Chemical Kinetics

C1A **Chemical Kinetics** is that branch of physical chemistry which deals with the study of the speed of a chemical reaction. Such studies also enable us to understand the mechanism by which the reaction occurs.

C1B **Rate of reaction :**

The rate of reaction is defined as the amount of change in concentration divided by the corresponding time interval or rate is the concentration change per unit time.

$$\text{Rate of reaction} = \frac{\textbf{Change in conc.}}{\textbf{time}} = \frac{\textbf{dx}}{\textbf{dt}}$$

For the reaction $aA + bB \rightarrow cC + dD$

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

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

–ve sign. indicates decrease of conc. of reactants with time t.

$$\text{Rate of disappearance of A} = -\frac{d[A]}{dt}, \quad \text{Rate of formation of C} = \frac{d[C]}{dt}$$

* Rate of reaction and rate of formation or rate of disappearance expression can be same if stoichiometric coefficient is one.

Practice Problems :

1. **In the reaction $A + 2B \rightarrow 3C + D$ which of the following expressions does not correctly describe changes in the concentration of various species as a function of time ?**

(a) $\dfrac{d[C]}{dt} = \dfrac{-3d[A]}{dt}$

(b) $\dfrac{3d[D]}{dt} = \dfrac{d[C]}{dt}$

(c) $\dfrac{3d[B]}{dt} = \dfrac{-2d[C]}{dt}$

(d) $\dfrac{2d[B]}{dt} = \dfrac{d[A]}{dt}$

2. **Rate of formation of SO_3 in the following reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is 100 kg min^{-1}. Hence rate of disappearance of SO_2 will be :**
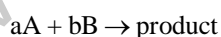
(a) 100 kg min^{-1} (b) 80 kg min^{-1} (c) 64 kg min^{-1} (d) 32 kg min^{-1}

[Answers : (1) **d** (2) **b**]

C2A **Rate law, molecularity and order of reaction**

According to the rate law the "rate of reaction is directly proportional to the concentration of reactant and reactants are raise to some power which may or may not be equal to stoichiometry coefficient".

For a reaction :

$aA + bB \rightarrow$ product

rate $= k[A]^m[B]^n$ .....   [A], [B] are the molar concentrations or active masses.

k = rate constant, specific rate constant or velocity constant

Order of reaction w.r.t. A = m, B = n. Overall order of reaction = m + n

molecularity = a + b

molecularity always a whole number (> O)

C2B Difference between order and molecularity :

Molecularity		Order	
1.	In elementary reactions, it is the total number of atoms or molecules taking part in the balanced equation, whereas for the complex reactions it has no significance.	1.	The order of the reaction is defined as the sum of the powers of the concentration terms represented in the rate expression of the reaction.
2.	It is the theoretical concept based on the number of molecules of an elementary equation	2.	It is an experimental property derived from the experimental rate law.
3.	It will not change with the change in conditions i.e. temperature, pressure etc.	3.	It will change with conditions.
4.	It is always an integer i.e. never be zero	4.	It may be an integer, fractional or even zero.

*   for Pseudo molecular reaction – order and molecularity are different

*   units of rate : mol L^{-1} time^{-1}

C3A Rate constant :

units of k – for reaction of nth order

$$k = \frac{1}{time} \times \frac{1}{[Conc.]^{n-1}}$$

C3B Integrated equation for rate constant of different order reactions :

A → Products

Let A_0 = initial concentration of reactant.

$A_0 - x$ = remaining conc. of reactant at time 't', x = concentration of reactant decomposed at time 't'

T_{50} = half-life period which is the time required by the reaction to undergo 50% conversion into the

products. i.e., at t = T_{50}, x = $\frac{[A_0]}{2}$.

C3C Zero order reaction :

                        A → Product

at t = 0 A_0 0

at time t $A_0 - x$ x

Rate expression of a zero order reaction as shown as r = k

for zero order : $k = \frac{x}{t}$, k has a unit mol lt^{-1} time^{-1}

for e.g. photochemical reaction like ($H_2 + Cl_2 \rightarrow 2HCl$) is a zero order reaction.

At t = T_{50}, x = $\frac{A_0}{2}$, $T_{50} = \frac{[A_0]}{2k}$

C3D First order reaction :

                        A → product

at time t = 0 A_0 0

at time t $A_0 - x$ x

Rate law expression for the first order reaction is
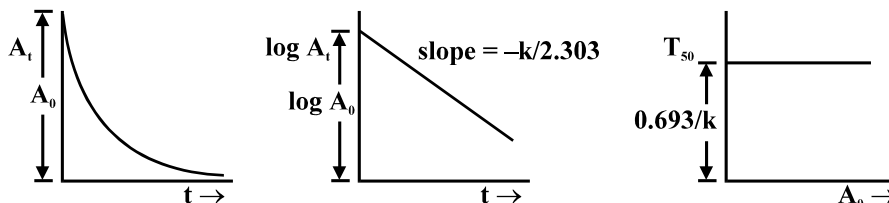
                r = k[A]

for first order :

$$A_t = A_0 e^{-kt}, \quad k = \frac{2.303}{t} \log \frac{A_0}{(A_0 - x)}, \quad \text{At } t = T_{50} \quad k = \frac{0.693}{T_{50}}, \quad T_{75\%} = 2T_{50\%}, \quad T_{99.9\%} \approx 10T_{50\%}$$

* Amount after n half lives for Ist order

$$[A]_t = [A]_0 (1/2)^n$$

Graph of first order reaction :

Practice Problems :

1. Ethylene is produced by $\underset{\text{Cyclobutane}}{C_4H_8} \xrightarrow{\Delta} 2C_2H_4$. The rate constant is $2.48 \times 10^{-4} \text{ sec}^{-1}$. In what time will

   the molar ratio of the ethylene to cyclobutane in reaction mixture attain the value 1

   (a) 27.25 minute   (b) 28.25 minute   (c) 25 minute   (d) 20 minute

2. Mathematical expression for $t_{1/4}$ i.e. when $(1/4)^{th}$ reaction is over following first order kinetics can be given by

   (a) $t_{1/4} = \frac{2.303}{K} \log 4$ (b) $t_{1/4} = \frac{2.303}{K} \log 2$

   (c) $t_{1/4} = \frac{2.303}{K} \log \frac{4}{3}$ (d) $t_{1/4} = \frac{2.303}{K} \log \frac{3}{4}$

3. The rate constant of a first order reaction is $4 \times 10^{-3} \text{ sec}^{-1}$. At a reactant concentration of 0.02 M, the rate of reaction would be

   (a) $8 \times 10^{-5} \text{ M sec}^{-1}$ (b) $4 \times 10^{-3} \text{ M sec}^{-1}$

   (c) $2 \times 10^{-1} \text{ M sec}^{-1}$ (d) $4 \times 10^{-1} \text{ M sec}^{-1}$

4. In a first order reaction, the concentration of reactant is decreased from 1.0 M to 0.25 M in 20 minute. The rate constant of the reaction would be

   (a) 10 min^{-1} (b) 6.931 min^{-1} (c) 0.6931 min^{-1} (d) 0.06931 min^{-1}

   [Answers : (1) a (2) c (3) a (4) d]

C3E   **Second order reaction :**

               $A \rightarrow$ **product**

at time t = 0 A_0 0

at time t $A_0 - x$ x
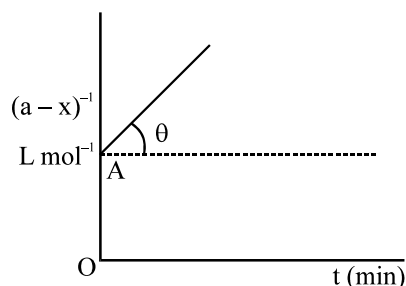
Rate law expression for the second order reaction is

         $r = k[A]^2$

$$k = \frac{1}{t}\left[\frac{1}{A_t} - \frac{1}{A_0}\right], \quad T_{50} = \frac{1}{A_0} \cdot \frac{1}{k}, \quad \text{for nth order : } t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

Practice Problems :

1. Following is the graph between $(a - x)^{-1}$ and time t for second order reaction $\theta = \tan^{-1}(0.5)$ OA = 2 L mol^{-1}.
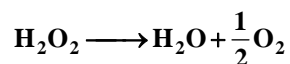

    hence rate at the start of the reaction is :

    (a) $1.25 \text{ L mol}^{-1} \text{ min}^{-1}$ (b) $0.5 \text{ L mol}^{-1} \text{ min}^{-1}$

    (c) $0.125 \text{ L mol}^{-1} \text{ min}^{-1}$ (d) $1.25 \text{ L mol}^{-1} \text{ min}^{-1}$

    [Answers : (1) c]

C4A   Experimental determination of rate constant of different first order reaction

   (i)   decomposition of hydrogen peroxide

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

hence V_0 = volume of KMnO$_4$ at start $\propto A_0$

                 V_t = volume of KMnO$_4$ at time t $\propto (A_0 - x)$

   hence for the first order reaction : $k = \dfrac{2.303}{t} \log \dfrac{V_0}{V_t}$

   (ii)   Acid hydrolysis of Ethyl Acetate :

$$CH_3COOC_2H_5 + H_2O \xrightarrow{\ H^+\ } CH_3COOH + C_2H_5OH$$
$$\text{excess}$$

V_0 = volume of NaOH at start $\propto$ catalyst [H$^+$], V_t = volume of NaOH at time $\propto$ x + [H$^+$]

V_∞ = volume of NaOH at infinite time $\propto$ [A$_0$] + [H$^+$]

Hence for Pseudo first order reaction : $k = \dfrac{2.303}{t} \log \dfrac{V_\infty - V_0}{V_\infty - V_t}$

   (iii)   Pressure change method :

            This is to be used in gaseous phase reaction. As reaction proceeds there may be a change in total pressure. By measuring initial and total pressure at the start and after time t, value of A$_0$ and $(A_0 - x)$ can be determined in terms of pressures.

$$A(g) \longrightarrow y\,B(g)$$

            at t = 0 P_0 0

            at time t $(P_0 - P)$ yP

Total pressure at time 't' $P_t = P_A + P_B$

                                             $P_t = P_0 - P + yP$

Therefore, $P_0 - P \propto (A_0 - x)$

$$P_0 \propto A_0$$

$$k = \frac{2.303}{t} \log \frac{P^0}{P^0 - P}$$

<u>Practice Problems :</u>

1. For the first order reaction $A(g) \rightarrow 2B(g) + C(g)$, the initial pressure $P_A = 90$ mm Hg, the pressure after 10 minutes is found to be 180 mm Hg. The rate constant of the reaction is

(a) 1.15×10^{-3} sec^{-1} (b) 2.3×10^{-3} sec^{-1}

(c) 3.45×10^{-3}sec^{-1} (d) 4.6×10^{-3} sec^{-1}

2. The reaction $A(g) + 2B(g) \rightarrow C(g) + D(g)$. Initial pressure of A and B are respectively $p_A = 0.60$ atm, $p_B = 0.80$ atm. When $p_C = 0.20$ atm, the rate of the reaction, relative to the initial rate, is :

(a) $\dfrac{1}{48}$ (b) $\dfrac{1}{24}$ (c) $\dfrac{1}{6}$ (d) $\dfrac{1}{4}$

3. At 100^{0}C, a gaseous reaction $A \rightarrow B + 2C$; is observed to be of first order. On starting with pure A, at the end of 14 minutes, the total pressure was found to be 264 mm of Hg. After a long time the total pressure of the system was 450 mm of Hg. Thus the Initial pressure of A is

(a) 57   (b) 150   (c) 114   (d) 190

[Answers : (1) a (2) c (3) b]

C4B Different methods for determining the order of reaction :

(i) Rate law method

(ii) Half life method

(iii) Integrated rate equation method

<u>Practice Problems :</u>

1. For the reaction, $2A + 2B \rightarrow$ Products the following initial rates were obtained at various given initial concentrations

S.No.	[A]	[B]	Rate(mol L^{-1} sec^{-1})
1.	0.1	0.2	0.46
2.	0.2	0.2	1.84
3.	0.2	0.1	0.92

The specific rate constant for the reaction is

(a) 2.3 sec^{-1} (b) 0.46 L mol^{-1} sec^{-1}

(c) 2.3×10^2 L^2 mol^{-2} sec^{-1} (d) 1.125×10^2 L^2 mol^{-2} sec^{-1}

2. The following data pertains to a reaction between A and B

S.No.	[A] mol/lit.	[B] mol/lit.	Rate (mol/ lit) time^{-1}
1.	1×10^{-2}	2×10^{-2}	2×10^{-4}
2.	2×10^{-2}	2×10^{-2}	4×10^{-4}
3.	2×10^{-2}	4×10^{-2}	8×10^{-4}

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

1. Rate constant of the reaction is 10^{-4}

2. Rate law of the reaction is K[A][B]

3. Rate of reaction increases four times on doubling the concentration of both the reactants. Select the correct answer using the codes given below

| (a) | 1, 2 and 3 | (b) | 1 and 2 | (c) | 2 and 3 | (d) | 3 alone |

3. From the following data, the activation energy for the reaction (cal/mol) $H_2 + I_2 \rightarrow 2HI$

T, K	1/T, K⁻¹	$\log_{10}K$
769	1.3×10^{-3}	2.9
667	1.5×10^{-3}	1.1

| (a) | 4×10^4 | (b) | 2×10^4 | (c) | 8×10^4 | (d) | 3×10^4 |

[Answers : (1) d (2) c (3) a]

C5A Effect of temperature on reaction rate :

The rate of chemical reaction generally increases on increasing the temperature.

* Temperature coefficient of a reaction is defined as the ratio of rate constant at two temperatures differing by 10 K (generally 25⁰ and 35⁰C). Observed value usually lies between 2 and 3 for most of the reactions.

* Larger the value of E_a, smaller the value of rate constant.

* Larger the value of E_a, greater is the effect of a given temperature on k.

* At lower temperature, increase in temperature causes more change in the value of k than that at higher temperature.
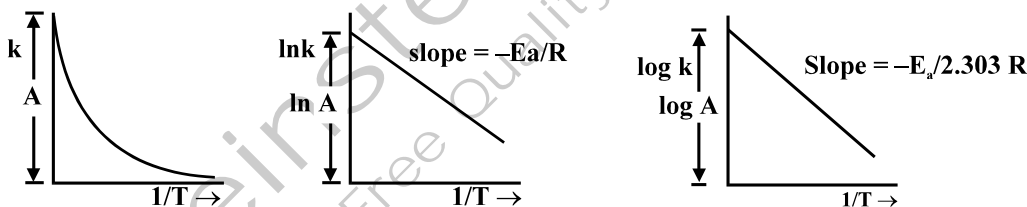
C5B Arrhenius equation :

Variation of rate constant k with temperature T(K) is given by Arrhenius equation.

$$k = Ae^{-Ea/RT}, \qquad \ln k = \ln A - \frac{E_a}{RT}, \qquad \log k = \log A - \frac{E_a}{2.303RT}$$

Where A is called the frequency factor or the pre-exponential factor. Collectively A and E_a are called the Arrhenius parameters of the reaction.

when $T \rightarrow \infty$, then k = A

C5C Graph on rate constant :

* $\log \dfrac{k_2}{k_1} = \dfrac{E_A}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$, where k_1 and k_2 are rate constants at temperature T_1 and T_2 respectively.

* Temperature coefficient $= \dfrac{\text{Rate constant } (T+10)^0 C}{\text{rate constant at } T^0 C}$

Practice Problems :

1. For a gaseous reaction the plot of log k against 1/T gave a straight line with a slope of -8×10^3. The activation energy E for the reaction is

| (a) | $\dfrac{8 \times 10^3 \times 2.303}{R}$ | (b) | $\dfrac{8 \times 10^3 \times R}{2.303}$ |
| (c) | $8 \times 10^3 \times 2.303 \, R$ | (d) | $\dfrac{8 \times 10^3}{R \times 2.303}$ |

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2. The rate of reaction is doubled for evergy 10^0 rise in temperature. The increase in reaction rate as a result of temperature rise from 10^0 to 100^0 is

(a)   112   (b)   512   (c)   400   (d)   614

3. Milk turns sour at 40^0C three times as faster as at 0^0C. Hence E_a in cal (activation energy) of turning of milk sour is :
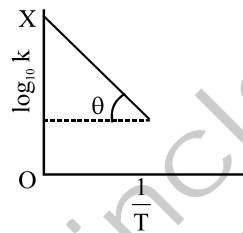
(a) $\dfrac{2.303 \times 2 \times 313 \times 273}{40} \log 3$

(b) $\dfrac{2.303 \times 2 \times 313 \times 273}{40} \log\left(\dfrac{1}{3}\right)$

(c) $\dfrac{2.303 \times 2 \times 40}{273 \times 313} \log 3$

(d) $\dfrac{2.303 \times 2 \times 40}{273 \times 313} \log\left(\dfrac{1}{3}\right)$

4. In presence of catalyst E_a is lowered by 2 kcal at 27^0C. Hence rate will be :

(a)   20 times   (b)   14 times   (c)   28 times   (d)   2 times

5. Graph between log k and $\dfrac{1}{T}$ [k is rate constant (s^{-1}) and T the temperature (K)] is a straight line with OX = 5, $\theta = \tan^{-1}\left(-\dfrac{1}{2.303}\right)$. Hence E_a will be :

(a) 2.303×2 cal   (b) $\dfrac{2}{2.303}$ cal   (c)   2 cal   (d)   none

6. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25^0C are $3.0 \times 10^{-4} s^{-1}$, 104.4 kJ mol^{-1} and $6.0 \times 10^{14} s^{-1}$ respectively. The value of the rate constant as $T \to \infty$ is

(a) $2.0 \times 10^{18} s^{-1}$ (b) $6.0 \times 10^{14} s^{-1}$ (c)   Infinity   (d) $3.6 \times 10^{30} s^{-1}$

7. For a first order reaction, when log k was plotted against 1/T, a straight line with a slope of –6000 was obtained. The activation energy for the reaction is

(a) 13.8×10^3 R   (b)   27600 cal   (c) 114.732×10^3 (d) 1.14×10^7

8. The rate constant for the first order decomposition of a certain reaction is given by the equation

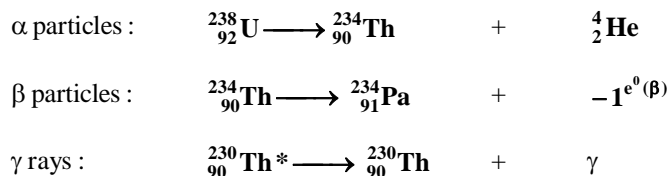$\ln k(\sec^{-1}) = 14.34 - \dfrac{1.25 \times 10^4}{T}$. The energy of activation in cal./mol is

(a) 2.5×10^2 (b)   250   (c) 2.5×10^3 (d) 2.5×10^4

[Answers : (1) c (2) b (3) a (4) c (5) c (6) b (7) a (8) d]

NUCLEAR CHEMISTRY

C1A Nuclear Chemistry involves the study of the nuclear changes i.e., the conversion of one element into the another element. It was observed by various scientists that the atomic nucleus of certain element undergo spontaneous disintegration into smaller fragments emitting powerful radiations. This phenomenon was defined as **"Radioactivity"** and is always independent of the external conditions such as temperature, pressure etc.

C1B **Active Radiation emitted during the spontaneous disintegration of certain nuclei are :**

α particles : $\qquad {}^{238}_{92}U \longrightarrow {}^{234}_{90}Th \qquad + \qquad {}^{4}_{2}He$

β particles : $\qquad {}^{234}_{90}Th \longrightarrow {}^{234}_{91}Pa \qquad + \qquad {}_{-1}e^{0 (\beta)}$

γ rays : $\qquad {}^{230}_{90}Th* \longrightarrow {}^{230}_{90}Th \qquad + \qquad \gamma$

Types of Radioactive Decay

Types of Decay	Radiation	Process	Nuclear change At. No.	Mass No.	Nuclear Condition
Alpha emission (α)	${}^{4}_{2}He$	—	–2	–4	$Z > 83$
Beta emission (β)	${}^{0}_{-1}e$	${}^{1}_{0}n \rightarrow {}^{1}_{1}p + {}^{0}_{-1}e$	+1	0	$\dfrac{N}{Z}$ too large
Positron emission (β^+)	${}^{0}_{1}e$	${}^{1}_{1}p \rightarrow {}^{1}_{0}n + {}^{0}_{1}e$	–1	0	$\dfrac{N}{Z}$ too small
Electron capture (Ec)	X rays	${}^{1}_{1}p + {}^{0}_{-1}e \rightarrow {}^{1}_{0}n$	–1	0	$\dfrac{N}{Z}$ too small
Gamma emission (γ)	${}^{0}_{0}\gamma$	—	0	0	Excited nucleus

C1C **Group displacement law :**

Emission of an α-particle (a helium nucleus) lowers the atomic number by two and mass number by four; emission of a β^--particle (an electron of nuclear origin) raises the atomic number by one and leaves the mass number unchanged. Thus, the new element may be displaced either to the left (two places in case of α-emission) or to the right (one place in case of β^- emission) in the periodic table. This displacement is known as Group Displacement Law.

C2A **Process of Radioactive Disintegration :**

The atoms of radioactive element are inharently unstable, thus they undergo spontaneous disintegration and emitting α or β particles and resulting in the formation of new element which is physically and chemically different from its parent element.

* Radioactive decay follows first order kinetics.

C2B **Rate of radioactive disintegration :**

The rate of distingration of a radioactive material the decay rate is directly proportional to the number of atoms present.

$$-\frac{dN}{dt} \propto N \quad , \quad -\frac{dN}{dt} = \lambda N$$

where $-\dfrac{dN}{dt}$ represents rate of decay in disintegration of atoms per unit time (say second), N the number of atoms disintegrating at that time and λ the disintegration constant (also called decay constant).

If N_0 is the number of atoms at the start of decay and N the number of atoms at a given time then by first order kinetics.

$$N = N_0 e^{-\lambda t}, \quad \lambda = \frac{2.303}{t}\log_{10}\left(\frac{N_0}{N}\right), \qquad At\ t = T_{50} \qquad \lambda = \frac{0.693}{T_{50}}.$$

Thus half-life period is independent of number of atoms present at a given time then $N = N_0\left(\frac{1}{2}\right)^n$

and in activity terms $A_t = A_0\left(\frac{1}{2}\right)^n$

The average life period is related to T_{50} and disintegration constant as : $t_{av} = \frac{1}{\lambda} = \frac{T_{50}}{0.693}$
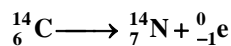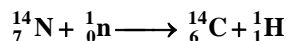
Practice Problems :

1. **The half-life of a radioactive element is 160 days. After 800 day 1 g of the element will reduce to**

   (a) $\frac{1}{10}$ g   (b) $\frac{1}{20}$ g   (c) $\frac{1}{8}$ g   (d) $\frac{1}{32}$ g

2. **Tritium $_1^3H$ has a half-life of 12.26 years. A 5.00 mL sample of tritiated water has an activity of 2.40×10^9 cpm. How many years will it take for the activity to fall to 3.00×10^8 cpm. ?**

   (a) 6.13   (b) 12.26   (c) 24.52   (d) 36.78

3. **Two substances A and B are present such that [A] = 4[B] and the half life of A is 5 min. and that of B is 15 minutes. If they start decaying at the same instant (first order), then how much time later will the concentration of both of them would be equal ?**

   (a) 15 minutes   (b) 10 minutes   (c) 5 minutes   (d) 12 minutes

4. **Two I-order reactions have half-lives in the ratio 3 : 2. Calculate the ratio of time intervals $t_1 : t_2$; t_1 is the time period for 25% completion of the first reaction and t_2 for 75% completion of the second reaction.**

   (a) 0.311 : 1   (b) 0.420 : 1   (c) 0.273 : 1   (d) 0.119 : 1

[Answers : (1) d (2) d (3) a (4) a]

C3   Radio Carbon Dating :

The application of the C-14 dating is based on the fundamental assumption that the intensity of cosmic ray and hence of ^{14}C in the atmosphere has been remaining constant over many thousands of years. This gives the initial activity of C-14 corresponding to the time when the plant or animal died and assimilation of radioactive carbon ceased to continue.

$$_7^{14}N + _0^1n \longrightarrow _6^{14}C + _1^1H$$
$$_6^{14}C \longrightarrow _7^{14}N + _{-1}^0e$$
$$Age = \frac{2.303}{\lambda}\log\frac{original\,activity\,(N_0)}{final\,activity\,(N)}$$
$$N = N_0\left(\frac{1}{2}\right)^n \quad where \quad n = \frac{t}{T_{50}}$$

Practice Problems :

1. **Weight of ^{14}C to have radioactivity 1 curie [λ (disintegration constant) = 4.4×10^{-12} sec^{-1}] is :**
   (a) 2×10^{-4} kg   (b) 0.9×10^{-4} kg   (c) 1.7×10^{-4} kg   (d) 3.7×10^{-10} kg

2. **An old wooden chair shows a $_6C^{14}$ activity which is 80% of the activity found today. The age of the sample is. ($t_{1/2}$ of $_6C^{14}$ = 5770 years).**

(a) **1.85×10^3** (b) **5.22×10^3** (c) **6.23×10^3** (d) **7.55×10^3**

[Answers : (1) a (2) a]

C4 **Rock Dating :**

It is based on the kinetic of radioactive decay. It is assumed that no lead was initially present is the sample and the whole of it came from the uranium.

Initial radioactivity = [U] + [Pb] = N_0 in terms of gram atoms

Final radioactive = [U] = N

We have assumed that due to high value of T_{50} of Uranium, its amount remains unchanged.

$$\frac{N_0}{N} = \frac{[U]+[Pb]}{[U]} = 1 + \frac{[Pb]}{[U]}$$

Thus $$t = \frac{2.303}{T_{50}} \log\left(\frac{N_0}{N}\right) = \frac{2.303}{T_{50}} \log\left[1 + \frac{[Pb]}{[U]}\right]$$

Practice Problems :

1. **"Landing on the moon" was the giant leap for the manking of the 'twentieth' century. Rock from there had equal number of atoms of $^{238}_{92}U$ and $^{206}_{82}Pb$. If half life of $^{238}_{92}U$ is 4.5×10^9 years, moon is ...... years old :**

(a) **9.0×10^9** (b) **4.5×10^9** (c) **2.25×10^9** (d) **none**

[Answers : (1) b]