

CHEMISTRY

- $t = 5 \times t_{1/2} = 5 \times \frac{\ln 2}{\lambda} = 5 T \ln 2$
 Hence, (B) is the correct answer.
- $t_1 = \frac{(t_{1/2})_1}{0.693} \ln \left(\frac{1}{1 - (1/4)} \right)$; $t_2 = \frac{(t_{1/2})_2}{0.693} \ln \left(\frac{1}{1 - 3/4} \right)$; $\frac{t_1}{t_2} = \frac{8}{1} \times \frac{\ln(4/3)}{\ln(4)} = 1 : 0.62$
- $$\begin{array}{ccccccc} \text{A(g)} & + & 2\text{B(g)} & \rightarrow & \text{C(g)} & & \\ t = 0 & & 0.4 \text{ atm} & & 1 \text{ atm} & & 0 \text{ atm} \\ t = t & & (0.4 - 0.3) \text{ atm} & & (1 - 0.6) \text{ atm} & & 0.3 \text{ atm} \end{array}$$
 Since reaction is elementary.
 So, Rate of reaction w.r.t. A & B will be of order equal to stoichiometric coefficient
 $\text{Rate} = K [\text{A}] [\text{B}]^2$; $\text{Rate}_{(\text{Initial})} = K [0.4] [1]^2$; $\text{Rate}_{(\text{after } t = t)} = K [0.1] [0.4]^2$

$$\frac{R_{(t=t)}}{R_{(t=0)}} = \frac{K[0.1][0.4]^2}{K[0.4][1]^2} = \frac{1}{25}$$
- $t_{1/2} \propto \frac{1}{a^{n-1}}$; $t_{1/2} = k \frac{1}{a^{n-1}}$; $\ln t_{1/2} = \ln k - (n - 1) \log_e a$.
 Hence, (A) is the correct answer.
- $$\begin{array}{ccc} \text{C}_7\text{H}_{14} & \rightarrow & 2\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6 \\ a & & 0 \quad 0 \\ a - x & & 2x \quad x \end{array}$$

$$\frac{a-x}{2x} = 1, x = \frac{a}{3}$$
 ; $1 \times 10^{-4} = \frac{2.303}{t} \log \frac{a}{2a/3}$; $t = 67.59 \text{ min.}$
- The information suggest that rate = $k[\text{A}]^2$
 This is satisfied by (D),
 In (A) and (C) B is involved in slow step, ; In (B), if we solve, B will appears in rate law.
- For zero order reaction, $x = kt$; $\therefore \frac{a}{2} \times k \times t_{1/2}$ i.e. $t_{1/2} = \frac{a}{2k}$ (i)
 For first order reaction, $t_{1/2} = \frac{\log_e 2}{k}$ (ii)
 From (i) and (ii), $\frac{a}{2k} = \frac{\log_e 2}{k}$; $a = \log_e 4 \text{ M}$; Hence, (A) is the correct answer.
- Fact based
- $$\text{I.E.} = \frac{n h c}{\lambda} = \frac{(6.022 \times 10^{23}) \times (6.62 \times 10^{-34})}{242 \times 10^{-9}} \times 3 \times 10^8 = 494.730 \text{ kJ/mol}$$
- At nodes, $\psi = 0$
 $\Rightarrow (\sigma - 1)(\sigma^2 - 8\sigma + 12) = 12$ $\Rightarrow \sigma = 1 \text{ and } (\sigma - 6)(\sigma - 2) = 0$
 $\Rightarrow \sigma = 6 \quad \sigma = 2$; Nearest radial node $\sigma = 1$ $\Rightarrow \frac{2Zr}{\alpha_0} = 1$
 $\Rightarrow r = \frac{\alpha_0}{2Z}$ Farthest radial node $\sigma = 6$; $\Rightarrow r = \frac{3\alpha_0}{Z}$

11. The listed reactions are first order reactions

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

$$\frac{d[C]}{dt} = k_2[B] + 2k_3[D] \quad ; \quad -\frac{d[A]}{dt} = k_1[A] + 2k_4[A] \quad ; \quad k_{\text{eff}} = k_1 + 2k_4$$

$$\Rightarrow E_{\text{eff}} = \frac{k_1 E_1 + 2k_4 E_4}{k_1 + 2k_4}$$

12. $r_n \propto n^2$

$$\text{But } r_{n+1} - r_n = r_{n-1} \quad ; \quad (n+1)^2 - n^2 = (n-1)^2 \quad ; \quad n = 4$$

Hence, (D) is the correct answer.

13. Activity after 'n' half lives = $\frac{A_0}{2^n}$ so, $0.01 = \frac{A_0}{2^6}$ Hence $A_0 = 0.64 \mu\text{Ci}$

14. $mvr = \frac{nh}{2\pi}$

$$\frac{nh}{2\pi} = 4.2178 \times 10^{-34} \quad ; \quad n = \frac{4.1278 \times 10^{-34} \times 2 \times 3.14}{6.625 \times 10^{-34}} = 4 \quad ; \quad \frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

The wavelength for transition from $n = 4$ to $n = 3$

$$\frac{1}{\lambda} = 109678 \left[\frac{1}{3^2} - \frac{1}{4^2} \right] \quad ; \quad \lambda = 1.8 \times 10^{-4} \text{ cm.}$$

15. $\Delta p = m\Delta v$
 $= 200 \times 1.6 \times 10^{-24} \times 10^{-3} \times 100 = 3.2 \times 10^{-23} \text{ kgm/sec}$

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad ; \quad \Rightarrow \quad \Delta x \geq \frac{h}{4\pi\Delta p} \quad \Rightarrow \quad \Delta x \geq \frac{6.4 \times 10^{-34}}{4 \times 3.14 \times 3.2 \times 10^{-23}}$$

$$\Rightarrow \Delta x \geq 1.59 \times 10^{-12} \text{ m}$$

16. $A \rightarrow \text{Products.}$

$$t_{1/2} = [\text{conc.}]^{1-n} \quad ; \quad n \rightarrow \text{order of reaction.} \quad \frac{100}{50} = \left(\frac{0.1}{0.025} \right)^{1-n} \quad 2 = 2 - 2n \Rightarrow 2n = 1$$

$$\Rightarrow n = \frac{1}{2} \quad \text{order of reaction is } \frac{1}{2} \quad ; \quad \frac{100}{t_{1/2}} = \left(\frac{0.1}{1} \right)^{1/2}$$

$$\Rightarrow t_{1/2} = 100\sqrt{10} \text{ min for } [A_0] = 1\text{M. } (t_{1/2} = 100\sqrt{10} \text{ min } [A_0] = 1\text{M})$$

17. $A_4 \longrightarrow 4A$

$$\begin{array}{ll} a & 0 \\ a-x & 4x \end{array}$$

$$\text{At 30 hrs,} \quad \begin{array}{l} a - x = 4x \\ a = 5x \end{array}$$

$$x = \frac{a}{5}$$

Hence reaction is 20% complete.

$$k = \frac{1}{30} \ln \frac{a}{4a/5} \quad ; \quad k = \frac{1}{30} \ln \frac{5}{4}$$

$$\Rightarrow t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2 \times 30}{\ln 5 - \ln 4} = \frac{\log 2 \times 30}{\log 5 - \log 4} = \frac{0.3 \times 30}{0.7 - 0.6} = \frac{9}{0.1} = 90 \text{ hrs}$$

\Rightarrow rate follows exponential decay with time.

In first order reaction, $t_{x\%}$ is independent of initial concentration.



18. Element A = $1s^2 2s^2 2p^1$

Element B = $1s^2 2s^2 2p^6 3s^2 3p^5$; atomic number of X = $5 + 17 = 22$

X is Ti

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$; M shell contain $2 + 6 + 2 = 10$ electron

Total number of electron with $l = 1$

$$= 6 + 6 = 12$$

Total number of electrons with $m = 0$

$$= 2 + 2 + 2 + 2 + 2 + 2 + 1 = 13$$

As d orbitals contain electrons, so d orbitals can be involved in back bonding.

19. (A) $[\text{Ar}] 3d^1 4s^2$ (B) $[\text{Ar}] 3d^{10} 4s^1$ (D) $[\text{Xe}] 6s^2 5d^1$

20. $\sqrt{n(n+2)} = \sqrt{24} \Rightarrow n = 4$

Hence, 4 unpaired electron. ; $\text{Fe}^{2+} \rightarrow 4$ unpaired electron ($3d^6$)

$\text{Cr}^{2+} \rightarrow 3d^4$ (4 unpaired electron) ; $\text{Mn}^{2+} \rightarrow 3d^5$ (5 unpaired electron)

$\text{Co}^{3+} \rightarrow 3d^6$ (4 unpaired electron) ; $\sqrt{n(n+2)} = \sqrt{24} \Rightarrow n = 4$

26. $E_4 - E_1 = 204 \text{ eV}$

$$\Rightarrow \frac{-13.6 \times Z^2}{4^2} + 13.6Z^2 = 204 \quad \Rightarrow \quad Z^2 \times 13.6 \times \frac{15}{16} = 204$$

$$\Rightarrow \quad Z^2 = 204 \times \frac{16}{15} \times \frac{1}{13.6} \quad \Rightarrow \quad Z = 4$$

$$\text{B.E. (2nd State)} = 0 - E_2 = 0 - \left(-13.6 \times \frac{4^2}{2^2} \right)$$

$$= 13.6 \times 4 = 54.4 \text{ eV}$$

$$\text{I.E.} = 0 - E_1 = -E_1 = +13.6 \times \frac{4^2}{1^2} = 217.6 \text{ eV} \quad \Rightarrow \quad \text{Ionisation potential} = 217.6 \text{ V}$$

27. $r = k[A]^x [B]^y$

$$1 = k \quad \dots(1)$$

$$8 = k(2)^x (4)^y \quad \dots(2)$$

$$27 = k(3)^x (9)^y \quad \dots(3)$$



$$\Rightarrow \frac{1}{8} = \frac{1}{2^x \cdot 2^{2y}} \Rightarrow x + 2y = 3 \quad \text{and} \quad \frac{1}{27} = \frac{1}{3^x \cdot 3^{2y}} \Rightarrow x + 2y = 3$$

$x = 1, y = 2$ does not satisfy this relation. ; $x = 2, y = 1$ does not satisfy this relation.
 $x = 2, y = 1/2$ satisfy this relation ; $x = 1/2, y = 2$ does not satisfy this relation.

So, ans is $r = k[A]^2 [B]^{1/2}$

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

$$1 = k \quad \dots(1) \quad 8 = k(2)^x (4)^y \quad \dots(2) \quad 27 = k(3)^x (9)^y \quad \dots(3)$$

$$\Rightarrow \frac{1}{8} = \frac{1}{2^x \cdot 2^{2y}} \Rightarrow x + 2y = 3$$

28. $r = 1 \times [4]^2 [2]^{1/2}$

$$= 16\sqrt{2} = 22.6 \text{ M/min.}$$

29. Let the order be first order. Then

$$K = \frac{1}{10} \ln \frac{0 - 22.8}{0 - 13.8} = \frac{1}{10} \ln \frac{228}{138} = \frac{1}{10} \ln \frac{114}{69}$$

$$= \frac{1}{10} \times 0.50 = 0.05 \quad ; \quad \text{and} \quad k = \frac{1}{20} \ln \frac{22.8}{8.25} = \frac{1}{20} \times 1.01 = 0.05$$

As both K are similar, assumption is correct. It is a first order reaction.

30. $t_{1/2} = \frac{\ln 2}{K} = \frac{0.693}{0.05} = 13.86 \text{ minutes.}$

32. $\int \frac{df}{1-f} = \int k dt$



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

$$t = t \quad 1 - x \quad 3x$$

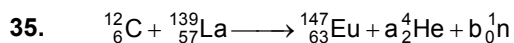
$$\text{at } t = 4, 1 - x = 3x$$

$$x = 1/4$$

for zero order reaction

$$C_t = C_0 - kt \quad ; \quad \frac{3}{4} = 1 - k \times 4 \quad ; \quad 4k = \frac{1}{4} \quad ; \quad k = \frac{1}{16} \quad \text{and} \quad t_{1/2} = \frac{C_0}{2k}$$

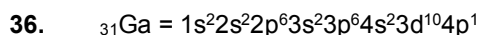
$$t_{1/2} = \frac{1}{2 \times \frac{1}{16}} = 8$$



$$6 + 57 = 63 + 2a$$

$$a=0 \text{ and } 139 + 12 = 147 + b \Rightarrow b = 4$$

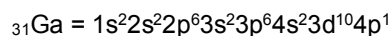
$$\text{Hence } a + b = 4.$$

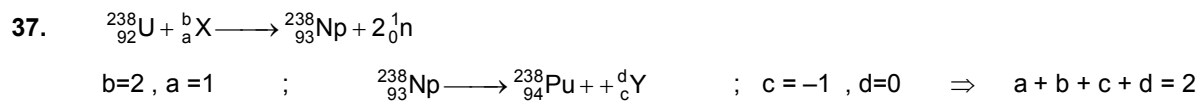


Orbitals having atleast one radial node = 2s, 3s, 3p, 4s, 4p

Hence maximum electrons with spin $+\frac{1}{2}$

$$= 1+1+3+1+1=7$$





$t=0$ a 0

$t=t$ $a-x$ x

$t=t_{\text{eq}}$ $a-x_{\text{eq}}$ x_{eq}

at equilibrium $\frac{x_{\text{eq}}}{a-x_{\text{eq}}} = \frac{\text{K}_1}{\text{K}_2}$; From graph $\frac{\text{K}_1}{\text{K}_2} = 4$

39. $[\text{A}]_t = \text{A}_0 e^{-6kt}$

$[\text{C}]_t = \frac{4k}{3k+2k+k} [1 - e^{-6kt}]$; $[\text{C}]_{\infty} = \frac{4k}{6k} [1 - e^{-\infty}] = \frac{2}{3} = 0.67$

40. Let the activity due to impurity be 'a' cpm.

\therefore due to Na it is $(1000 - a)$ cpm.

After 30 hrs 'a' would be reduced to $\left(\frac{1}{2}\right)^{10} a$ cpm

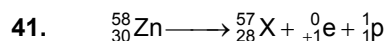
and $(1000 - a)$ would be reduced to $\frac{1}{4} (1000 - a)$ cpm

\therefore total activity after 30 hrs would be ; $\left(\frac{1}{2}\right)^{10} a + \frac{1}{4} (1000 - a) = 200$ (given)

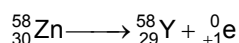
solving we get

$250 - \frac{1}{4} a \cong 200$ $\therefore \frac{1}{4} a = 50 \Rightarrow a = 200$

Hence 20% activity was due to impurity.



Neutrons = $57 - 28 = 29$



neutrons

= 29

\Rightarrow total neutrons in X and Y = $29 + 29 = 58$

42. $K = \frac{1}{t} \ln \frac{h_{\infty} - h_0}{h_{\infty} - h_t} = \frac{1}{3600} \ln \frac{1-11}{1-1-\frac{10}{e}}$

$= \frac{1}{3600} \ln e = \frac{1}{3600} / \text{sec} = \frac{1}{3600} \times 60 \times 60 \times 24 = 24 / \text{day}$

$\Rightarrow \text{rate} = K \cdot [\text{C}_2\text{H}_4\text{O}] = 24 \times \frac{22}{44} = 12 \text{ M/day.}$

$-\ln(1-f) = kt + c$ $t=0, f=0$ $-\ln(1-f) = kt$

From Figure $k = -\frac{3}{200}$ $f = (1 - e^{-3t/200})$; For 50% grow $t = \frac{200}{3} \times \ln(0.5) = 46.20 \text{ h}$

43. (a) $E_n^{-y} \propto r_n$

$$\left(\frac{Z^2}{n^2} \times 13.6 \text{ eV} \right) \propto \left(\frac{n^2}{Z} \times 0.529 \text{ \AA} \right)$$

$$y = 1$$

(b) $\ell_n \propto n^x$

$$\frac{nh}{2\pi} \propto n^x$$

$$x = 1$$

(c) Potential energy = 2 total energy

(d) $T_n \propto \frac{n^3}{Z^2}$ $t = -2$ $m = -3$

44. In radioactive species

(A) Activity = $\lambda N = \lambda N_0 e^{-\lambda t}$ and λ is independent of temperature and time.

So, Activity varies with time and $\log(\text{activity}) = \log \lambda N_0 - \frac{\lambda t}{2.303}$

Hence graph is linear.

(B) $t_{1/2}$ is independent of time and also temperature.

(C) $N = N_0 e^{-\lambda t}$

Hence, N depends on time and its log vs time graph is straight line.

(D) Explained in (A)

45. (A) $t_{1/2} \propto \frac{1}{a}$

order is second and $[A] = \frac{[A_0]}{1 + kt[A_0]}$

(B) Unit of k suggest that order is second and $[A] = \frac{[A_0]}{1 + kt[A_0]}$

(C) $K = \frac{k_f}{k_b}$ is infinitely large when $k_f > k_b$. This happens when E_a of forward reaction is less than of backward reaction.

(D) Addition of catalyst increases the rate greatly when the uncatalysed reaction is very slow. i.e. when its activation energy is very large.