{234}$  ?  
 (a)  $\alpha$                       (b)  $\beta$                       (c)  $\beta^+$  (positron)                      (d)  $\gamma$ -emission
121.  ${}_{83}\text{Bi}^{214}$  decays to A by  $\alpha$ -emission; A then decays to B by beta emission, which decays to C by another beta emission. Element C decays to D by still another beta emission, and D decays by  $\alpha$ -emission to a stable isotope E. What is an element E?  
 (a)  ${}_{81}\text{Tl}^{207}$                       (b)  ${}_{80}\text{Hg}^{206}$                       (c)  ${}_{79}\text{Au}^{206}$                       (d)  ${}_{82}\text{Pb}^{206}$
122. The activity of a radioactive nuclide ( $\text{X}^{100}$ ) is 6.023 curie at a certain time 't'. If its disintegration constant is  $3.7 \times 10^4 \text{ s}^{-1}$  the mass of X after t sec is :  
 (a)  $6.022 \times 10^6 \text{ g}$                       (b)  $10^{-13} \text{ g}$                       (c)  $10^{-15} \text{ g}$                       (d)  $10^{-17} \text{ g}$
123. Activity of a radioactive substance is  $A_1$  at time  $t_1$  and  $A_2$  at time  $t_2$  ( $t_2 > t_1$ ), then the ratio of  $\frac{A_2}{A_1}$  is :  
 (a)  $e^{\lambda(t_2 + t_1)}$                       (b)  $e^{\lambda(t_1 - t_2)}$                       (c)  $e^{-\lambda(t_1 + t_2)}$                       (d)  $\frac{t_2}{t_1}$

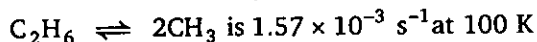
124. The half-life of  ${}^6\text{C}^{14}$  is 5730 year. What fraction of it's original  $\text{C}^{14}$  would left after 22920 year of storage?  
 (a) 0.50 (b) 0.25 (c) 0.125 (d) 0.0625
125. A radioactive sample had an initial activity of 56 dpm. After 69.3 minutes, it was found to have an activity of 28 dpm. Find the number of atoms in a sample having an activity of 100 dpm.  
 (a) 693 (b) 100 (c) 1000 (d) 10,000
126. A radioactive sample has initial activity of 28 dpm 30 minutes later its activity 14 dpm. How many atoms of nuclide were present initially?  
 (a) 2800 (b) 1217 (c) 528 (d) 2802
127. The half-life of  $\text{Co}^{60}$  is 5.27 year ( $\lambda = 2.5 \times 10^{-7} \text{ min}^{-1}$ ). The activity of 2.09 of the sample is nearly :  
 (a)  $5 \times 10^5$  dpm (b)  $2.5 \times 10^{10}$  dpm (c)  $5 \times 10^{10}$  dpm (d)  $10^{10}$  dpm
128. Half-life ( $t_{1/2}$ ) for a radioactive decay is 6930 sec. The time required to fall the rate of decay by  $\left(\frac{1}{100}\right)^{\text{th}}$  of it's initial value is :  
 (a) 69.3 sec (b) 20,000 sec (c) 23030 sec (d) none of these
129. A sample of radioactive substance is found 90% of it's initial amount after one day. What % of the original sample can be found after 3 days?  
 (a) 81 (b) 72.9 (c) 25 (d) 65.61
130. If time  $t$  is required for a radioactive substance to become one third of it's initial amount, what fraction would be left after  $0.5 t$ ?  
 (a)  $\frac{1}{2}$  (b)  $\frac{1}{\sqrt{3}}$  (c)  $\frac{1}{3}$  (d)  $\sqrt{\frac{2}{3}}$
131. The present activity of the hair of Egypt mummy is 1.75 dpm.  $t_{1/2}$  of  ${}^6\text{C}^{14}$  is 5770 year and disintegration rate of fresh sample of  $\text{C}^{14}$  is 14 dpm. Find out age of mummy.  
 (a) 23080 year (b) 138480 year (c) 11998.3 year (d) 17313.6 year
132. The amount of  ${}^6\text{C}^{14}$  isotope in a piece of wood is found to one fourth ( $1/4$ ) of that present in a fresh piece of wood. Calculate the age of the piece of wood ( $t_{1/2}$  of  ${}^6\text{C}^{14} = 5770$  years)  
 (a) 7999 year (b) 11540 year (c) 16320 year (d) 23080 year
133. A radioactive element undergoing decay is left 20% of it's initial weight after certain period of time  $t$ , how many such periods should elapse from the start for the 50% of the element to be left over?  
 (a) 3 (b) 4 (c) 5 (d) None of these
134. In a sample of wood, the reading of a counter is 32 dpm and in a fresh sample of tree it is 122dpm. Due to error counter gives the reading 2 dpm in absence of  ${}^{14}\text{C}$ . Half life of  ${}^{14}\text{C}$  is 5770 years.  
 The approximate age (in years) of wood sample is:  
 (a) 7997.2 (b) 57570 (c) 11,540 (d) 15140
135. A 0.50g sample of rock was found to have  $2.5 \times 10^{-6}$  mol of  ${}^{40}_{19}\text{K}$  ( $t_{1/2} = 1.3 \times 10^9$  yr) and  $7.5 \times 10^{-6}$  mol of  ${}^{40}_{20}\text{Ca}$ . How old is the rock ?  
 (a)  $6.5 \times 10^8$  yr (b)  $1.3 \times 10^9$  yr (c)  $2.6 \times 10^9$  yr (d)  $5.2 \times 10^9$  yr

136. Indium-112 is radioactive and has a very short half-life ( $t_{1/2} = 14$  min). Its decay constant and average life are respectively :
- (a)  $0.0495 \text{ min}^{-1}$ , 9.7 min (b)  $0.495 \text{ min}^{-1}$ , 20.2 min  
(c)  $9.7 \text{ min}^{-1}$ , 20.2 min (d) 0.0495, 20.2 min
137. The half-life of radioactive element is 100 minutes. The time interval between the stages to 50% and 87.5% decay will be :
- (a) 100 min (b) 50 min (c) 200 min (d) 25 min
138. The half-life of  $\text{Tc}^{99}$  is 6.0 hr. The total residual activity in a patient 30 hr after receiving an injection containing  $\text{Tc}^{99}$  must be more than  $0.01 \mu\text{Ci}$ . What is the maximum activity (in  $\mu\text{Ci}$ ) that the sample injected an have?
- (a) 0.16 (b) 0.32 (c) 0.64 (d) 0.08
139. A pure radio-chemical preparation was observed to disintegrate at the rate of 2140 counts/minutes at 12.35 PM. At 3.55 PM. of the same day, the disintegration rate of the sample was only 535 count/minutes. What is the half-life of the material?
- (a) 50 min (b) 100 min (c) 200 min (d) None of these
140. A certain radioactive isotope  ${}_Z X^A$  ( $t_{1/2} = 100$  days) decays to  ${}_{Z-2} Y^{A-8}$ . If 1 mole of  ${}_Z X^A$  is kept in sealed container, how much He gas will accumulate at STP in 200 days?
- (a) 11.2 litre (b) 33.6 litre (c) 22.4 litre (d) 44.8 litre
141. A radioactive substance decay 25% in 10 minute. If at start there are  $4 \times 10^{20}$  atoms present, after what time will the number of atoms be reduced to  $10^{20}$  atoms? (given  $\ln 3 = 1.098$ )
- (a) 10.98 min (b) 21.97 min (c) 48.19 min (d) None of these
142. The time of decay for a nuclear reaction is given by  $t = 4 t_{1/2}$ . The relation between the mean life ( $T$ ) and time of decay ( $t$ ) is given by :
- (a)  $2 T \ln 2$  (b)  $4 T \ln 2$  (c)  $2 T^4 \ln 2$  (d)  $\frac{1}{T^2} \ln 2$
143. Two radio isotopes A and B of atomic weight X and Y are mixed in equal amount by weight. After 20 days, their weight ratio is found to be 4 : 1. Isotope A has a half-life of 1 day. The half-life of isotope B is :
- (a)  $1.11 \frac{Y}{X}$  day (b)  $0.11 \frac{X}{Y}$  day (c) 0.6237 day (d) 1.11 day
144. Two radioactive nuclides A and B have half-lives 50 min and 10 min respectively. A fresh sample contains the nuclide of B to be eight time that of A. How much time should elapse so that the number of nuclides of A becomes double of B?
- (a) 30 (b) 40 (c) 50 (d) 100
145. A radioactive nuclide is produced at a constant rate of  $\alpha$  per second. It's decay constant is  $\lambda$ . If  $N_0$  be the no. of nuclei at time  $t = 0$ , then max. no. of nuclei possible are :
- (a)  $N_0$  (b)  $\alpha/\lambda$  (c)  $N_0 + \frac{\alpha}{\lambda}$  (d)  $\frac{\lambda}{\sigma} + N_0 s$
146. An analysis of the rock shows that the relative number of  $\text{Sr}^{87}$  and  $\text{Rb}^{87}$  ( $t_{1/2} = 4.7 \times 10^{10}$  year) atoms is 0.05. What is the age of the rock? Assume all  $\text{Sr}^{87}$  to be formed from  $\text{Rb}^{87}$  only.
- (a)  $7.62 \times 10^9$  year (b)  $1.43 \times 10^9$  year  
(c)  $3.28 \times 10^9$  year (d)  $4.32 \times 10^8$  year



# Level 2

1. The forward rate constant for the elementary reversible gaseous reaction



What is the rate constant for the backward reaction at this temperature if  $10^{-4}$  moles of  $\text{CH}_3$  and 10 moles of  $\text{C}_2\text{H}_6$  are present in a 10 litre vessel at equilibrium.

- (a)  $1.57 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  (b)  $1.57 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$   
 (c)  $1.57 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$  (d)  $1.57 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$
2. For a hypothetical reaction,



If these reactions are carried simultaneously in a reactor such that temperature is not changing. If rate of disappearance of B is  $y \text{ M sec}^{-1}$  then rate of formation (in  $\text{M sec}^{-1}$ ) of Q is:

- (a)  $\frac{2}{3}y$  (b)  $\frac{3}{2}y$  (c)  $\frac{4}{3}y$  (d)  $\frac{3}{4}y$
3. The kinetic data for the given reaction  $A(g) + 2B(g) \xrightarrow{k} C(g)$  is provided in the following table for three experiments at 300 K

Ex. No.	[A/M]	[B/M]	Initial rate ( $\text{M sec}^{-1}$ )
1.	0.01	0.01	$6.930 \times 10^{-6}$
2.	0.02	0.01	$1.386 \times 10^{-5}$
3.	0.02	0.02	$1.386 \times 10^{-5}$

In another experiment starting with initial concentration of 0.5 and 1 M respectively for A and B at 300 K, find the rate of reaction after 50 minutes from start of experiment (in  $\text{M/sec}$ ).

- (a)  $6.93 \times 10^{-4}$ , (b)  $0.25 \times 10^{-7}$  (c)  $4.33 \times 10^{-5}$  (d)  $3.46 \times 10^{-4}$
4. The reaction  $A(g) + 2B(g) \longrightarrow C(g)$  is an elementary reaction. In an experiment involving this reaction, the initial partial pressures of A and B are  $P_A = 0.40 \text{ atm}$  and  $P_B = 1.0 \text{ atm}$  respectively. When  $P_C = 0.3 \text{ atm}$ , the rate of the reaction relative to the initial rate is:
- (a)  $\frac{1}{12}$  (b)  $\frac{1}{50}$  (c)  $\frac{1}{25}$  (d) none of these
5. Which of the following is incorrect statement ?
- (a) Stoichiometry of a reaction tells about the order of the elementary reactions  
 (b) For a zero order reaction, rate and the rate constant are identical.  
 (c) A zero order reaction is controlled by factors other than concentration of reactants  
 (d) A zero order reaction is an elementary reaction

6. Two first order reaction have half-lives in the ratio 8 : 1. Calculate the ratio of time intervals  $t_1 : t_2$ . The time  $t_1$  and  $t_2$  are the time period for  $\left(\frac{1}{4}\right)^{\text{th}}$  and  $\left(\frac{3}{4}\right)^{\text{th}}$  completion.

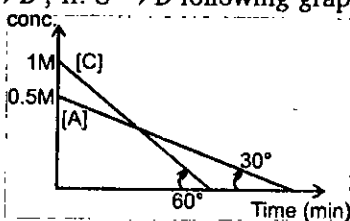
(a) 1 : 0.301                      (b) 0.125 : 0.602                      (c) 1 : 602                      (d) none of these

7. Reaction  $A + B \longrightarrow C + D$  follows rate law,  $r = k[A]^{1/2} [B]^{1/2}$  starting with 1 M of A and B each. What is the time taken for concentration of A become 0.1 M?

[Given  $k = 2.303 \times 10^{-2} \text{ sec}^{-1}$ ].

(a) 10 sec                      (b) 100 sec                      (c) 1000 sec                      (d) 434 sec

8. For the two reactions I:  $A \rightarrow B$ ; II:  $C \rightarrow D$  following graph is obtained.



Which of the following is true:

(a) If  $[B] = [A]$  then at that time  $[B] < [D]$                       (b) If  $[C] = [A]$  then at that time  $[B] > [D]$

(c)  $(t_{100\%})_{\text{Reaction I}} : (t_{100\%})_{\text{Reaction II}}$                       (d)  $[A] = [C]$  at  $t = \frac{\sqrt{3}}{2}$  min.

9. The reaction  $A(g) \longrightarrow B(g) + 2C(g)$  is a first order reaction with rate constant  $2.772 \times 10^{-3} \text{ s}^{-1}$ . 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 at 300 K.

(a) 0.0125 M                      (b) 0.025 M                      (c) 0.05 M                      (d) none of these

10. For a first order homogeneous gaseous reaction,  $A \longrightarrow 2B + C$

If the total pressure after time  $t$  was  $P_t$  and after long time ( $t \rightarrow \infty$ ) was  $P_\infty$  then  $k$  in terms of  $P_t$ ,  $P_\infty$  and  $t$  is :

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

(c)  $k = \frac{2.303}{t} \log \left( \frac{2P_\infty}{3(P_\infty - P_t)} \right)$                       (d) none of these

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

Time                       $t$                        $\infty$

moles of reagent     $n_1$                        $n_2$

Reaction progress is measure with the help of titration of reagent 'R'. If all A, B and C reacted with reagent and have 'n' factors [n factor; eq. wt. =  $\frac{\text{mol. wt.}}{n}$ ] in the ratio of 1 : 2 : 3 with the

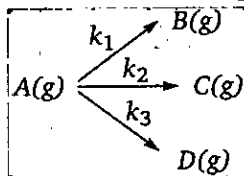
reagent. The  $k$  in terms of  $t$ ,  $n_1$  and  $n_2$  is :

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

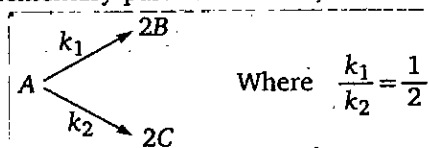
$$(c) k = \frac{1}{t} \ln \left( \frac{4n_2}{n_2 - n_1} \right)$$

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

12. The gaseous decomposition reaction,  $A(g) \longrightarrow 2B(g) + C(g)$  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  $\text{hr}^{-1}$ ) is : [Given : vapour pressure of  $\text{H}_2\text{O}$  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) none of these
13. The reaction, Sucrose  $\xrightarrow{\text{H}^+}$  Glucose + Fructose, takes place at certain temperature while the volume of solution is maintained at 1 litre. At time zero the initial rotation of the mixture is 34°. After 30 minutes the total rotation of solution is 19° and after a very long time, the total rotation is -11°. Find the time when solution was optically inactive.  
 (a) 135 min (b) 103.7 min (c) 38.7 min (d) 45 min
14. A gaseous compound A reacts by three independent first order processes (as shown in figure) with rate constant  $2 \times 10^{-3}$ ,  $3 \times 10^{-3}$  and  $1.93 \times 10^{-3} \text{sec}^{-1}$  for products B, C and D respectively. If initially pure A was taken in a closed container with  $P = 8 \text{ atm}$ , then the partial pressure of B (in atm) after 100 sec from start of experiment.



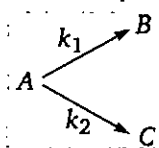
- (a) 0.288 (b) 0.577 (c) 1.154 (d) none of these
15. A compound A dissociate by two parallel first order paths at certain temperature
- $$A(g) \xrightarrow{k_1(\text{min}^{-1})} 2B(g) \quad k_1 = 6.93 \times 10^{-3} \text{ min}^{-1}$$
- $$A(g) \xrightarrow{k_2(\text{min}^{-1})} C(g) \quad k_2 = 6.93 \times 10^{-3} \text{ min}^{-1}$$
- The reaction 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?  
 (a) 1.25 (b) 0.75 (c) 1.50 (d) 2.50
16. For given hypothetical elementary parallel reaction,



- Initially only 2 moles of A are present. The total no. of moles of A, B and C at the end of 75% reaction are:  
 (a) 2 (b) 3 (c) 4 (d) 3.5



17. The reaction  $\text{cis-X} \xrightleftharpoons[k_b]{k_f} \text{trans-X}$  is first order in both directions. At 25°C, the equilibrium constant is 0.10 and the rate constant  $k_f = 3 \times 10^{-4} \text{ s}^{-1}$ . In an experiment starting with the pure *cis*-form, how long would it take for half of the equilibrium amount of the *trans*-isomer to be formed?  
 (a) 150 sec (b) 200 sec (c) 240 sec (d) 210 sec
18. 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 with same frequency factor, the temperature required is 400 K. What is the activation energy of the reaction, if the catalyst lowers the activation energy barrier by 16 kJ/mol?  
 (a) 100 kJ/mol (b) 80 kJ/mol (c) 60 kJ/mol (d) None of these
19. Consider the reaction.

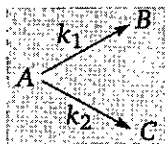


- The rate constant for two parallel reactions were found to be  $10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $4 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . If the corresponding energies of activation of the parallel reaction are 100 and 120 kJ/mol respectively, what is the net energy of activation ( $E_a$ ) of A?  
 (a) 100 kJ/mol (b) 120 kJ/mol (c) 116 kJ/mol (d) 220 kJ/mol
20. A reaction takes place in various steps. The rate constant for first, second, third and fifth steps are  $k_1, k_2, k_3$  and  $k_5$  respectively. The overall rate constant is given by

$$k = \frac{k_2}{k_3} \left( \frac{k_1}{k_5} \right)^{1/2}$$

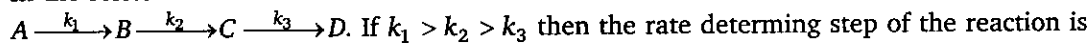
if activation energy are 40, 60, 50 and 10 kJ/mol respectively, the overall energy of activation (kJ/mol) is :

- (a) 10 (b) 20 (c) 25 (d) none of these
21. For reaction  $A \longrightarrow B$ , the rate constant  $k_1 = A_1 e^{-E_{a1}/(RT)}$  and for the reaction  $X \longrightarrow Y$ , the rate constant  $k_2 = A_2 e^{-E_{a2}/(RT)}$ . If  $A_1 = 10^8$ ,  $A_2 = 10^{10}$  and  $E_{a1} = 600 \text{ cal/mol}$ ,  $E_{a2} = 1800 \text{ cal/mol}$ , then the temperature at which  $k_1 = k_2$  is (Given :  $R = 2 \text{ cal/K}\cdot\text{mol}$ )  
 (a) 1200 K (b)  $1200 \times 4.606 \text{ K}$  (c)  $\frac{1200}{4.606} \text{ K}$  (d)  $\frac{600}{4.606} \text{ K}$
22. For first order parallel reaction  $k_1$  and  $k_2$  are 4 and  $2 \text{ min}^{-1}$  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 at which B and C will be obtained in equimolar ratio is :

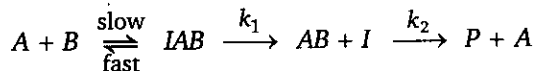


- (a) 757.48 K      (b) 378.74 K      (c) 600 K      (d) none of these

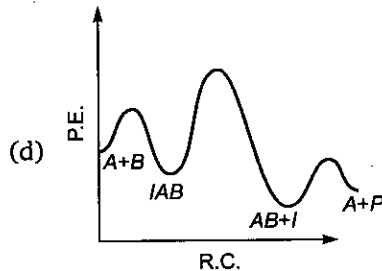
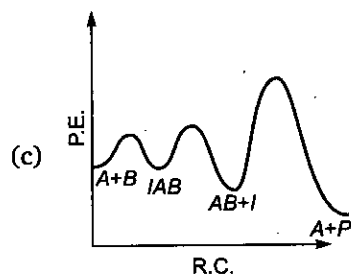
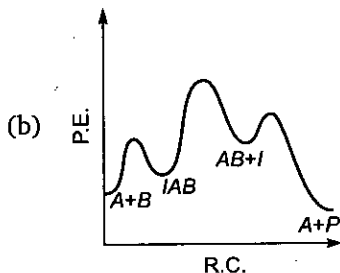
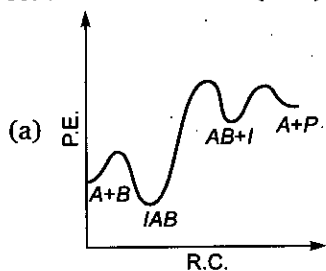
23. In the series reaction



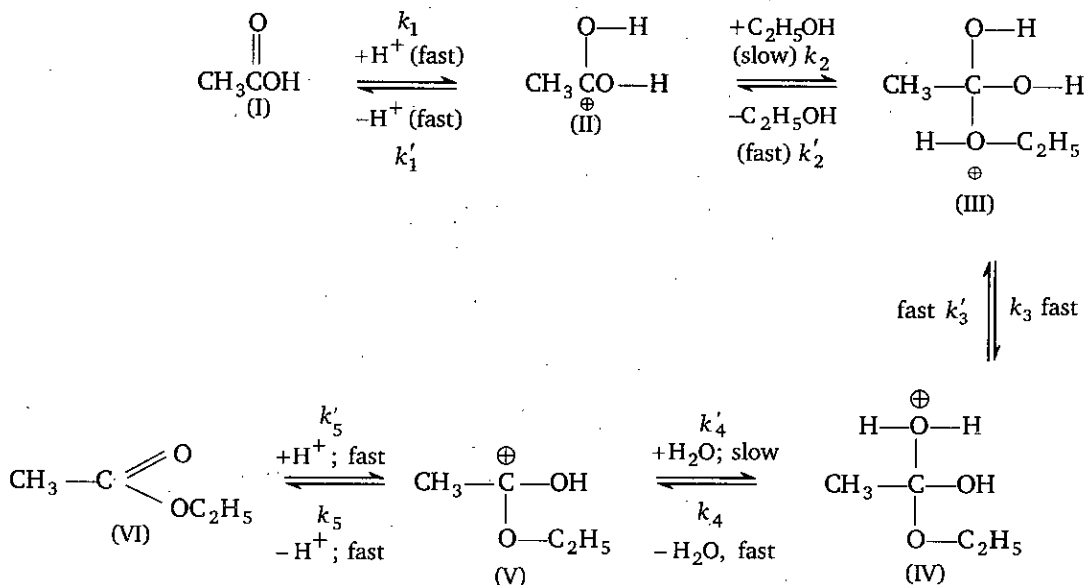
- (a)  $A \rightarrow B$       (b)  $C \rightarrow D$   
 (c)  $B \rightarrow C$       (d) Any step
24. The following mechanism has been proposed for the exothermic catalyzed complex reaction



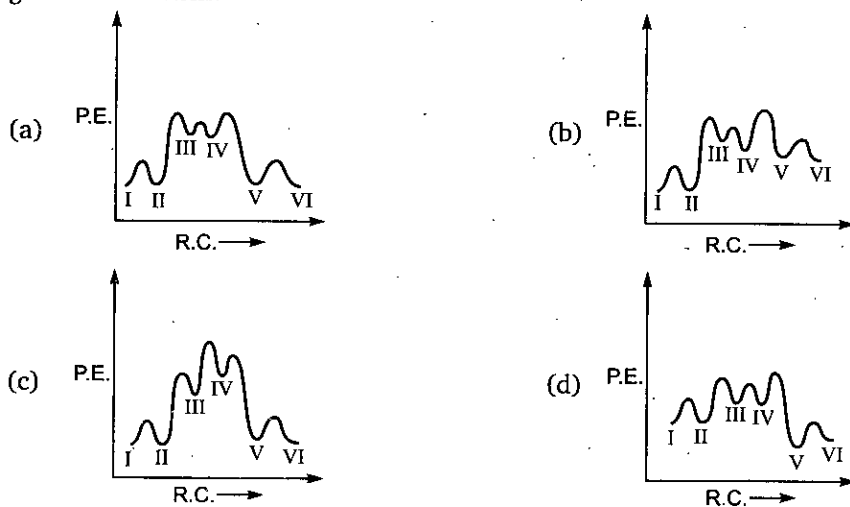
If  $k_1$  is much smaller than  $k_2$ , the most suitable qualitative plot of potential energy (P.E.) versus reaction co-ordinate (R.C.) for the above reaction



25. The mechanism of esterification in presence of acid catalyst ( $\text{H}_2\text{SO}_4$ ) is proposed as follows :



Which of the following potential energy Vs reaction co-ordinate diagram is consistent with given mechanism?

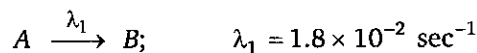


26. For the first order reaction  $A \longrightarrow B + C$ , carried out at  $27^\circ\text{C}$  if  $3.8 \times 10^{-16}\%$  of the reactant molecules exists in the activated state, the  $E_a$  (activation energy) of the reaction is :
- (a) 12 kJ/mol      (b) 831.4 kJ/mol      (c) 100 kJ/mol      (d) 88.57 kJ/mol
27. Upon irradiating californium with neutrons, a scientist discovered a new nuclide having mass number of 250 and a half-life of 30 min. After 90 min. of irradiation, the observed radioactivity due to nuclide was 100 dis/min. How many atoms of the nuclide were prepared initially?
- (a)  $2.4 \times 10^4$       (b)  $3.46 \times 10^4$       (c) 1900      (d) 800

28. A radioactive isotope  $X$  with half-life of  $6.93 \times 10^9$  years decay to  $Y$  which is stable. A sample of rock from the moon was found to contain both the elements  $X$  and  $Y$  in the mole ratio 1 : 7. What is the age of the rock?

- (a)  $2.079 \times 10^{10}$  years (b)  $1.94 \times 10^{10}$  years  
(c)  $1.33 \times 10^9$  years (d)  $10^{10}$  years

29. The average (mean) life of a radio nuclide which decays by parallel path is



- (a) 52.63 sec (b) 500 sec (c) 50 sec (d) none of these

30. The radioactive decay  ${}_{83}\text{Bi}^{211} \longrightarrow {}_{81}\text{Tl}^{207}$ , takes place in 100 L closed vessel at  $27^\circ\text{C}$ . Starting with 2 moles of  ${}_{83}\text{Bi}^{211}$  ( $t_{1/2} = 130$  sec), the pressure development in the vessel after 520 sec will be :

- (a) 1.875 atm (b) 0.2155 atm (c) 0.4618 atm (d) 4.618 atm

31. A fresh radioactive mixture containing short lives species  $A$  and  $B$ . Both emitting  $\alpha$ -particles initially of 8000  $\alpha$ -particles per minute. 20 minutes later, they emits at the rate of 3500  $\alpha$ -particles per minute. If the half-lives of the species  $A$  and  $B$  are 10 minutes and 500 hours respectively, then the ratio of activities of  $A : B$  in the initial mixture was :

- (a) 4 : 6 (b) 6 : 4 (c) 3 : 4 (d) 3 : 1

32. In order to determine the volume of blood in an animal, a 1.0 mL sample of solution of  $10^3$  dpm of  ${}^3\text{H}$  is injected into the animal blood stream. After sufficient time for circulatory equilibrium to be established, 2 mL of blood is found to have activity to 10 dpm. The volume of blood in animal is :

- (a) 199 mL (b) 198 mL (c) 200 mL (d) 20 mL

33. The ratio of activities of two radio nuclides  $X$  and  $Y$  in a mixture at time  $t = 0$  was found to be 4 : 1. After two hours, the ratio of activities become 1 : 1. If the  $t_{1/2}$  of radio nuclide  $X$  is 20 min then  $t_{1/2}$  [in minutes] of radio nuclide  $Y$  is :

- (a) 10 (b) 20 (c) 30 (d) 40

34. Find the age of an ancient Egyptian wooden article (in years) from the given information.

- (i) Activity of 1 g of carbon obtained from ancient wooden article = 7 counts/min/g  
(ii) Activity of 1 g carbon obtained from fresh wooden sample = 15.4 counts per min/g  
(iii) Percentage increase in level of  $\text{C}^{14}$  due to nuclear explosions in past 100 years is 10%  
(iv)  $t_{1/2}$  of  ${}^6\text{C}^{14} = 5770$  years

- (a)  $5.770 \times 10^3$  (b)  $16.87 \times 10^3$  (c) 2488 (d) none of these

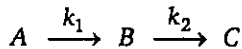
35. The isotopes  ${}^{238}\text{U}$  and  ${}^{235}\text{U}$  occur in nature in the weight ratio 140 : 1. It is assumed that initially they were found in equal weight. If half life ( $t_{1/2}$ ) of  ${}^{238}\text{U} = 4.5 \times 10^9$  and  $t_{1/2}$  of  ${}^{235}\text{U} = 5 \times 10^8$  year respectively then the age of earth is ( $\log 7 = 0.846$ ;  $\log 2 = 0.3$ )

- (a)  $4.02 \times 10^9$  year (b)  $2.01 \times 10^9$  year (c)  $8.72 \times 10^9$  year (d) None of these

# Level 3

## PASSAGE 1

Two consecutive irreversible first order reactions can be represented by



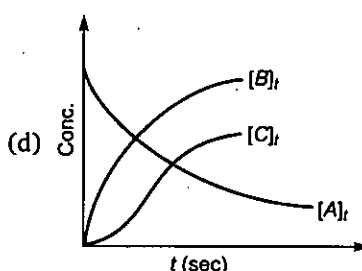
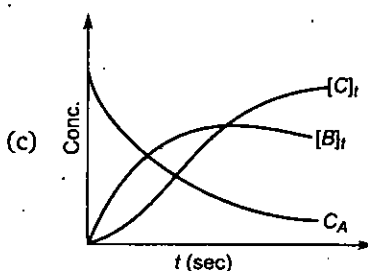
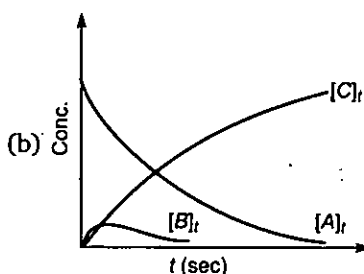
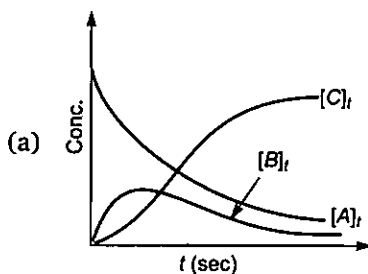
The rate equation for  $A$  is readily integrated to obtain

$$[A]_t = [A]_0 \cdot e^{-k_1 t}; \text{ and } [B]_t = \frac{k_1 [A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

1. At what time will  $B$  be present in greatest concentration?

- (a)  $\frac{k_1}{k_2 - k_1}$       (b)  $\frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$       (c)  $\frac{1}{k_2 - k_1} \ln \frac{k_1}{k_2}$       (d) None of these

2. When  $k_1 = 1 \text{ s}^{-1}$  and  $k_2 = 50 \text{ s}^{-1}$ ; select most appropriate graph



3. If  $k_1$  and  $k_2$  both are almost same then which graph is most suitable :

- (a) graph A      (b) graph B      (c) graph C      (d) graph D

4. Select the correct statement for given reaction :

- (a)  $A$  decreases linearly  
 (b)  $B$  rises to a max. and then constant  
 (c)  $B$  rises to a max. and then falls  
 (d) The slowest rate of increases of  $C$  occurring where  $B$  is max.

**PASSAGE 2**

Arrhenius studied the effect of temperature on the rate of a reaction and postulated that rate constant varies with temperature exponentially as  $k = Ae^{-E_a/RT}$ . This method is generally used for finding the activation energy of a reaction. Keeping temperature constant, the effect of catalyst on the activation energy has also been studied.

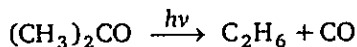
- The pre-exponential factor in the Arrhenius equation of a first order reaction has the units-  
 (a)  $\text{mol L}^{-1}\text{s}^{-1}$       (b)  $\text{L mol}^{-1}\text{s}^{-1}$       (c)  $\text{s}^{-1}$       (d) dimensionless
- If  $x$  is the fraction of molecules having energy greater than  $E_a$ , it will be given by-  
 (a)  $x = -\frac{E_a}{RT}$       (b)  $\ln x = -\frac{E_a}{RT}$       (c)  $x = e^{E_a/RT}$       (d) Any of these
- If the rate of reaction doubles for  $10^\circ\text{C}$  rise of temperature from  $290\text{K}$  to  $300\text{K}$ , the activation energy of the reaction will be approximately:  
 (a)  $40 \text{ kcal mol}^{-1}$       (b)  $12 \text{ kcal mol}^{-1}$       (c)  $60 \text{ kcal mol}^{-1}$       (d)  $70 \text{ kcal mol}^{-1}$

**PASSAGE 3**

An important parameter of a photochemical reaction is the quantum efficiency or quantum yield ( $\phi$ ) which is defined as

$$\phi = \frac{\text{moles of the substance reacted}}{\text{moles of photons absorbed}}$$

Absorption of UV radiation decompose acetone according to the reaction



- The quantum yield of the reaction at  $330 \text{ nm}$  is  $0.4$ . A sample of acetone absorbs monochromatic radiation at  $330 \text{ nm}$  at the rate of  $7.2 \times 10^{-3} \text{ Js}^{-1}$  (Given :  $N_A = 6 \times 10^{23}$ ;  $h = 6.6 \times 10^{-34}$  in S.I. unit). The rate of formation of  $\text{CO}$  (mol/s) is :  
 (a)  $2 \times 10^{-8}$       (b)  $8 \times 10^{-8}$       (c)  $8 \times 10^{-9}$       (d) none of these
- If quantum yield in  $0.8$  then rate of formation of  $\text{C}_2\text{H}_6$  (mol/s) is :  
 (a)  $2 \times 10^{-8}$       (b)  $1.6 \times 10^{-9}$       (c)  $16 \times 10^{-9}$       (d)  $8 \times 10^{-9}$

**PASSAGE 4**

Radioactive disintegration is a first order reaction and its rate depends only upon the nature of nucleus and does not depend upon external factors like temperature and pressure. The rate of radioactive disintegration (Activity) is represented as

$$-\frac{dN}{dt} = \lambda N$$

Where  $\lambda$  = decay constant;  $N = N_0$  of nuclei at time  $t$ ;  $N_0$  = initial no. of nuclei

The above equation after integration can be represented as

$$\lambda = \frac{2.303}{t} \log \left( \frac{N_0}{N} \right)$$

- Half-life period of  $U^{237}$  is  $2.5 \times 10^5$  years. In how much time will the amount of  $U^{237}$  remaining be only 25% of the original amount?  
(a)  $2.5 \times 10^5$  years    (b)  $1.25 \times 10^5$  years    (c)  $5 \times 10^5$  years    (d)  $10^6$  years
- Calculate the half-life period of a radioactive element which remains only 1/16 of its original amount in 4740 years :  
(a) 1185 years    (b) 2370 years    (c) 52.5 years    (d) none of these
- What is the activity in Ci (curie) of 1.0 mole of Plutonium-239? ( $t_{1/2} = 24,000$  years)  
(a) 1.49 Ci    (b) 14.9 Ci    (c)  $5.513 \times 10^{11}$  Ci    (d) None of these

### PASSAGE

5)

Size of nucleus was obtained by the equation  $r = R_0 A^{1/3}$ , where  $r$  is the radius of nucleus of mass no.  $A$  and  $R_0$  is a constant whose value is equal to  $1.5 \times 10^{-15}$  metre.

(Given 1 amu =  $1.66 \times 10^{-24}$  g)

- What is the density of a nucleus of mass number  $A$ ?  
(a)  $\frac{4}{3} \pi (1.5 \times 10^{-15})^3 A$     (b)  $1.17 \times 10^{17}$  g/cm<sup>3</sup>    (c)  $1.17 \times 10^{-17}$  kg/m<sup>3</sup>    (d) None of these
- Nucleus radius of  ${}_6C^{12}$  is  $3 \times 10^{-15}$  metre. What is density ratio of  $d_C/d_{H_2O}$ ?  
(a)  $1.76 \times 10^{17}$     (b)  $1.76 \times 10^{14}$     (c)  $17.6 \times 10^7$     (d)  $17.6 \times 10^{17}$

### ONE OR MORE ANSWERS IS/ARE CORRECT

- Select the correct statement(s):  
(a) Rate constants are never negative  
(b) Partial orders are never negative  
(c) Molecularity and order of reaction both are equal for elementary reactions  
(d) Order of reaction may be change with change in practical conditions (temp. and pressure)
- Select the correct statement(s) :  
(a) The rate of reaction decreases with decrease in temperature  
(b) The rate of reaction is uniform in zero order reaction  
(c) The rate of reaction depends upon the surface area of the solid reactants  
(d) Average and instantaneous rate of reaction defined for micro and macro-scopic time interval respectively

3. Select the correct statement(s) :

- (a) The rate law of the elementary reaction;  $2A \longrightarrow B + C$ , must be  $r = k[A]^2$   
 (b) The rate law for the complex reaction  
 $A + B \longrightarrow C$ , might not be  $r = k[A][B]$   
 (c) If the partial orders differ from the coefficients in the balanced reaction, the reaction must be complex  
 (d) If the partial orders are equal to corresponding coefficients in the balanced reaction, the reaction must be elementary

4. Select the correct statement(s):

- (a) Every substance that appears in the rate law of reaction must be a reactant or product in that reaction  
 (b) If we know the rate law of a reaction; we can deduce it's mechanism must be  
 (c) If the reaction has rate  $r = k[A][B]^{3/2}$  then reaction may be elementary  
 (d) A zero order reaction must be a complex reaction

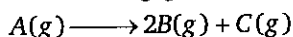
5. Select the correct statement(s) :

- (a) When  $T \rightarrow \infty$  or  $E_a \rightarrow 0$  then  $k = A$   
 (b) A positive catalyst can change  $\Delta H$  of the reaction  
 (c) A mixture of reactants may be thermodynamically unstable but kinetically stable  
 (d) A negative catalyst increases the activation energy of the reaction

6. Consider a reaction  $A + B \rightarrow C$ , in which both reactants are in the same phase may be

- (a) unimolecular elementary reaction  
 (b) Exothermic  
 (c) Heterogeneous  
 (d) Photochemical

7. In the following gaseous phase first order reaction



initial pressure was found to be 400 mm of Hg and it changed to 1000 mm of Hg after 20 min. Then

- (a) Half life for A is 10 min  
 (b) Rate constant is  $0.0693 \text{ min}^{-1}$   
 (c) Partial pressure of C at 30 min is 350 mm of Hg  
 (d) Total pressure after 30 min is 1150 mm of Hg

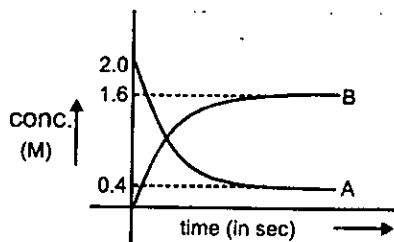
8. Identify the true statement(s)

- (a) A catalyst is chemically unchanged at the end of a reaction  
 (b) A catalyst may appear in the kinetic rate equation of the reaction  
 (c) A catalyst will not affect the composition of an equilibrium mixture  
 (d) A catalyst cannot cause a non-spontaneous ( $\Delta G > 0$ ) reaction to proceed

9. For the reaction  $A \xrightleftharpoons[k_2 \text{sec}^{-1}]{k_1 \text{sec}^{-1}} B$  following graph is given,

$k_1 = 4 \times 10^{-2} \text{ sec}^{-1}$ . Which is/are correct statement (s) ( $\ln 2 = 0.7$ ,  $\ln 8/7 = 0.14$ )





- (a) Equilibrium constant is 4.0  
 (b) Time taken for the completion of 50% of equilibrium conc. of B is 14 sec.  
 (c) Time taken for the completion of 10% of initial conc. of A is 2.8 sec.  
 (d) Rate constant of backward reaction is  $10^{-2} \text{ sec}^{-1}$

10. Select the correct statement(s) :

- (a)  $\alpha$ -particles are simply helium atoms  
 (b)  $\gamma$ -rays travel with higher speed as compare to  $\alpha$ -particle and have higher ionization power as compare to  $\beta$ -particle  
 (c) A loss of  $\beta$ -particles results in the production of isobars  
 (d)  $\beta$ -particles are considered as the best bombarding particles

11. Select the correct statement(s) :

- (a) In the reaction  ${}_{92}\text{U}^{235} + {}_0n^1 \longrightarrow {}_{56}\text{Ba}^{140} + 2{}_0n^1 + x$ , produced  $x$  is  ${}_{36}\text{Kr}^{94}$   
 (b) In the reaction  ${}_{11}\text{Na}^{23} + z \longrightarrow {}_{12}\text{Mg}^{23} + {}_0n^1$ , the bombarding particle  $z$  is deuteron  
 (c) Very large amount of energy is produced during nuclear fission and nuclear fusion  
 (d) In a fission reaction, a loss in mass occurs releasing a vast amount a energy

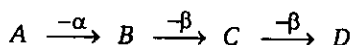
12. Select the correct statement(s):

- (a) SI unit of radioactivity is becquerel (Bq)  
 (b)  $1 \text{ Ci} = 3.7 \times 10^7 \text{ Bq}$   
 (c)  ${}_3\text{Li}^7 + {}_1\text{H}^1 \longrightarrow {}_2\text{He}^4$  is ( $P, \alpha$ ) type reaction  
 (d) The half-life of a particular radioactive isotope is a characteristics constant of that isotope

13. Select the correct statement(s) :

- (a) On bombarding  ${}_7\text{N}^{14}$  nuclei with  $\alpha$ -particle, the nuclei of the product formed after release of proton would be  ${}_8\text{O}^{17}$   
 (b) Decay constant does not depend upon temperature  
 (c) Nuclide and it's decay product after  $\alpha$ -emission are called isodiaphers  
 (d) Half-life of radium is 1580 years. It's average life will be 1097.22 years

14. In the decay process



- (a) A and B are isobars  
 (b) A and D are isotopes

- (c) *B*, *C* and *D* are isobars  
(d) *A* and *C* are isotones
15. In electron capture (radioactive process)  
(a) a neutron is formed (b) a proton is consumed  
(c)  $\gamma$ -ray emission takes place (d) X-ray emission takes place
16. Select the correct statement (s) for positron emission by unstable nucleus:  
(a) X-ray emission takes place (b) A neutron is formed  
(c)  $\frac{n}{p}$  of daughter nucleus increases (d) A neutron is consumed
17. Select the correct statement (s)  
(a) Mass number remains constant when positron emission takes place  
(b) One neutron converts into proton in  $\beta$  ( ${}_{-1}^0e$ ) emission process  
(c) Activity of a radioactive substance double when temp. increases from 300 K to 310 K  
(d) Isodiaphers formed when one alpha particle emitted and isotopes formed when 2 beta particles emitted

### MATCH THE COLUMN

Column-I and Column-II contains four entries each. Entries of Column-I are to be matched with some entries of Column-II. One or more than one entries of Column-I may have the matching with the same entries of Column-II.

1. **Column-I**
- (A) Unit of  $k$  is always equals to  
 (B) Unit of  $k$  in zero order  
 (C) Unit of  $k$  in first order  
 (D) Unit of  $k$  in second order
- Column-II**
- (P) 1/time  
 (Q)  $M/\text{time}$   
 (R)  $\text{Time}^{-1} M^{-1}$   
 (S) Unit of  $A$  (pre-exponential factor)

2. **Column-I**
- (A) Molecularity of a reaction  
 (B) Order of reaction  
 (C) The dissociation of  $\text{H}_2\text{O}_2$  (aq) is  
 (D)  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \xrightarrow{h\nu} 2\text{HCl}$  is
- Column-II**
- (P) 0, 1 Possible  
 (Q) 1, 2 Possible  
 (R) First order reaction  
 (S) Zero order reaction

3. **Column-I (Curve)**
- (A)  $C$  Vs  $t$  (abscissa) for zero order  
 (B)  $\log C$  Vs  $t$  (abscissa) for first order  
 (C)  $\left(\frac{-dc}{dt}\right)$  Vs  $C$  for zero order  
 (D)  $\ln\left(\frac{-dc}{dt}\right)$  Vs  $\ln C$  for first order
- Column-II (Curve)**
- (P) unity  
 (Q) zero  
 (R)  $-k$   
 (S)  $-\frac{k}{2.303}$

4. **Column-I**
- Linear plots (with non zero slope)**
- (A)  $\ln\left[-\frac{d[A]}{dt}\right]$  vs.  $\ln [A]$   
 (B)  $\log_e k$  vs.  $\frac{1}{T}$   
 (C)  $\log t_{1/2}$  vs.  $\log [A]_0$   
 (D)  $\frac{-d[A]}{dt}$  vs.  $[A]^2$
- Column-II (Order)**
- (P) 2  
 (Q)  $\frac{1}{2}$   
 (R) 0  
 (S) 1

$[A]$  = Reactant concentration at time 't'

$k$  = rate constant

$T$  = Absolute temperature

5.

Column-I

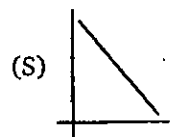
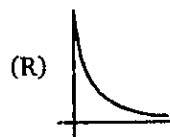
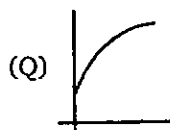
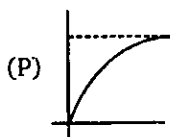
(A)  $\log[B]$  vs  $t$

(B)  $[A]$  vs  $t$

(C)  $\frac{1}{[A]}$  vs  $t$

(D)  $\ln k$  vs  $\frac{1}{T}$

Column-II



6.

Column-I

(A) Isotones

(B) Isobars

(C) Isotopes

(D) Isodiaphers

Column-II

(P)  ${}_{19}\text{Pa}^{234}$  and  ${}_{90}\text{Th}^{234}$

(Q)  ${}_{6}\text{C}^{12}$  and  ${}_{6}\text{C}^{14}$

(R)  ${}_{19}\text{K}^{39}$  and  ${}_{9}\text{F}^{19}$

(S)  ${}_{18}\text{Ar}^{39}$  and  ${}_{19}\text{K}^{40}$

7.

Column-I

(A)  $\alpha$ -emission

(B)  $\beta$ -emission

(C)  $\gamma$ -emission

(D)  $\beta^+$  (Positron) emission

Column-II

(P) Change in mass no.

(Q) No change in atomic no. and mass no.

(R) Atomic no. decreases

(S) Atomic no. increases

### ASSERTION-REASON TYPE QUESTIONS

Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason).

Examine the statements carefully and mark the correct answer according to the instructions given below :

- (A) If both the statements are TRUE and STATEMENT-2 is the correct explanation of STATEMENT-1  
 (B) If both the statements are TRUE but STATEMENT-2 is NOT the correct explanation of STATEMENT-1  
 (C) If STATEMENT-1 is TRUE and STATEMENT-2 is FALSE  
 (D) If STATEMENT-1 is FALSE and STATEMENT-2 is TRUE

1. **STATEMENT-1 :** Molecularity has no meaning for a complex reaction  
**STATEMENT-2 :** Molecularity defined only for RDS
2. **STATEMENT-1 :** An elementary reaction cannot have fractional order.  
**STATEMENT-2 :** Stoichiometric coefficients in an elementary reaction can be fractional.
3. **STATEMENT-1 :** Concentration of reactant in zero order reaction is constant.  
**STATEMENT-2 :** For zero order reaction  $A \longrightarrow B$ , successive half life of reaction decreases with the progress of the reaction.
4. **STATEMENT-1 :** Acid catalysed hydrolysis of esters is pseudo first order reaction.  
**STATEMENT-2 :** Water is present in excess in given reaction.
5. **STATEMENT-1 :** The order of reaction can have fractional value.  
**STATEMENT-2 :** For an elementary reaction, the partial orders are determined by the reaction stoichiometry.
6. **STATEMENT-1 :** Catalyst can increase that rate constant to a large extent.  
**STATEMENT-2 :** By using suitable catalyst, we can significantly increase yield.
7. **STATEMENT-1 :** For each  $10^\circ\text{C}$  rise of temperature the  $k$  is nearly double.  
**STATEMENT-2 :** Energy wise distribution of molecules in a gas sample is an exponential function of temperature so  $e^{-E_a/RT}$  is doubled.
8. **STATEMENT-1 :** Product can form only when the required orientation and energy conditions are met.  
**STATEMENT-2 :** All collisions between reactants yield the desired product.
9. **STATEMENT-1 :** The plot of  $k$  versus  $1/T$  is linear.  
**STATEMENT-2 :**  $k = A \cdot e^{-E_a/(RT)}$
10. **STATEMENT-1 :** For exothermic reaction equilibrium constant decreases with increase in temperature.  
**STATEMENT-2 :** For exothermic reaction rate constant decreases with decrease in temperature.
11. **STATEMENT-1 :** If the activation energy of reaction is zero, temperature will have no effect on the rate constant.  
**STATEMENT-2 :** Lower the activation energy fasten is the reaction.
12. **STATEMENT-1 :** Active complex is an intermediate product.  
**STATEMENT-2 :** Active complex is unstable with high vibrational energy.

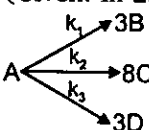
13. **STATEMENT-1 :** The pre-exponential factor  $A$  has the same units for all reactions.  
**STATEMENT-2 :**  $e^{-E_a/RT}$  has no unit.
14. **STATEMENT-1 :**  $\gamma$ -rays have very high penetrating power.  
**STATEMENT-2 :**  $\gamma$ -rays are electromagnetic radiations of high energy.
15. **STATEMENT-1 :** Nuclide  ${}_{13}\text{Al}^{30}$  is less stable than  ${}_{20}\text{Ca}^{40}$ .  
**STATEMENT-2 :** Nuclide having odd number of protons and neutrons are generally unstable.
16. **STATEMENT-1 :** Disintegration of  ${}_{1}\text{H}^3$  (tritium) is accompanied by  $\beta$ -emission.  
**STATEMENT-2 :** Tritium has high  $n/p$  ratio.
17. **STATEMENT-1 :** The life of radioactive object (organic origin) can found with the help of carbon dating.  
**STATEMENT-2 :**  ${}_{6}\text{C}^{14}$  is a  $\alpha$  and  $\beta$ -emitter.
18. **STATEMENT-1 :** Neutrons are the best bombarding particles.  
**STATEMENT-2 :** Neutrons are neutral particles.
19. **STATEMENT-1 :** Nucleus does not contain free electrons, yet it emit beta-particles  
**STATEMENT-2 :** At high  $n/p$  ratio, one neutron supposed to give 1 proton and 1  $e^-$  ( $\beta$ ).
20. **STATEMENT-1 :** Rate of disintegration of thorium increases with the increase in moles of thorium.  
**STATEMENT-2 :** Rate of disintegration does not depend upon temperature, pressure

## SUBJECTIVE PROBLEMS

- The rate of decomposition of  $\text{NH}_3(\text{g})$  at 10 atm on platinum surface is zero order. What is rate of formation (in  $M \text{ min}^{-1}$ ) of  $\text{H}_2(\text{g})$ , if rate constant of reaction  $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$  is  $2.0 M \text{ min}^{-1}$  ?
- $5A \rightarrow \text{Product}$   
 In above reaction, half-life period is directly proportional to initial concentration of reactant. The initial rate of reaction is  $400 \text{ mol lit}^{-1} \text{ min}^{-1}$ .  
 Calculate the half-life period (in sec) when initial concentration of reactant is  $200 \text{ mol lit}^{-1}$ .
- In an elementary reaction  $A(\text{g}) + 2B(\text{g}) \rightarrow C(\text{g})$  the initial pressure of  $A$  and  $B$  are  $P_A = 0.40$  atm and  $P_B = 0.60$  atm respectively. After time  $T$ , if pressure of  $C$  is observed 0.1 atm, then find the value of 
$$\frac{r_i \text{ (initial rate of reaction)}}{r_t \text{ (rate of reaction after time } t)}$$
- The rate of decomposition of  $\text{NH}_3(\text{g})$  at 10 atm on platinum surface is zero order. What is rate of formation (in  $M \text{ min}^{-1}$ ) of  $\text{H}_2(\text{g})$  if rate constant of reaction  $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$  is  $2.0 M \text{ min}^{-1}$
- Carbon monoxide reacts with  $\text{O}_2$  to form  $\text{CO}_2$ :  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$   
 information on this reaction is given in the table below.

[CO] mol/L	[O <sub>2</sub> ] mol/L	Rate of reaction (mol/L. min)
0.02	0.02	$4 \times 10^{-5}$
0.04	0.02	$1.6 \times 10^{-4}$
0.02	0.04	$8 \times 10^{-5}$

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

6. Half-life for the zero order reaction,  $A(g) \rightarrow B(g) + C(g)$  and half-life for the first order reaction  $X(g) \rightarrow Y(g) + Z(g)$  are equal. If completion time for the zero order reaction is 13.86 min, then calculate the rate constant (in  $\text{hr}^{-1}$ ) for the reaction  $X(g) \rightarrow Y(g) + Z(g)$ .
7. For any acid catalysed reaction,  $A \xrightarrow{H^+} B$   
Half-life period is independent of concentration of A at given pH. At same concentration of A half -life time is 10min at pH = 2 and half-life time is 100min at pH = 3. If the rate law expression of reaction is  $r = k[A]^x [H^+]^y$  then calculate the value of  $(x + y)$ .
8. For a reaction,  $A \rightleftharpoons B$  equilibrium constant is 1.66 and  $k_{\text{forward}} = 0.166 \text{ hr}^{-1}$ .  
Calculate the time (in hours) when concentration of B is 80% of its equilibrium concentration.  
(Given :  $\ln 25 = 3.20$ )
9. For a reaction  $A \rightleftharpoons B$  equilibrium constant is 1.66 and  $k_{\text{forward}} = 0.166 \text{ hr}^{-1}$   
Calculate the time (in hours) when concentration of B is 80% of its equilibrium concentration.  
(Given:  $\ln 25 = 3.20$ )
10.  ; at time  $t = 0$  (initial mole) of A is 1.  
Overall half life of the reaction is 15 days then calculate the number of mole of C after 45 days in terms of  $10^2$  if the ratio of  $k_1 : k_2 : k_3$  is 2 : 2 : 3
11. Iodine-131 is a radioactive isotope. If 1.0 mg of  $^{131}\text{I}$  has an activity of  $4.6 \times 10^{12} \text{ Bq}$ . What is the half -life of  $^{131}\text{I}$  (in days) ?
12. The average life of a radioactive element is 7.2min. Calculate the time interval (in min.) between the stages of 33.33% and 66.66% decay
13. A, B and C are isodiaphers while C, D and E are isobars. Calculate the difference of protons between A and E  
 $^{206}_{82}\text{A} \rightarrow \text{B} \rightarrow \text{C} \rightarrow \text{D} \rightarrow \text{E}$   
Given : Isodiaphers and isobars are formed in successive  $\alpha$  and  $\beta$ -emission respectively.
14. In the given radioactive disintegration series  
 $^{232}_{90}\text{Th} \rightarrow \dots \rightarrow ^{208}_{82}\text{Pb}$   
Calculate value of  $(n + 2)$   
Where value of  $n$  is number of isobars formed in this series, suppose there is successive emission of  $\beta$ -particles.
15. In the given radioactive disintegration series  
 $^{235}_{92}\text{U} \rightarrow \dots \rightarrow ^{207}_{82}\text{Pb}$   
Calculate difference between number of  $\alpha$  and number of  $\beta$  particles emitted in this series.

# ANSWERS

## Level 1

1. (c)	2. (b)	3. (c)	4. (d)	5. (d)	6. (d)	7. (d)	8. (c)	9. (a)	10. (c)
11. (c)	12. (a)	13. (d)	14. (d)	15. (b)	16. (d)	17. (c)	18. (c)	19. (d)	20. (a)
21. (c)	22. (c)	23. (b)	24. (a)	25. (c)	26. (c)	27. (d)	28. (c)	29. (b)	30. (c)
31. (d)	32. (a)	33. (d)	34. (a)	35. (b)	36. (c)	37. (a)	38. (b)	39. (a)	40. (c)
41. (c)	42. (d)	43. (c)	44. (b)	45. (c)	46. (b)	47. (b)	48. (b)	49. (a)	50. (b)
51. (d)	52. (c)	53. (c)	54. (d)	55. (d)	56. (a)	57. (d)	58. (a)	59. (a)	60. (c)
61. (c)	62. (c)	63. (c)	64. (a)	65. (a)	66. (c)	67. (b)	68. (d)	69. (d)	70. (c)
71. (d)	72. (a)	73. (a)	74. (b)	75. (d)	76. (c)	77. (a)	78. (d)	79. (d)	80. (c)
81. (b)	82. (b)	83. (c)	84. (c)	85. (c)	86. (c)	87. (c)	88. (c)	89. (b)	90. (c)
91. (d)	92. (d)	93. (d)	94. (b)	95. (b)	96. (c)	97. (b)	98. (d)	99. (d)	100. (c)
101. (c)	102. (b)	103. (b)	104. (d)	105. (d)	106. (b)	107. (a)	108. (c)	109. (d)	110. (b)
111. (a)	112. (c)	113. (d)	114. (c)	115. (b)	116. (c)	117. (c)	118. (d)	119. (b)	120. (c)
121. (d)	122. (c)	123. (b)	124. (d)	125. (d)	126. (b)	127. (c)	128. (c)	129. (b)	130. (b)
131. (d)	132. (b)	133. (d)	134. (c)	135. (c)	136. (d)	137. (c)	138. (b)	139. (b)	140. (b)
141. (c)	142. (b)	143. (d)	144. (c)	145. (b)	146. (c)	147. (a)	148. (b)	149. (b)	150. (b)

## Level 2

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



# Level 3

Passage-1	1. (b)	2. (b)	3. (a)	4. (c)
Passage-2	1. (c)	2. (b)	3. (b)	
Passage-3	1. (c)	2. (c)		
Passage-4	1. (c)	2. (a)	3. (b)	
Passage-5	1. (b)	2. (b)		

### One or More Answers is/are Correct

1. (a,c,d) 2. (a,b,c) 3. (a,b,c) 4. (d) 5. (a,c,d) 6. (b,c,d) 7. (a,b,c,d) 8. (a,b,c,d)  
 9. (a,b,c,d) 10. (c) 11. (a,c,d) 12. (a,c,d) 13. (a,b,c) 14. (b,c) 15. (a,b) 16. (c,d)  
 17. (a,b)

### Match the Column

- |                 |                 |              |       |
|-----------------|-----------------|--------------|-------|
| 1. A → S;       | B → Q;          | C → P;       | D → R |
| 2. A → Q;       | B → P, Q;       | C → R;       | D → S |
| 3. A → R;       | B → S;          | C → Q;       | D → P |
| 4. A → P, Q, S; | B → P, Q, R, S; | C → P, Q, R; | D → P |
| 5. A → P;       | B → R;          | C → Q;       | D → S |
| 6. A → S;       | B → P;          | C → Q;       | D → R |
| 7. A → P, R;    | B → S;          | C → Q;       | D → R |

### Assertion-Reason Type Questions

1. (C) 2. (C) 3. (D) 4. (A) 5. (B) 6. (C) 7. (A) 8. (C) 9. (D) 10. (B)  
 11. (B) 12. (D) 13. (D) 14. (A) 15. (B) 16. (A) 17. (C) 18. (A) 19. (A) 20. (B)

### Subjective Problems

1. 6	2. 3	3. 3	4. 6	5. 5	6. 6	7. 2	8. 6	9. 6	10. 1
11. 8	12. 5	13. 2	14. 7	15. 3					

# Hints and Solutions

## Level 1

4. (d) Rate of reaction

$$= -\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt}$$

$$\text{or } \frac{k_1[A]^2}{2} = \frac{k_2[A]^2}{1} = \frac{k_3[A]^3}{3}$$

$$\frac{k_1}{2} = k_2 = \frac{k_3}{3}$$

7. (d)  $K_{eq} = \frac{k_f}{k_b} = \frac{\text{Conc. of products as per rate law}}{\text{Conc. of reactants as per rate law}}$   
stoichiometry of reaction is required.

8. (c)  $K_{eq}$  at 1400 =  $\frac{0.29}{1.1 \times 10^{-6}} = 2.63 \times 10^5$ ;  $K_{eq}$  at 1500 =  $9.28 \times 10^4$ ; Value of  $K_{eq}$  reduces with rise in temperature so reaction is exothermic.

11. (c)  $x = kt$

$$t_{\text{completion}} = \frac{a}{k} = \frac{0.5}{0.1} = 5 \text{ min}$$

20. (a)  $t_{1/2} = \frac{a}{2k} = k'$ ;  $\log(t_{1/2}) = \log k' + \log a$

23. (b)  $C = \frac{n}{V} = \frac{P}{RT}$   $\therefore \frac{dC}{dt} = \frac{1}{V} \frac{dn}{dt} = \frac{1}{RT} \frac{dP}{dt}$

28. (c) Order w.r.t. A = 1; order w.r.t. B = 1

$$\text{R.O.R.} = \frac{1}{2} \frac{d(AB)}{dt} = k_r[A][B];$$

$$\frac{1}{2} \times (2.5 \times 10^{-4}) = k_r (0.1)(0.1)$$

$$k_r = 1.25 \times 10^{-2}$$

29. (b) Rate of appearance of AB(g),

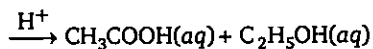
$$\frac{d(AB)}{dt} = k_b[A][B]$$

$$\therefore k_b = 2.5 \times 10^{-2}$$

31. (d) For elementary reaction molecularity of reaction = order of reaction.

$$34. (a) t_{1/2} = \frac{1}{(n-1)k} \left[ \frac{2^{n-1} - 1}{a^{n-1}} \right]$$

39. (a)  $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{H}_2\text{O}(\text{l})$



$$r = \frac{(k_{\text{net}})\text{H}_2\text{SO}_4}{(k_{\text{net}})\text{HCl}} = \text{R.O.R. in presence of}$$

$\text{H}_2\text{SO}_4 > \text{R.O.R. in presence of HCl}$

40. (c)  $r_1 = k[A]^2[B]$ ;  $r_2 = k[2A]^2[2B] = 8r_1$

41. (c)  $[A]_t = [A] - kt = 1 - 0.001 \times 10 \times 60$   
 $= 0.4 \text{ M}$

$$[B]_t = 0.001 \times 10 \times 60 = 0.6 \text{ M}$$

42. (d)  $t_{100\%} = \frac{a}{k} = \frac{1}{0.6} \text{ min} = 100 \text{ sec.}$

43. (c)  $x = kt$  so  $t_{1/2} = \frac{a}{2k}$  and  $T = \frac{a}{k}$ ;

$$t_{1/2} = \frac{1}{2 \times 0.001} = 500 \text{ sec and } T = 1000 \text{ sec}$$

45. (c)  $x = 0.1 - 0.08 = 0.02 \text{ M}$ ;

$$k = \frac{x}{t} = \frac{0.02}{10} = 2 \times 10^{-3} \text{ M min}^{-1}$$

$$\therefore t_{1/2} = \frac{[A]_0}{2k} = \frac{0.1}{2 \times 2 \times 10^{-3}} = 25 \text{ min}$$

$$t_{\text{completion}} = 2 \times t_{1/2} = 50 \text{ min};$$

50. (b)  $k = \frac{2.303}{t} \log \left( \frac{C_{A_0}}{C_A} \right)$ ;

$$2.303 \times 1 = 2.303 \log \left( \frac{C_{A_0}}{C_A} \right)$$

$$\frac{C_{A_0}}{C_A} = 10$$

$$\therefore C_A = \frac{1}{10} \Rightarrow 0.1$$

$$\therefore \text{rate after 1 min } r_1 = k \cdot C_A$$

$$\Rightarrow 2.303 \times 0.1 \Rightarrow 0.2303 \text{ M min}^{-1}$$

51. (d) Reaction is second order;  $k = 10^{-4} \text{ L/mol. min.}$

$$\therefore \frac{1}{3} \frac{d[A]}{dt} = k[A]^2$$

$$\begin{aligned} -\frac{d[A]}{dt} &= 10^{-4} \times 3 \times (0.5)^2 \\ &= 7.5 \times 10^{-5} \text{ M min}^{-1} \\ &= \frac{7.5 \times 10^{-5}}{60} = 1.25 \times 10^{-6} \text{ Ms}^{-1} \end{aligned}$$

$$\begin{aligned} 52. \text{ (c) } k &= \frac{2.303}{t} \log \left( \frac{a}{a-x} \right) \\ k &= \frac{2.303}{32} \log \left( \frac{100}{1} \right) \Rightarrow \frac{2.303}{16} \\ t &= \frac{2.303 \times 16}{2.303} \log \left( \frac{100}{0.1} \right) = 48 \text{ min} \end{aligned}$$

$$\begin{aligned} 55. \text{ (d) } k_t &= \frac{0.693}{30} \\ k_H &= \frac{a}{2t_{1/2}} = \frac{2}{2 \times t_{1/2}} = \frac{1}{t_{1/2}} = \frac{1}{30} \\ \frac{k_I}{k_H} &= \frac{0.693}{30 \times 1} \times 30 = 0.693 \end{aligned}$$

$$\begin{aligned} 57. \text{ (d) } A &\longrightarrow 3B; \quad P_T = P_0 + 2x \\ \text{After time } t & \quad P_0 - x \quad 3x \\ x &= \frac{P_T - P_0}{2} \quad k = \frac{1}{t} \ln \left( \frac{P_0}{P_0 - x} \right) \\ \text{After long time } t & \quad 3P_0 \\ x &= \frac{P_T - P_\infty}{2} \quad k = \frac{1}{t} \ln \left( \frac{\frac{P_\infty}{3}}{\frac{P_\infty}{3} - \left( \frac{3P_T - P_\infty}{6} \right)} \right) \\ P_\infty = 3P_0 \quad x &= \frac{3P_T - P_\infty}{6} \quad k = \frac{1}{t} \ln \left( \frac{\frac{P_\infty}{3}}{\frac{P_\infty}{2} - \frac{P_T}{2}} \right) \end{aligned}$$

$$\begin{aligned} 58. \text{ (a) } k &= \frac{0.693}{2.1} = 0.33 \text{ hr}^{-1} \\ \text{Let } t & \text{ be the time for 90\% decomposition,} \\ \text{so } a &= 100\% \quad x = 90 \text{ or } (a-x) = 10 \\ k &= \frac{2.303}{t} \log \left( \frac{a}{a-x} \right) \\ \Rightarrow t &= \frac{2.303}{0.33} \log \left( \frac{100}{10} \right); \quad t = 6.978 \text{ hr} \\ n_{\text{NH}_4\text{NO}_3} & \text{ taken} = \frac{6.2}{62} \Rightarrow 0.1; \\ \text{as per given no. of moles of } & \text{N}_2\text{O produced} \end{aligned}$$

$$= 0.1 \times \frac{90}{100}$$

$$\begin{aligned} \text{Vol. of N}_2\text{O produced at STP} \\ &= 0.09 \times 22.4 = 2.016 \text{ L} \end{aligned}$$

$$\begin{aligned} 60. \text{ (c) } k &= \frac{2.303}{t} \log \left( \frac{P_t}{P_0} \right); \quad (\text{CH}_3)_2\text{N}_2 \longrightarrow \text{C}_2\text{H}_6 + \text{N}_2 \\ t = 0 & \quad 200; \quad t \quad 200-x \quad x \quad x \\ \text{as per given } & 200 + x = 350 \quad x = 150 \\ \therefore k &= \frac{2.303}{t} \log \left( \frac{200}{200-150} \right) \end{aligned}$$

$$k = 5.77 \times 10^{-4} \text{ sec}^{-1}$$

$$\begin{aligned} 61. \text{ (c) } k &= \frac{1}{t} \ln \left( \frac{r_\infty - r_0}{r_\infty - r_t} \right) = \frac{1}{t} \ln \left( \frac{r_0 - r_\infty}{r_t - t_\infty} \right) \\ k &= \frac{1}{70} \ln \left( \frac{44+11}{16.5+11} \right) \\ k &= \frac{\ln 2}{70} \text{ when solution is optically inactive} \\ r_t &= 0 \\ \therefore k &= \frac{1}{t} \ln \left( \frac{r_0 - r_\infty}{O - r_\infty} \right) \\ \frac{\ln 2}{70} &= \frac{1}{t} \ln \left( \frac{44+11}{11} \right); \\ \frac{0.7}{70} &= \frac{1}{t} \times 1.6; \quad t = 160 \text{ min} \end{aligned}$$

$$\begin{aligned} 63. \text{ (c) } kt &= \frac{1}{n-1} \left[ \frac{1}{A_t^{n-1}} - \frac{1}{A_0^{n-1}} \right] \\ kt_{0.5} &= \frac{1}{n-1} \left[ \frac{2^{n-1} - 1}{A_0^{n-1}} \right] \quad \dots(1) \\ kt_{0.875} &= \frac{1}{n-1} \left[ \frac{8^{n-1} - 1}{A_0^{n-1}} \right] \\ \frac{t_{0.875}}{t_{0.5}} &= \frac{8^{n-1} - 1}{2^{n-1} - 1} \end{aligned}$$

$$\begin{aligned} 64. \text{ (a) } kt &= \ln \frac{\alpha_0}{\alpha_t}; \quad k \times 60 = \ln \frac{80}{75} \\ \Rightarrow k &= \frac{1}{60} \ln \frac{80}{75} \\ k \times 5 \times 60 &= \ln \frac{80}{r_t}; \quad 300 \times \frac{1}{60} \\ \ln \frac{80}{75} &= \ln \frac{80}{r_t}; \quad \ln \frac{80}{r_t} = 0.32 \end{aligned}$$

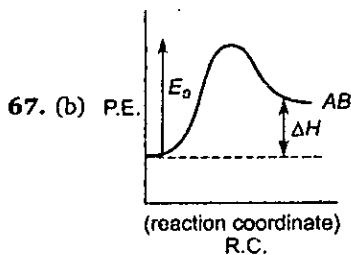
$t_i = 58$

optical rotation observed after 5 hrs

$= 58 + 2 = 60$

66. (c)  $\frac{1}{2} \frac{dC_B}{dt} = k_1 \cdot C_A$ ;  $\frac{dC_B}{2t} = 2k_1 C_A$

$\Rightarrow 2 \times 2 \times 10^{-3} \times 2 = 8 \times 10^{-3} M s^{-1}$



$E_a$  is always greater than  $\Delta H$

70. (c) First step is slow (require large activation energy) second step is fast (less activation energy) and overall reaction exothermic, so product energy level should be less as compare to reactants.

71. (d) Slow step require larger activation energy and product level is always more than reactant energy level in endothermic reaction.

75. (d)  $k = \left(\frac{k_1 \cdot k_2}{k_3}\right)^{2/3}$ ;  $E = \frac{2}{3} [E_{a_1} + E_{a_2} - E_{a_3}]$

$\Rightarrow \frac{2}{3} [180 + 80 - 50] = 140 \text{ kJ/mol}$

76. (c)  $A_1 e^{-E_{a_1}/RT} = A_2 e^{-E_{a_2}/RT}$

$\frac{A_2}{A_1} = e^{(E_{a_2} - E_{a_1})/RT}$

$10 = \text{Exp} \left( \frac{600}{RT} \right)$ ,  $R = 2 \text{ cal/K-mol}$

$\ln 10 = \frac{600}{2T}$

$T = \frac{300}{2.303} \text{ K}$

82. (b)  $k_{1(300)} = \frac{0.693}{20}$ ;  $k_{2(320)} = \frac{0.693}{5}$

$\ln \frac{k_{2(320)}}{k_{1(300)}} = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$

$E_a = \frac{2.303 RT_1 T_2}{(T_2 - T_1)} \log \frac{k_2}{k_1}$

$= \frac{2.303 \times 8.314}{20 \times 1000} \times 300 \times 320 \log 4$

$= 55.14 \text{ kJ/mol}$

87. (c)  $k_1 = A e^{-\frac{83.314}{R \times 500}}$ ;  $k_2 = A e^{-\frac{75}{R \times 500}}$

$\frac{k_2}{k_1} = \exp \left( \frac{8.314 \times 1000}{8.314 \times 500} \right)$

$\Rightarrow \exp(2) \Rightarrow 7.38$

104. (d) Isotones have same no. of neutron;

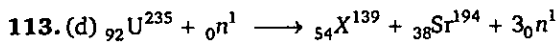
$17 - 9 = B - 8$

$B = 16$

Isobars have same mass no.

$A = B = 16$

no. of neutrons  $16 - 8 = 8$



116. (c)  $E_{\text{total}} = 200 \frac{(3^5 - 1)}{3 - 1}$

$= 100 \times 242 = 24200 \text{ MeV}$

122. (c)  $A = \lambda N$

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

$N = 6.023 \times 10^6 \text{ atoms}$

1 mole or  $6.023 \times 10^{23} \text{ atoms} = 100 \text{ g of X}$

$\therefore 6.023 \times 10^6 \text{ atoms}$

$\Rightarrow \frac{100}{6.023 \times 10^{23}} \times 6.023 \times 10^6 = 10^{-15} \text{ g}$

124. (d) Four half-lives (Total time =  $n \times$  half-life so,  $n = 4$ ), hence 0.0625

125. (d)  $\lambda = \frac{0.693}{69.3} = 10^{-2} \text{ min}^{-1}$ ;

$N = \frac{-\frac{dN}{dt}}{\lambda} = \frac{100}{10^{-2}} = 10,000$

129. (b) Equal fraction decay in equal periods of time, fraction of sample remaining after

3 days  $\Rightarrow (0.9)^3 = 0.729$

131. (d)  $\frac{N_0}{N} = \frac{A_0}{A} = 8$ ;

$t = \frac{1}{\lambda} \ln \left( \frac{A_0}{A} \right) \Rightarrow t = \frac{5770}{0.693} \ln 8$

$\Rightarrow 17313.6 \text{ year}$

133. (d)  $t$  for 20% left

$$\Rightarrow t_1 = \frac{2.303}{\lambda} \log \frac{1}{1-0.8}$$

$$= \frac{\ln 5}{\lambda}$$

$t$  for 50% left

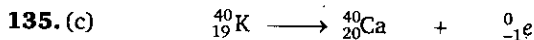
$$\Rightarrow t_2 = \frac{1}{\lambda} \ln 2$$

$$\frac{t_2}{t_1} = \frac{\frac{1}{\lambda} \ln 2}{\frac{1}{\lambda} \ln 5} = 0.43$$

$$t_2 = 0.43 t_1$$

134. (c)  $t = \frac{t_{0.5}}{0.693} \ln \frac{r_0}{r} = \frac{5770}{0.693} \times \ln \frac{120}{30}$ ;

$$t = \frac{5770}{0.693} \times 2 \times 0.693 = 11,540 \text{ years}$$



At present  $25 \times 10^{-6}$   $7.5 \times 10^{-6}$  mole

mole of  ${}_{19}^{40}\text{K}$  consumed =  $7.5 \times 10^{-6}$  mole

initial mole of  ${}_{19}^{40}\text{K}$  was  $(7.5 + 25) \times 10^{-6}$  mole

$$t = \frac{1}{\lambda} \ln \left( \frac{10 \times 10^{-6}}{2.5 \times 10^{-6}} \right) = \frac{1.3 \times 10^9}{\ln 2} \times \ln(4) =$$

$$1.3 \times 10^9 \times 2 = 2.6 \times 10^9 \text{ yr}$$

138. (b) Total time =  $nt_{1/2}$ ;  $n = 5$ ;  $\frac{\text{Initial activity}}{2^n}$

$$\text{Initial activity} = 0.01 \times 2^5 = 0.32 \mu\text{Ci}$$

139. (b)  $\lambda t = \ln \left( \frac{A_0}{A} \right)$

$$= \frac{0.693}{t_{1/2}} \times 200 = \ln \left( \frac{2140}{535} \right)$$

$$= t_{1/2} = 100 \text{ min.}$$

141. (c)  $\lambda = \frac{1}{10} \ln \left( \frac{100}{100-25} \right)$

$$t = \frac{1}{\lambda} \ln \left( \frac{N_0}{N} \right)$$

$$t = \frac{10}{\ln \left( \frac{4}{3} \right)} \times \ln \left( \frac{4 \times 10^{20}}{10^{20}} \right)$$

$$t = 48.19$$

142. (b)  $t_{1/2} = \frac{t}{4}$ ;  $t_{1/2} = T \ln 2$

$$\text{so } \frac{t}{4} = T \ln 2; t = 4T \ln 2$$

143. (d)  $W_0 =$  initial wt.;  $W \Rightarrow$  wt. after 20 days

$$\lambda_A = \frac{2.303}{t} \log \left( \frac{W_0}{W_A} \right);$$

$$\lambda_B = \frac{2.303}{t} \log \left( \frac{W_0}{W_B} \right)$$

$$\lambda_A - \lambda_B = \frac{2.303}{t} \log \left( \frac{W_B}{W_A} \right)$$

$$\text{so } \lambda_B = 0.6237$$

$$\therefore (t_{1/2})_B = \frac{0.693}{0.6237} = 1.11 \text{ day}$$

144. (c) Given  $(n_0)_B = 8 \times (n_0)_A$ ;  $(n)_A = 2 \times (n)_B$

$$\lambda_A - \lambda_B = \frac{2.303}{t} \log \left[ \frac{(N_A)_0}{(N_A)} \times \frac{(N_B)}{(N_B)_0} \right];$$

$$t = \frac{\ln \left( \frac{1}{16} \right)}{\frac{0.693}{50} - \frac{0.693}{10}}$$

$$= 50 \text{ min}$$

145. (b) as per given  $\frac{dN}{dt} = \alpha - \lambda N$  for max. no. of nuclei;

$$\frac{dN}{dt} = 0; \alpha = \lambda \cdot N, N = \frac{\alpha}{\lambda}$$

146. (c)  $\frac{\text{Atoms of Sr}}{\text{Atoms of Rb}} = 0.05$

or  $\frac{\text{Atoms of (Sr + Rb)}}{\text{atoms of Rb}} = 1.05$

so,  $\frac{\text{Initial no. of atoms of Rb}}{\text{Present no. of atoms of Rb}} = 1.05$

$$t = \frac{2.303}{\lambda} \log (n_0/n)$$

$$= \frac{2.303}{0.693} \times 4.7 \times 10^{10} \log (1.05)$$

$$= 3.28 \times 10^9 \text{ year}$$

147. (a)  $\lambda_A N_A = \lambda_B N_B$

( $\because$  rate of disintegration are same)

$$\frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A}$$

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

148. (b)  $N = N_0 \cdot e^{-\lambda t}$ ; where  $N =$  Parent remaining ( $p$ )

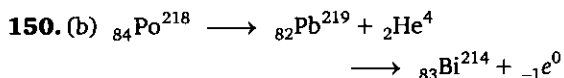
and  $N_0 =$  Initial parent = Parent remaining ( $p$ ) + daughter formed ( $d$ )

$$p = (p + d) \cdot e^{-\lambda t} \text{ or } \ln \frac{(p + d)}{p} = \lambda t$$

$$t = \frac{1}{\lambda} \ln \left( 1 + \frac{d}{p} \right)$$

149. (b)  $\lambda = \lambda_1 + \lambda_2$ ;  $\lambda = \frac{0.693}{22}$  and  $\frac{\lambda_1}{\lambda_2} = \frac{2}{98}$

$$\lambda_1 = 0.00063 \text{ year}^{-1}; \lambda_2 = 0.03087 \text{ year}^{-1}$$



$\text{Pb}^{214}$  to reach max. no. of nuclei

$$t_{\text{max}} = \frac{1}{\lambda_1 - \lambda_2} \ln \frac{\lambda_1}{\lambda_2}$$

$$= 247.5 \text{ sec}$$

where  $\lambda_1 = \frac{0.693}{183}$ ;  $\lambda_2 = \frac{0.693}{161}$

**Level 2**

1. (d)  $K_{\text{eq}} = \frac{k_f}{k_b} \Rightarrow \frac{[\text{CH}_3]^2}{[\text{C}_2\text{H}_6]}$

$$\therefore [\text{CH}_3] = \frac{10^{-4}}{10} = 10^{-5} \text{ M}$$

$$\frac{1.57 \times 10^{-3}}{k_b} = \frac{(10^{-5})^2}{1}$$

$$\Rightarrow k_b = 1.57 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$$

3. (c)  $r_1 = k[0.01]^a [0.01]^b = 6.93 \times 10^{-6} \dots$  (i)

$r_2 = k[0.02]^a [0.01]^b = 1.386 \times 10^{-5} \dots$  (ii)

$r_3 = k[0.02]^a [0.02]^b = 1.386 \times 10^{-5} \dots$  (iii)

From data  $a = 1$ ;  $b = 0$ ;

overall order = 1;  $k = 6.93 \times 10^{-4} \text{ sec}^{-1}$

$$6.93 \times 10^{-4} = \frac{1}{50 \times 60} \ln \frac{A_0}{A_t}; 0.693 = \ln \frac{A_0}{A_t}$$

$$\Rightarrow A_t = 0.0625$$

rate of reaction =  $6.93 \times 10^{-4} \times 0.0625$   
 $= 4.33 \times 10^{-5} \text{ Ms}^{-1}$

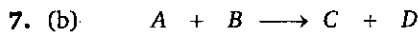
4. (c)  $\frac{r_2}{r_1} = \frac{P_{A_2} \cdot P_{B_2}^2}{P_{A_1} \cdot P_{B_1}^2} = \frac{0.1 \times (0.4)^2}{0.4 \times 1^2}$   
 $= \frac{1}{25}$

6. (c)  $t_1 = \frac{(t_{1/2})_1}{0.693} \ln \left( \frac{1}{(1 - 1/4)} \right)$

$$t_2 = \frac{(t_{1/2})_2}{0.693} \ln \left( \frac{1}{(1 - 3/4)} \right)$$

$$\frac{t_1}{t_2} = \frac{8}{1} \times \frac{\ln(4/3)}{\ln(4)}$$

$$= \frac{8 \times 0.125}{0.602} = 1 : 602$$



$$t=0 \quad 1 \quad 1 \quad \quad \quad x \quad x$$

$$t \quad 1-x \quad 1-x \quad \quad \quad x \quad x$$

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

$$\Rightarrow \frac{dx}{dt} = k(1-x)^{1/2}(1-x)^{1/2}$$

or  $\frac{dx}{dt} = k(1-x)$

$$\Rightarrow t = \frac{1}{k} \ln \left( \frac{1}{1-x} \right);$$

$$t = \frac{2.303}{2.303 \times 10^{-2}} \log \left( \frac{1}{0.1} \right)$$

$$= 100 \text{ sec}$$

8. (c)

(a) False because  $(t_{1/2})_I \neq (t_{1/2})_{II}$

(b) False if  $[C] = [A]$  then at that time  $[B] < [D]$

(c) True  $t_{100\%} = \frac{a}{k}$  (for zero order)

$$\frac{(t_{100\%})_I}{(t_{100\%})_{II}} = \frac{a_I \cdot k_{II}}{a_{II} \cdot k_I} = \frac{0.5}{1} \times \frac{\sqrt{3}}{1/\sqrt{3}} = \frac{3}{2}$$

(d)  $[A]_t = [A]_0 - k_I t$  or  $[A]_t = 0.5 - \frac{1}{\sqrt{3}} t$

$[C]_t = [C]_0 - k_{II} t$  or  $[C]_t = 1 - \sqrt{3} t$

if  $[A] = [C]_t$

i. e.  $0.5 - \frac{1}{\sqrt{3}} t = 1 - \sqrt{3} t$  or  $(\sqrt{3} - \frac{1}{\sqrt{3}}) t = 0.5$

$$t = \frac{\sqrt{3}}{4} \text{ min.}$$

9. (a)  $t_{1/2} = \frac{0.693}{k}$   
 $= \frac{0.693}{2.772 \times 10^{-3}}$   
 $= 250 \text{ sec}$

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

$$V_f = \frac{n_f}{n_i} \times V_i = \frac{0.05 + 0.15}{0.1} \times 2$$

$$= 4 \text{ litre}$$

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



$$\begin{array}{l} t=0 \quad P_i \quad 0 \quad 0 \\ t \quad P_i - x \quad 2x \quad x \\ t \rightarrow \infty \quad 0 \quad 2P_i \quad P_i \end{array}$$

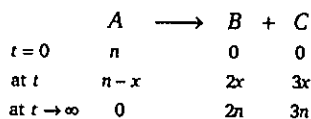
$$P_\infty = 3P_i \text{ or } P_i = \frac{P_\infty}{3}; P_i + 2x = P_t$$

$$x = \frac{P_t - P_i}{2}$$

$$\text{As we know } k = \frac{2.303}{t} \log \left( \frac{P_i}{P_i - x} \right)$$

$$\text{so } k = \frac{2.303}{t} \log \left( \frac{2P_\infty}{3(P_\infty - P_t)} \right)$$

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

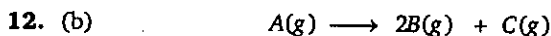


$$\therefore 5n = n_2 \Rightarrow n = \frac{n_2}{5}$$

$$n + 4x = n_1 \Rightarrow x = \frac{n_1 - n}{4}$$

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

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



$$\begin{array}{l} \text{Let initial pressure} \quad P_0 \quad 0 \quad 0 \\ \text{After 10 min.} \quad (P_0 - x) \quad 2x \quad x \\ \text{After long time } (t \rightarrow \infty) \quad 0 \quad 2P_0 \quad P_0 \end{array}$$

as per given  $(P_0 - x) + 2x + x + \text{vapour pressure of H}_2\text{O} = 188$

$$P_0 + 2x = 160 \text{ and } 3P_0 + 28 = 388$$

$$\text{so, } P_0 = 120 \text{ and } x = 20 \text{ torr}$$

$$k = \frac{1}{t} \ln \left( \frac{P_0}{P_0 - x} \right)$$

$$\Rightarrow \frac{1}{10} \ln \left( \frac{120}{100} \right) = \frac{1}{10} \times (\ln 4 + \ln 3 - \ln 10) \\ = 0.02 \text{ min}^{-1} = 1.2 \text{ hr}^{-1}$$

13. (b)  $k = \frac{2.303}{t} \log \left( \frac{r_\infty - r_0}{r_\infty - r_t} \right)$

$$= \frac{2.303}{30} \log \left( \frac{-11 - 34}{-11 - 19} \right) \\ = 1.35 \times 10^{-2} \text{ min}^{-1}$$

when solution is optically inactive  $r_t = 0$ ;

$$t = \frac{1}{k} \ln \left( \frac{-45}{-11} \right) = 103.7 \text{ min}$$

14. (c) Overall rate constant

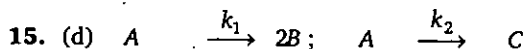
$$= k = k_1 + k_2 + k_3 = 6.93 \times 10^{-3}$$

$$t_{1/2} = \frac{0.693}{6.93 \times 10^{-3}} = 100 \text{ sec;}$$

After half-life,  $P_B + P_C + P_D = 4 \text{ atm}$

$$\frac{P_B}{P_B + P_C + P_D} = \frac{k_1}{k_1 + k_2 + k_3} = \frac{200}{693}$$

$$P_B = 4 \times \frac{200}{693} \\ = 1.154 \text{ atm}$$



$$\begin{array}{l} a_0 - x - y \quad 2x \quad a_0 - x - y \quad y \\ \frac{d[A]}{dt} = (k_1 + k_2)[A]; \quad \frac{[B]}{[C]} = \frac{2k_1}{k_2} = \frac{2x}{y} \end{array}$$

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

$$\therefore k_1 = k_2 = x = y$$

$$(k_1 + k_2)t = \ln \frac{A_0}{A_t}$$

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

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

$\therefore x = a_0/4$ . 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

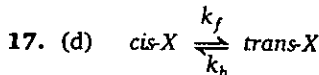
$$= 2 \times 1.25 = 2.5 \text{ atm}$$

16. (d) 1 mole of A will form 2 moles of B and C

after completion of reaction when 75% A

converted into B and C then total no. of

$$\text{moles} = 0.5 + 2 \times 1.5 = 3.5 \text{ moles}$$



$$\text{Initial} \quad a \quad 0; K_{(eq)} = \frac{k_f}{k_b}; k_b = \frac{3 \times 10^{-4}}{0.1} = 3 \times 10^{-3}$$

$$\text{at time } t \quad a-x \quad x$$

$$\text{at eqm} \quad a-x_e \quad x_e$$

As we know  $(k_f + k_b) = \frac{1}{t} \ln \left( \frac{x_e}{x_e - x} \right)$

given  $x = \frac{x_e}{2}$

$\therefore (k_f + k_b) = \frac{1}{2} \ln 2$

or  $(3 \times 10^{-3} + 3 \times 10^{-4}) = \frac{0.693}{t}$

$t = 210 \text{ sec}$

18. (b)  $k = A \cdot e^{-E_a/RT}$ ;  $A \cdot e^{-\frac{E_a}{RT_1}} = A \cdot e^{-\frac{(E_a - x)}{RT_2}}$

$\frac{E_a}{500} = \frac{(E_a - 16)}{400} = E_a = 80 \text{ kJ/mol}$

19. (c) For parallel reaction

$E_a = \frac{k_1 E_{a1} + k_2 E_{a2}}{k_1 + k_2}$

$= \frac{10^{-2} \times 100 + 4 \times 10^{-2} \times 120}{10^{-2} + 4 \times 10^{-2}}$

$E_a = 116 \text{ kJ/mol}$

20. (c)  $k = A \cdot e^{-E_a/(RT)}$

$\therefore$  Effective overall energy of activation

$E_a = E_{a(2)} - E_{a(3)} + \frac{1}{2} E_{a(1)} - \frac{1}{2} E_{a(5)}$

$= 60 - 50 + \frac{1}{2} \times 40 - \frac{1}{2} \times 10$

$= 25 \text{ kJ/mol}$

21. (d)  $A_1 \cdot e^{-E_{a1}/RT} = A_2 \cdot e^{-E_{a2}/RT}$ ;

$\frac{A_2}{A_1} = e^{(E_{a2} - E_{a1})/RT}$

$10^2 = \text{Exp} \left\{ \frac{1200}{RT} \right\}$ ;  $2 \ln 10 = \frac{1200}{2T}$

$T = \left\{ \frac{600}{4.606} \right\} \text{K}$

22. (b)  $\ln \frac{k_1'}{k_1} = \frac{E_1}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$  ... (i)

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

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

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

$T_2 = 378.74 \text{ K}$

24. (b)  $A + B \xrightleftharpoons[\text{fast}]{\text{slow}} IAB$ ; So  $E_{a(f)}$  is high and  $E_{a(b)}$  is low.  $k_1 \ll k_2$ ; So,  $E_a$  for this step is very high and next step is low and overall reaction is exothermic.

25. (a) Activation energy

$E_1 \approx E_{II} \approx E_V \approx E_{VI}$

$E_{1(f)} \approx E_{1(b)} \approx E_{2(b)} \approx E_{3(f)} \approx E_{3(b)}$

$\approx E_{4(f)} \approx E_{5(f)} \approx E_{6(b)}$

$E_{2(f)} \approx E_{4(b)}$  (slow steps so larger)

26. (c)  $e^{-\frac{E_a}{RT}} \times 100 = 3.8 \times 10^{-16}$ ;  $e^{-\frac{E_a}{RT}} = 3.8 \times 10^{-18}$

$-\frac{E_a}{RT} = \ln(3.8 \times 10^{-18})$ ;

$R = 8.314$  and  $T = 300$

$E_a = 100 \text{ kJ/mol}$

27. (b)  $\lambda t = \ln \left( \frac{A_0}{A} \right)$

$= \frac{0.693}{30} \times 90 = \ln \frac{A_0}{A} = A_0 = A \times 8$

$\therefore N_0 = \frac{A_0}{\lambda} = \frac{800}{0.693} \times 30 = 3.46 \times 10^4 \text{ atoms}$

28. (a) at time  $X \xrightarrow[n_0 - x]{\nu_0 - x} Y$ ;  $\frac{n_0 - x}{x} = \frac{1}{7}$ ;  $n_0 = \frac{8x}{7}$ ;

$\lambda = \frac{0.693}{6.93 \times 10^9} \Rightarrow 10^{-10} \text{ years}^{-1}$

$t = \frac{2.303}{\lambda} \log \left( \frac{w_0}{w_0 - x} \right)$

$= \frac{2.303}{10^{-10}} \log(8)$

$= 2.079 \times 10^{10} \text{ years}$

29. (c)  $\lambda_{\text{net}}$  or  $\lambda = \lambda_1 + 2\lambda_2 = 1.8 \times 10^{-3} + 2 \times 10^{-3} = 2 \times 10^{-2}$

Average life  $(T_{av}) = \frac{1}{\lambda}$

$= \frac{1}{2 \times 10^{-2}} = 50 \text{ sec}$



30. (c)  ${}_{83}\text{Bi}^{211} \longrightarrow {}_{81}\text{Tl}^{207} + {}_2\text{He}^4$ ; total time  
 $= n \times \text{half-life}$

moles of substance left after  $n$  halves

$$= \frac{\text{initial moles}}{2^n} = \frac{2}{2^4} = 0.125$$

moles of He produced

$$= 2 - 0.125 = 1.875$$

Pressure developed due to

$$\text{He} = \frac{1.875 \times 0.0821 \times 300}{100}$$

$$= 0.4618 \text{ atm}$$

31. (d) Let initial activities of A and B are  $A_0$  and  $B_0$

( $\therefore$  after 2 half-lives of activity of A will remain  $\frac{A_0}{4}$ )

$$A_0 + B_0 = 8000 \text{ and also } \frac{A_0}{4} + B_0 = 3500$$

(we can assume that activity of B remains constant due to larger half-life)

$$\text{so } \frac{3A_0}{4} = 4500; A_0 = 6000; B_0 = 2000;$$

$$\frac{A_0}{B_0} = \frac{6000}{2000} = \frac{3}{1}$$

32. (a) No change in activity of sample during establishment of circulatory equilibrium.

Let volume of blood is  $V$  mL, so total vol. =  $(V + 1)$  mL after injection of sample.

2 mL sample has activity of 10 dpm, so  $(V + 1)$  mL sample has activity of  $\frac{10}{2} \times (V + 1)$

Since rate is constant so

$$\frac{10}{2} \times (V + 1) = 1000; V = 199 \text{ mL}$$

33. (c)  $\frac{A_{0(x)}}{A_{0(y)}} = \frac{4}{1}; \frac{A_x}{A_y} = 1,$

$$\lambda_y - \lambda_x = \frac{1}{t} \ln \left( \frac{(A_0)_y}{(A_0)_x} \times \frac{A_x}{A_y} \right)$$

$$(\lambda_y - \lambda_x)t = \ln \left( \frac{1}{4} \right); (t_{1/2})_y = 30 \text{ min.}$$

34. (a) Corrected  $\text{C}^{14}$  content :

Let initial  $\text{C}^{14}$  count =  $A_0$ ;

$$A_0 + A_0/10 = 15.4; A_0 = 14$$

$$t = \frac{1}{\lambda} \log \frac{14}{7} = 5.770 \times 10^3 \text{ years}; t = \frac{\ln 2}{\lambda}$$

$$= t_{1/2}; t = 5770 \text{ years}$$

35. (a) For  $\text{U}^{238}$ ;  $\lambda_1 t = \ln \left( \frac{n_0}{n_1} \right)$ ;

$$\text{For } \text{U}^{235}; \lambda_2 t = \ln \left( \frac{n'_0}{n_2} \right)$$

$$(\lambda_1 - \lambda_2)t = \ln \left( \frac{n_0 \times n_2}{n_1 \times n'_0} \right);$$

$$\ln 2 \left[ \frac{1}{0.5 \times 10^9} - \frac{1}{4.5 \times 10^9} \right] t = \ln (140)$$

$$t = 4.02 \times 10^9 \text{ year}$$

### Level 3

#### Passage-1

1. (b) For max. con. of B;

$$\frac{d[B]}{dt} = 0; \text{ so } t_{\text{max}} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

3. (c) from if  $k_2 \gg k_1$  then major portion of B formed will dissociate and if  $k_1 = k_2$  then relatively larger accumulation of B at the max. concentration.

#### Passage-4

2. (a)  $\frac{N}{N_0} = \left( \frac{1}{x} \right)^n$ ; where  $n$  = no. of halves;

$$\frac{N}{N_0} = \frac{1}{10} = \left( \frac{1}{x} \right)^n$$

$$= n = 4$$

Total time =  $n \times t_{1/2}$

$$= 4740 = 4 \times t_{1/2};$$

$$t_{1/2} = 1185 \text{ years}$$

3. (b)  $-\frac{dN}{dt} = \lambda \times N \Rightarrow \frac{0.693}{t_{1/2}} \times n \times N_A$

$$-\frac{dN}{dt} = \frac{0.693}{24,000 \times 365 \times 24 \times 60 \times 60}$$

$$\times 1 \times 6.02 \times 10^{23} \text{ dps or } 14.9 \text{ Ci}$$

#### Passage-5

1. (b)  $r = R_0 A^{1/3}$

$\therefore$  Volume of nucleus (4/3)

$$\pi r^3 = \frac{4}{3} \pi (1.5 \times 10^{-15})^3 \text{ A m}^3$$

$$\text{density } d = \frac{m}{V} = \frac{A \times 1.66 \times 10^{-27} \text{ kg}}{4/3 \pi (1.5 \times 10^{-15})^3 \text{ A}}$$

$$= 1.17 \times 10^{17} \text{ kg/m}^3$$

2. (b)

$$d_c = \frac{\text{Mass}}{\text{Volume}} = \frac{12 \times 1.66 \times 10^{-27}}{(4/3) \times 3.14 \times (3 \times 10^{-15})^3}$$

$$= 1.76 \times 10^{17} \text{ kg/m}^3$$

$$d_{\text{H}_2\text{O}} = 1000 \text{ kg/m}^3$$

$$\frac{d_c}{d_{\text{H}_2\text{O}}} = \frac{1.76 \times 10^{17}}{1,000} = 1.76 \times 10^{14}$$

**Subjective Problems**

$$4. \quad 2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$$

$$\frac{dx}{dt} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{1}{2} \frac{d[\text{N}_2]}{dt}$$

$$= \frac{1}{2} \frac{d[\text{H}_2]}{dt} = k[\text{NH}_3]^2$$

$$\frac{d[\text{H}_2]}{dt} = 3K = 3 \times 2 = 6$$

$$9. \quad (K_f + K_b)t = \ln \frac{x_e}{x_e - x} = \ln \frac{x_e}{x_e - 0.8x_e};$$

$$(K_f + K_b)t = \ln \frac{x_e}{0.2x_e} = \ln 5 = 1.6;$$

$$\frac{K_f}{K_b} = K \Rightarrow K_b = 0.1t = 6 \text{ hrs.}$$

$$14. \quad \text{Number of } \alpha\text{-particle} = \alpha = \frac{232 - 208}{4} = 6$$

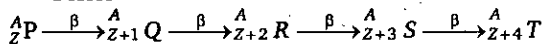
$$Z_2 = Z_1 - 2x + y$$

 (where  $x$  = number of  $\alpha$  and  $y$  = number of  $\beta$ )

$$82 = 90 - 12 + y$$

$$y = 4$$

Series



Total number of isobars = 5

$$n = 5, \text{ so } n + 2 = 7$$

$$15. \quad \text{Number of } \alpha\text{-particle} = \alpha = \frac{235 - 207}{4} = 7$$

$$Z_2 = Z_1 - 2x + y$$

 (where  $x$  = number of  $\alpha$  and  $y$  = number of  $\beta$ )

$$82 = 92 - 14 + y$$

$$y = 4$$

 Number of  $\alpha$  particle - number of  $\beta$  particle = 3

**One or More Answers is/are Correct**

9. (a, b, c, d)

$$k = \frac{B_e}{A_e} = \frac{1.6}{0.4} = 4; k = 4 \frac{k_1}{k_2} = \frac{4 \times 10^{-2}}{k_2}$$

$$\Rightarrow k_2 = 10^{-2}$$

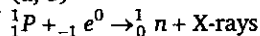
$$t_{0.5x_e} = \frac{1}{k + k_2} \ln \frac{x_e}{x_e - x}$$

$$= \frac{1}{5 \times 10^{-2}} \ln 2 = \frac{70}{2}; t_{0.5x_e} = 14 \text{ min};$$

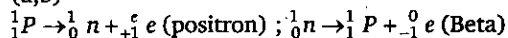
$$t_{0.1a} = \frac{1}{5 \times 10^{-2}} \times \ln \frac{x_e}{x_e - x} = \frac{1}{5 \times 10^{-2}} \ln \frac{1.6}{1.6 - 0.2}$$

$$= \frac{100}{5} \ln \frac{16}{14} = 20 \times 0.14 = 2.8$$

15. (a, b)



17. (a, b)



Activity =  $\lambda N$ , Decay constant  $\lambda$  does not depend upon temperature.

By the emission of  $\alpha$ -particle, isodiaphe 4r formed.

By the emission of  $\beta$ -particle, isobars formed.