

VOLUME I

ANSWERS

UNIT-I

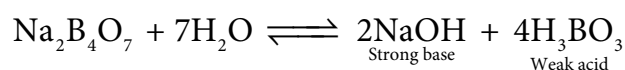
Choose the correct answer

1. b) $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ 2. c) SO_2 3. c) $\text{MgCO}_3 \longrightarrow \text{MgO} + \text{CO}_2$
4. b) Al_2O_3 5. a) Al
6. d) Carbon and hydrogen are suitable reducing agents for metal sulphides.
7. c) A-iv , B-ii , C-iii , D-i
8. d) Electromagnetic separation
9. b) $\text{Cu(s)} + \text{Zn}^{2+}(\text{aq}) \longrightarrow \text{Zn(s)} + \text{Cu}^{2+}(\text{aq})$
10. c) Sodium
11. b) Infusible impurities to soluble impurities
12. c) Galena
13. a) Lower the melting point of alumina
14. a) Carbon reduction
15. c) Displacement with zinc
16. c) Mg
17. b) Van Arkel process
18. d) Both (a) and (c)
19. d) In the metallurgy of gold, the metal is leached with dilute sodium chloride solution
20. b) Impure copper
21. b) ΔG^0 Vs T
22. c) $\left(\frac{\Delta G^0}{\Delta T} \right)$ is negative
23. b) $\text{Al}_2\text{O}_3 + 2\text{Cr} \longrightarrow \text{Cr}_2\text{O}_3 + 2\text{Al}$
24. b) The graph for the formation of CO_2 is a straight line almost parallel to free energy axis.

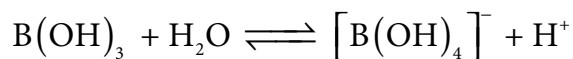
UNIT-2

Choose the correct answer:

1. c) basic



2. d) accepts OH^- from water, releasing proton.



3. b) B_3H_6

nido borane : B_nH_{4+n}

arachno borane : B_nH_{6+n}

B_3H_6 is not a borane

4. a) Aluminium

5. c) four

There are two $3\text{c} - 2\text{e}^-$ bonds i.e., the bonding in the bridges account for 4 electrons.

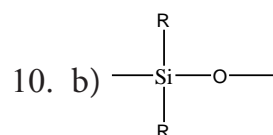
6. c) Lead

7. c) sp^2 hybridised

8. a) +4

Example : CH_{4+} in which the oxidation state of carbon is +4

9. d) $(\text{SiO}_4)^{4-}$



11. a) Me_3SiCl

12. d) dry ice

dry ice – solid CO_2 in which carbon is in sp hybridized state

13. a) Tetrahedral

14. d) Feldspar is a three dimensional silicate

15. a) A-b, B-1, C-4, D-3

16. d) Al, Cu, Mn, Mg

Al-95%, Cu-4%, Mn-0.5%, Mg-0.5%

17. a) Metal borides

18. a) $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$

stability of +1 oxidation state increases down the group due to inert pair effect

UNIT-3

Choose the correct answer:

1. a) Nessler's reagent

2. d) ability to form $p\pi - p\pi$ bonds with itself

3. d) $1s^2 2s^2 2p^6 3s^2 3p^3$

4. b) P_4 (white) and PH_3

5. a) H_3PO_3

6. a) H_3PO_3

7. b) 2

8. a) 6N

9. d) Both assertion and reason are wrong.
The converse is true.

10. b) F_2

11. b) $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$

12. d) NeF_2

13. c) He

14. c) XeO_3

15. a) HI

16. d) $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$

17. d) $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$

18. c) $\text{Cu}(\text{NO}_3)_2$ and NO_2

UNIT-4

Choose the correct answer:

1. b) in case of Sc, 3d orbitals are partially filled but in Zn these are completely filled

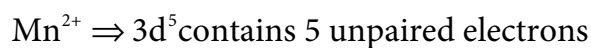
2. a) Cr



3. a) Ti

4. c) Ni^{2+}

5. a) 5.92BM



$$n=5 ; \therefore \sqrt{n(n+2)} \text{ BM}$$

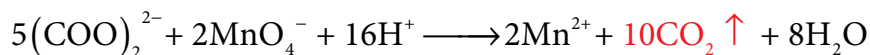
$$\therefore \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}$$

6. c) their ability to adopt variable oxidation states

7. a) $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$

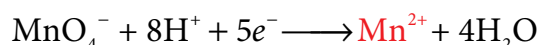


8. b) Carbon dioxide

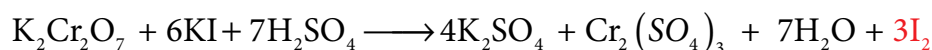


9. b) $\text{Na}_2\text{Cr}_2\text{O}_7$ is preferred over $\text{K}_2\text{Cr}_2\text{O}_7$ in volumetric analysis

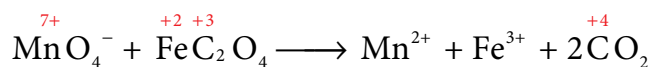
10. b) Mn^{2+}



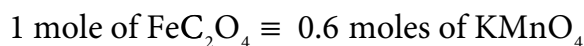
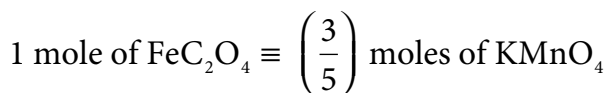
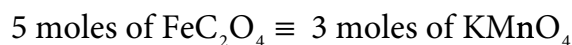
11. c) 3



12. c) 0.6



$5e^-$ acception $3e^-$ release



13. c) All the lanthanons are much more reactive than aluminium.

As we move from La to Lu, their metallic behaviour because almost similar to that of aluminium.

14. b) Yb^{2+}



15. d) +3

16. a) Both assertion and reason are true and reason is the correct explanation of assertion.

17. b) +3

18. a) Np, Pu, Am

19. a) $\text{La}(\text{OH})_2$ is less basic than $\text{Lu}(\text{OH})_3$

UNIT-5

Choose the correct answer:

1. In the complex $[\text{M}(\text{en})_2(\text{Ox})]\text{Cl}$ For the central metal ion M^{3+}

The primary valence is = +3

The secondary valence = 6

sum of primary valence and secondary valence = $3+6 = 9$

Answer : option (d)

2. The complex is $[\text{M}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$

1000 ml of 1M solution of the complex gives 2 moles of Cl^- ions

1000 ml of 0.01M solution of the complex will give

$$\frac{100 \text{ ml} \times 0.01\text{M} \times 2\text{Cl}^-}{1000 \text{ ml} \times 1\text{M}} = 0.002 \text{ moles of } \text{Cl}^- \text{ ions}$$

Answer : option (b)

3. Molecular formula: $\text{MSO}_4\text{Cl} \cdot 6\text{H}_2\text{O}$.

Formation of white precipitate with Barium chloride indicates that SO_4^{2-} ions are outside the coordination sphere, and no precipitate with AgNO_3 solution indicates that the Cl^- ions are inside the coordination sphere. Since the coordination number of M is 6, Cl^- and 5 H_2O are ligands, remaining 1 H_2O molecular and SO_4^{2-} are in the outer coordination sphere.

Answer : option (c)

4. $\left[\overset{+}{\text{Fe}}(\text{H}_2\text{O})_5 \overset{+}{\text{NO}} \right]^{2+} \text{SO}_4^{2-}$

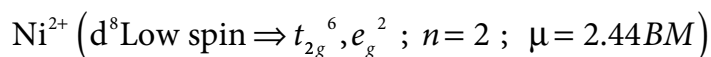
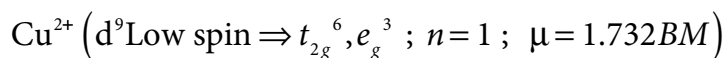
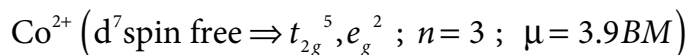
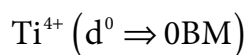
+1 and +1 respectively

Answer : option(d)

5. Answer : option(d)

6. Answer : option(d)

7. Answer : option(c)



8. Answer : option(b)

The electronic configuration t_{2g}^3, e_g^2

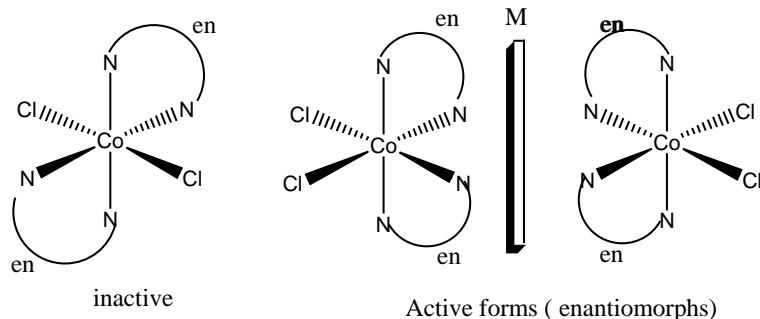
$$[3 \times (-0.4) + 2(0.6)]\Delta_0$$

$$[-1.2 + 1.2]\Delta_0 = 0$$

9. Answer : option(a)

In all the complexes, the central metal ion is Co^{3+} , among the given ligands CN^- is the strongest ligand, which causes large crystal field splitting i.e maximum Δ_0

10. Answer : option(b)



Complexes given in other options (a), (c) and (d) have symmetry elements and hence they are optically inactive.

11. Answer : option(d)



12. Three isomers. If we consider any one of the ligands as reference (say Py), the arrangement of other three ligands (NH_3 , Br^- and Cl^-) with respect to (Py) gives three geometrical isomers.

13. Answer : option(c)

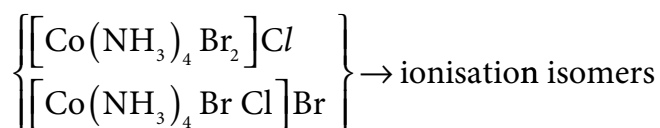
(a) coordination isomers

(b) no isomerism (different molecular formula)

(c) $\leftarrow \text{NCS}$, $\leftarrow \text{SCN}$ coordinating atom differs : linkage isomers

14. Answer : option(a)

For $[MA_4B_2]^{n+}$ complexes-geometrical isomerism is possible



15. Answer : option(d)

Option (a) and (b) – geometrical isomerism is possible

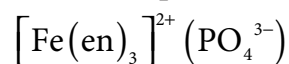
Option (c) – ionization isomerism is possible

Option (d) – no possibility to show either constitutional isomerism or stereo isomerism

16. Answer : option(c)

(a) Fe^{2+} (b) Fe^{3+} (c) Fe^0

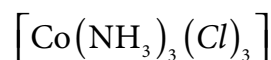
17. Answer : option(d)



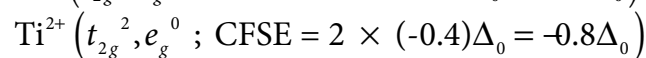
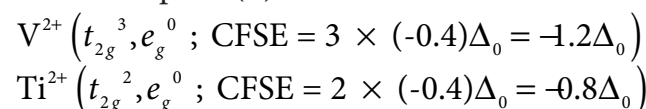
18. Answer : option(c)

- (a) Zn^{2+} ($d^{10} \Rightarrow$ diamagnetic)
 (b) Co^{3+} (d^6 Low spin $\Rightarrow t_{2g}^6, e_g^0$; diamagnetic)
 (c) Ni^{2+} (d^8 Low spin $\Rightarrow t_{2g}^6, e_g^2$; paramagnetic)
 (d) $[Ni(CN)_4]^{2-}$ (dsp^2 ; square planar, diamagnetic)

19. Answer : option(c)



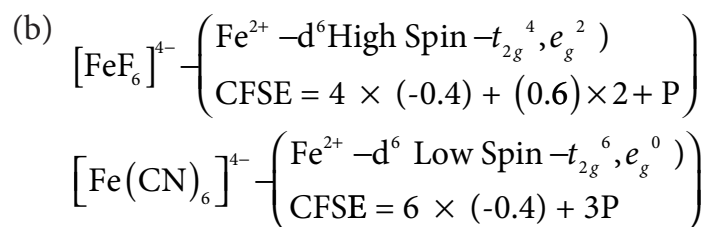
20. Answer : option(d)



Statements given in option (a) ,(b), and (c) are wrong.

The current statements are

(a) since, the crystal field stabilization is more in octahedral field , octahedral complexes are more stable than square planar complexes.



UNIT-6

Choose the correct answer:

1. c) both covalent crystals

2. b) AB_3

$$\text{number of A ions} = \left(\frac{N_c}{8} \right) = \left(\frac{8}{8} \right) = 1$$

$$\text{number of B ions} = \left(\frac{N_f}{2} \right) = \left(\frac{6}{2} \right) = 3$$

simplest formula AB_3

3. b) 1:2

if number of close packed atoms = N; then,

The number of Tetrahedral holes formed = $2N$

number of Octahedral holes formed = N

therefore $N:2N = 1:2$

4. c) molecular solid

lattice points are occupied by CO_2 molecules

5. a) Both assertion and reason are true and reason is the correct explanation of assertion.

6. c) 8 and 4

CaF_2 has cubical close packed arrangement

Ca^{2+} ions are in face centered cubic arrangement, each Ca^{2+} ions is surrounded by 8 F^- ions and each F^- ion is surrounded by 4 Ca^{2+} ions.

Therefore coordination number of Ca^{2+} is 8 and of F^- is 4

7. b) 6.023×10^{22}

in bcc unit cell,

2 atoms \equiv 1 unit cell

Number of atoms in 8g of element is ,

$$\text{Number of moles} = \frac{8g}{40 g mol^{-1}} = 0.2 \text{ mol}$$

1 mole contains 6.023×10^{23} atoms

0.2 mole contains $0.2 \times 6.023 \times 10^{23}$ atoms

$$\left(\frac{1 \text{ unit cell}}{2 \text{ atoms}} \right) \times 0.2 \times 6.023 \times 10^{23}$$

6.023×10^{22} unit cells

8. d) M_3N_2

if the total number of M atoms is n ,
then the number of tetrahedral voids
 $= 2n$

given that $\left(\frac{1}{3}\right)^{\text{rd}}$ of tetrahedral voids

are occupied i.e., $\left(\frac{1}{3}\right) \times 2n$ are occupied
by N atoms

$$\therefore M:N \Rightarrow n : \left(\frac{2}{3}\right)n$$

$$1 : \left(\frac{2}{3}\right)$$

$$3 : 2 \Rightarrow M_3N_2$$

9. c) 6

$$\frac{r_{C^+}}{r_{A^-}} = \frac{0.98 \times 10^{-10}}{1.81 \times 10^{-10}} = 0.54$$

it is in the range of 0.44–0.732, hence the
coordination number of each ion is 6

$$10. d) \left(\frac{\sqrt{3}}{2}\right) \times 400 \text{ pm}$$

$$\sqrt{3} a = r_{Cs^+} + 2r_{Cl^-} + r_{Cs^+}$$

$$\left(\frac{\sqrt{3}}{2}\right) a = (r_{Cs^+} + r_{Cl^-})$$

$$\left(\frac{\sqrt{3}}{2}\right) 400 = \text{inter ionic distance}$$

$$11. a) \left(\frac{100}{0.414}\right)$$

$$\text{for an fcc structure } \frac{r_{X^+}}{r_{Y^-}} = 0.414$$

$$\text{given that } r_{X^+} = 100 \text{ pm}$$

$$r_{Y^-} = \frac{100 \text{ pm}}{0.414}$$

12. c) 32%

packing efficiency = 68%

therefore empty space percentage =

$$(100 - 68) = 32\%$$

13. b) 848.5 pm

let edge length = a

$$\sqrt{2}a = 4r$$

$$a = \frac{4 \times 300}{\sqrt{2}}$$

$$a = 600 \times 1.414$$

$$a = 848.4 \text{ pm}$$

$$14. b) \left(\frac{\pi}{6}\right)$$

$$\left(\frac{\frac{4}{3}\pi r^3}{a^3}\right) = \left(\frac{\frac{4}{3}\pi \left(\frac{a}{2}\right)^3}{a^3}\right) = \left(\frac{\pi}{6}\right)$$

15. a) excitation of electrons in F centers

$$16. c) \left(\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a\right)$$

$$sc \Rightarrow 2r = a \Rightarrow r = \frac{a}{2}$$

$$bcc \Rightarrow 4r = \sqrt{3}a \Rightarrow r = \frac{\sqrt{3}a}{4}$$

$$fcc \Rightarrow 4r = \sqrt{2}a \Rightarrow r = \frac{\sqrt{2}a}{4} = \frac{a}{2\sqrt{2}}$$

$$\left(\frac{a}{2}\right) : \left(\frac{\sqrt{3}a}{4}\right) : \left(\frac{a}{2\sqrt{2}}\right)$$

$$17. d) \left(\frac{\sqrt{3}}{2}\right)a$$

if a is the length of the side, then the
length of the leading diagonal passing
through the body centered atom is $\sqrt{3}a$

$$\text{Required distance} = \left(\frac{\sqrt{3}}{2}\right)a$$

18. a) 915 kg m⁻³

$$\rho = \frac{n \times M}{a^3 N_A}$$

for bcc

$$n = 2$$

$$M = 39$$

$$\text{nearest distance } 2r = 4.52$$

$$a = \frac{4r}{\sqrt{3}} = \frac{2 \times 4.52 \times 10^{-10}}{\sqrt{3}} = 5.21 \times 10^{-10}$$

$$\rho = \frac{2 \times 39}{(5.21 \times 10^{-10})^3 \times (6.023 \times 10^{23})}$$

$$\rho = 915 \text{ Kg m}^{-3}$$

$$N_A$$

19. b) equal number of cations and anions are missing from the lattice

20. c) Frenkel defect

21. d) Both assertion and reason are false

22. b) FeO

23. a) XY_8

UNIT-7

Choose the correct answer:

1. option (c)

$$k = \left(\frac{2.303}{t} \right) \log \left(\frac{[A_0]}{[A]} \right)$$

$$k = \left(\frac{1}{t} \right) \ln \left(\frac{[A_0]}{[A]} \right)$$

$$e^{kt} = \left(\frac{[A_0]}{[A]} \right)$$

$$[A] = [A_0] e^{-kt}$$

In this case

$$k = x \text{ min}^{-1} \text{ and } [A_0] = 0.01M = 1 \times 10^{-2}M$$

$$t = 1 \text{ hour} = 60 \text{ min}$$

$$[A] = 1 \times 10^{-2} (e^{-60x})$$

2. option (c)



$$\text{for } n \neq 1 \quad t_{1/2} = \frac{2^{n-1} - 1}{(n-1) k [A_0]^{n-1}}$$

$$\text{for } n = 0 \quad t_{1/2} = \frac{1}{2 k [A_0]^1}$$

$$t_{1/2} = \frac{[A_0]}{2 k}$$

$$t_{1/2} \propto [A_0] \text{ ————— (1)}$$

given

$$[A_0] = 0.02 \text{ M} ; t_{1/2} = 10 \text{ min}$$

$$[A_0] = 0.04 \text{ M} ; t_{1/2} = ?$$

substitute in (1)

$$10 \text{ min} \propto 0.02 \text{ M} \text{ ————— (2)}$$

$$t_{1/2} \propto 0.04 \text{ M} \text{ ————— (3)}$$

$$\frac{(3)}{(2)}$$

$$\Rightarrow \frac{t_{1/2}}{10 \text{ min}} = \frac{0.04 \text{ M}}{0.02 \text{ M}}$$

$$t_{1/2} = 2 \times 10 \text{ min} = 20 \text{ min}$$

3. option (b)

$$k = A e^{\left(\frac{E_a}{RT}\right)}$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right) \left(\frac{1}{T}\right)$$

this equation is in the form of a straight line equation

$$y = c + m x$$

a plot of $\ln k$ vs $\left(\frac{1}{T}\right)$ is a straight line with negative slope

4. option (c)

For a first order reaction

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

$t_{1/2}$ does not depend on the initial concentration and it remains constant (whatever may be the initial concentration)

$$t_{1/2} = 2.5 \text{ hrs}$$

5. option(c)

$$\text{Rate} = \left(\frac{-1}{2}\right) \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \left(\frac{1}{3}\right) \frac{d[\text{H}_2]}{dt}$$

$$\left(\frac{1}{2}\right) k_1 [\text{NH}_3] = k_2 [\text{NH}_3] = \left(\frac{1}{3}\right) k_3 [\text{NH}_3]$$

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

$$1.5 k_1 = 3k_2 = k_3$$

6. option(a)

Given :

At low pressure the reaction follows first order, therefore

$$\text{Rate} \propto [\text{reactant}]^1$$

$$\text{Rate} \propto (\text{surface area})$$

At high pressure due to the complete coverage of surface area, the reaction follows zero order.

$$\text{Rate} \propto [\text{reactant}]^0$$

Therefore the rate is independent of surface area.

7. option(b)

$$\text{rate} = k[\text{A}]^n$$

$$\text{rate} = \frac{-d[\text{A}]}{dt}$$

$$\text{unit of rate} = \frac{\text{mol L}^{-1}}{\text{s}} = \text{mol L}^{-1} \text{s}^{-1}$$

$$\text{unit of rate constant} = \frac{(\text{mol L}^{-1} \text{s}^{-1})}{(\text{mol L}^{-1})^n} = \text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$$

in this case

$$\text{rate} = k[\text{Acetone}]^{3/2}$$

$$n = \frac{3}{2}$$

$$\text{mol}^{1-(3/2)} \text{L}^{(3/2)-1} \text{s}^{-1}$$

$$\text{mol}^{-(1/2)} \text{L}^{(1/2)} \text{s}^{-1}$$

8. option(b)

A catalyst provides a new path to the reaction with low activation energy. i.e., it lowers the activation energy.

9. option(a)

In zero order reactions, increase in the concentration of reactant does not alter the rate.

So statement (i) is wrong.

$$k = A e^{-\left(\frac{E_a}{RT}\right)}$$

if $E_a = 0$ so, statement (ii) is correct, and statement (iii) is wrong

$$k = A e^0$$

$$k = A$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$$

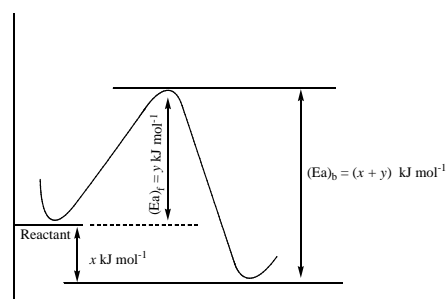
this equation is in the form of a straight line equation

$$y = c + m x$$

a plot of $\ln k$ vs $\left(\frac{1}{T}\right)$ is a straight line with negative slope

so statements (iv) and (v) are wrong.

10. option(d)



$$(x + y) \text{ kJ mol}^{-1}$$

$$(x + y) \times 10^3 \text{ J mol}^{-1}$$

11. option(c)

$$T_1 = 200\text{K} ; k = k_1$$

$$T_2 = 400\text{K} ; k = k_2 = 2k_1$$

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

$$\log\left(\frac{2k_1}{k_1}\right) = \frac{E_a}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{400 \text{ K} - 200 \text{ K}}{200 \text{ K} \times 400 \text{ K}}\right)$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 200 \text{ K} \times 400 \text{ K}}{200 \text{ K}}$$

$$E_a = 2305 \text{ J mol}^{-1}$$

$$E_a = 2.305 \text{ kJ mol}^{-1}$$

12. option(a)

$$k = \left(\frac{2.303}{t} \right) \log \left(\frac{[A_0]}{[A]} \right)$$

$$2.303 \times 10^{-2} \text{ hour}^{-1} = \left(\frac{2.303}{1806 \text{ min}} \right) \log \left(\frac{0.25}{[A]} \right)$$

$$\left(\frac{2.303 \times 10^{-2} \text{ hour}^{-1} \times 1806 \text{ min}}{2.303} \right) = \log \left(\frac{0.25}{[A]} \right)$$

$$\left(\frac{1806 \times 10^{-2}}{60} \right) = \log \left(\frac{0.25}{[A]} \right)$$

$$0.301 = \log \left(\frac{0.25}{[A]} \right)$$

$$\log 2 = \log \left(\frac{0.25}{[A]} \right)$$

$$2 = \left(\frac{0.25}{[A]} \right)$$

$$[A] = \left(\frac{0.25}{2} \right) = 0.125 \text{ M}$$

13. option(b)

$$k = \left(\frac{2.303}{t} \right) \log \left(\frac{[A_0]}{[A]} \right)$$

$$[A_0] = 100 ; [A] = 25$$

$$6.909 = \left(\frac{2.303}{t} \right) \log \left(\frac{100}{25} \right)$$

$$t = \left(\frac{2.303}{6.909} \right) \log(4)$$

$$t = \left(\frac{1}{3} \right) \log 2^2$$

$$t = \left(\frac{2}{3} \right) \log 2$$

14. option(c)

$$k = \left(\frac{1}{t} \right) \ln \left(\frac{[A_0]}{[A]} \right)$$

$$[A_0] = 0.1 ; [A] = 0.05$$

$$k = \left(\frac{1}{t_{1/2}} \right) \ln \left(\frac{0.1}{0.05} \right)$$

$$k = \left(\frac{1}{t_{1/2}} \right) \ln(2)$$

$$t_{1/2} = \frac{\ln(2)}{k}$$

15. option(b)

$$\text{rate}_1 = k[0.1]^n [0.1]^m \text{ ———(1)}$$

$$\text{rate}_2 = k[0.2]^n [0.1]^m \text{ ———(2)}$$

$$\frac{(2)}{(1)}$$

$$\frac{2x}{x} = \frac{k[0.2]^n [0.1]^m}{k[0.1]^n [0.1]^m}$$

$$\frac{2x}{x} = 2^n \quad \therefore n = 1$$

$$\text{rate}_3 = k[0.1]^n [0.2]^m \text{ ———(3)}$$

$$\text{rate}_4 = k[0.2]^n [0.2]^m \text{ ———(4)}$$

$$\frac{(4)}{(2)}$$

$$\frac{8x}{2x} = \frac{k[0.2]^n [0.2]^m}{k[0.2]^n [0.1]^m}$$

$$\frac{8}{2} = 2^m \quad \therefore m = 2$$

$$\therefore \text{rate} = k[A]^1 [B]^2$$

16. option(c)

For a first reaction, If the concentration of reactant is doubled, then the rate of reaction also doubled.

Rate constant is independent of concentration and is a constant at a constant temperature,

17. option(a)

The unit of rate constant is s^{-1} and it indicates that the reaction is first order.

18. option(c)

$$\text{Rate} = \frac{d[\text{N}_2\text{O}_5]}{dt} = \left(\frac{1}{2}\right) \frac{d[\text{NO}_2]}{dt} = \frac{2 d[\text{O}_2]}{dt}$$

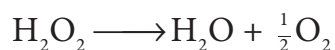
Given that

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = 6.5 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}$$

$$\frac{d[\text{NO}_2]}{dt} = 2 \times 6.5 \times 10^{-2} = 1.3 \times 10^{-1} \text{ mol L}^{-1}\text{s}^{-1}$$

$$\frac{d[\text{O}_2]}{dt} = \frac{6.5 \times 10^{-2}}{2} = 3.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}$$

19. option(d)



$$\text{Rate} = \frac{-d[\text{H}_2\text{O}_2]}{dt} = \frac{d[\text{H}_2\text{O}]}{dt} = \frac{2d[\text{O}_2]}{dt}$$

$$\text{no of moles of oxygen} = \left(\frac{48}{32}\right) = 1.5 \text{ mol}$$

$$\therefore \text{rate of formation of oxygen} = 1.5 \text{ mol min}^{-1}$$

$$\therefore \text{rate of formation of water} = 2 \times 1.5 = 3 \text{ mol min}^{-1}$$

20. option(a)

For a first order reaction $t_{1/2}$ is independent of initial concentration i.e., $\therefore n \neq 1$; for such cases

$$t_{1/2} \propto \frac{1}{[A_0]^{n-1}} \quad \text{----- (1)}$$

$$\text{If } [A_0] = 2[A_0] ; \text{ then } t_{1/2} = 2t_{1/2}$$

$$2 t_{1/2} \propto \frac{1}{[2 A_0]^{n-1}} \quad \text{----- (2)}$$

$$\frac{(2)}{(1)} \Rightarrow$$

$$2 = \frac{1}{[2A_0]^{n-1}} \times \frac{[A_0]^{n-1}}{1}$$

$$2 = \frac{[A_0]^{n-1}}{[2A_0]^{n-1}}$$

$$2 = \left(\frac{1}{2}\right)^{n-1}$$

$$2 = (2^{-1})^{n-1}$$

$$2^1 = (2^{-n+1})$$

$$n = 0$$

21. Answer : option(a)

	A	→	B	C	D
Initial	a		0	0	0
Reacted at time t	x		–	–	–
After time t	(a – x)		x	x	x
Total number of moles		= (a + 2x)			

$$a \propto P_0$$

$$(a + 2x) \propto P$$

$$\frac{a}{(a + 2x)} = \frac{P_0}{P}$$

$$x = \frac{(P - P_0)a}{2P_0}$$

$$(a - x) = a - \left(\frac{(P - P_0)a}{2P_0} \right)$$

$$(a - x) = a \left\{ \frac{3P_0 - P}{2P_0} \right\}$$

$$k = \left(\frac{2.303}{t} \right) \log \frac{[A_0]}{[A]}$$

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

$$k = \left(\frac{2.303}{t} \right) \log \left(\frac{a}{a \left\{ \frac{3P_0 - P}{2P_0} \right\}} \right)$$

$$k = \left(\frac{2.303}{t} \right) \log \left(\frac{2P_0}{3P_0 - P} \right)$$

22. Answer : option(b) 30min

$$t_{75\%} = 2t_{50\%}$$

$$t_{50\%} = \left(\frac{t_{75\%}}{2} \right) = \left(\frac{60}{2} \right) = 30 \text{ min}$$

23. Answer : option(d)

in 140 days \Rightarrow initial concentration reduced to $\left(\frac{1}{2} \right) g$

in 280 days \Rightarrow initial concentration reduced to $\left(\frac{1}{4} \right) g$

in 420 days \Rightarrow initial concentration reduced to $\left(\frac{1}{8} \right) g$

in 560 days \Rightarrow initial concentration reduced to $\left(\frac{1}{16} \right) g$

24. Answer : option(b)

For a first order reaction

$$t_{1/2} = \frac{0.6932}{k}$$

For a second order reaction

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1) k [A_0]^{n-1}}$$

$$n = 2$$

$$t_{1/2} = \frac{2^{2-1} - 1}{(2-1) k [A_0]^{2-1}}$$

$$t_{1/2} = \frac{1}{k [A_0]}$$

25. Answer : option(c)

$$1 \xrightarrow{t_{1/2}} \left(\frac{1}{2} \right) \xrightarrow{t_{1/2}} \left(\frac{1}{4} \right) \xrightarrow{t_{1/2}} \left(\frac{1}{8} \right) \xrightarrow{t_{1/2}} \left(\frac{1}{16} \right)$$

$$\therefore 4 t_{1/2} = 2 \text{ hours}$$

$$t_{1/2} = 30 \text{ min}$$

Answer the following:

10 solution

$$\text{Rate} = k[A]^2[B][L]^{\frac{3}{2}} \text{ -----(1)}$$

(i) when $[L] = [4L]$

$$\text{Rate} = k[A]^2[B][4L]^{\frac{3}{2}}$$

$$\text{Rate} = 8 \left(k[A]^2[B][L]^{\frac{3}{2}} \right) \text{ -----(2)}$$

Comparing (1) and (2) ; rate is increased by 8 times.

(ii) when $[A] = [2A]$ and $[B] = [2B]$

$$\text{Rate} = k[2A]^2[2B][L]^{\frac{3}{2}}$$

$$\text{Rate} = 8 \left(k[A]^2[B][L]^{\frac{3}{2}} \right) \text{ -----(3)}$$

Comparing (1) and (3) ; rate is increased by 8 times.

(iii) when $[A] = \left[\frac{A}{2} \right]$

$$\text{Rate} = k \left[\frac{A}{2} \right]^2 [B][L]^{\frac{3}{2}}$$

$$\text{Rate} = \left(\frac{1}{4} \right) \left(k[A]^2[B][L]^{\frac{3}{2}} \right) \text{ -----(4)}$$

Comparing (1) and (4) ; rate is reduced to $\frac{1}{4}$ times.

(iv) when $[A] = \left[\frac{A}{3} \right]$ and $[L] = [4L]$

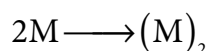
$$\text{Rate} = k \left[\frac{A}{3} \right]^2 [B][4L]^{\frac{3}{2}}$$

$$\text{Rate} = \left(\frac{8}{9} \right) \left(k[A]^2[B][L]^{\frac{3}{2}} \right) \text{ -----(5)}$$

Comparing (1) and (5) ; rate is reduced to $\frac{8}{9}$ times.

11. solution

Let us consider the dimerisation of a monomer M



$$\text{Rate} = k[M]^n$$

Given that $n=2$ and $[M] = 0.05 \text{ mol L}^{-1}$

$$\text{Rate} = 7.5 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$$

$$k = \frac{\text{Rate}}{[M]^n}$$

$$k = \frac{7.5 \times 10^{-3}}{(0.05)^2} = 3 \text{ mol}^{-1} \text{Ls}^{-1}$$

12. Solution

$$\text{rate} = k[x]^{\left(\frac{3}{2}\right)}[y]^{\left(\frac{1}{2}\right)}$$

$$\text{overall order} = \left(\frac{3}{2} + \frac{1}{2}\right) = 2$$

i.e., second order reaction.

Since the rate expression does not contain the concentration of z, the reaction is zero order with respect to z.

15. Solution:

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{1 \text{ min}} \log \frac{[0.08]}{[0.04]}$$

$$k = 2.303 \log 2$$

$$k = 2.303 \times 0.3010$$

$$k = 0.6932 \text{ min}^{-1}$$

$$k = \left(\frac{0.6932}{60}\right) \text{ s}^{-1}$$

$$k = 1.153 \times 10^{-2} \text{ s}^{-1}$$

19. Solution

$$k = A e^{-\left(\frac{E_a}{RT}\right)}$$

$$k = 1.6 \times 10^{13} \text{ s}^{-1} e^{-\left(\frac{200 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 600 \text{ K}}\right)}$$

$$k = 1.6 \times 10^{13} \text{ s}^{-1} e^{-(40.1)}$$

$$k = 1.6 \times 10^{13} \text{ s}^{-1} \times 3.8 \times 10^{-18}$$

$$k = 6.21 \times 10^{-5} \text{ s}^{-1}$$

20. Solution

$$\text{rate} = k[x]^n [y]^m$$

$$0.15 = k[0.2]^n [0.02]^m \text{ —————(1)}$$

$$0.30 = k[0.4]^n [0.02]^m \text{ —————(2)}$$

$$1.20 = k[0.4]^n [0.08]^m \text{ —————(3)}$$

$$\frac{(3)}{(2)}$$

$$\frac{1.2}{0.3} = \frac{k[0.4]^n [0.08]^m}{k[0.4]^n [0.02]^m}$$

$$4 = \left(\frac{[0.08]}{[0.02]} \right)^m$$

$$4 = (4)^m$$

$$\therefore m = 1$$

$$\frac{(2)}{(1)}$$

$$\frac{0.30}{0.15} = \frac{k[0.4]^n [0.02]^m}{k[0.2]^n [0.02]^m}$$

$$2 = \left(\frac{[0.4]}{[0.2]} \right)^n$$

$$2 = (2)^n$$

$$\therefore n = 1$$

$$\text{Rate} = k[x]^1 [y]^1$$

$$0.15 = k[0.2]^1 [0.02]^1$$

$$\frac{0.15}{[0.2]^1 [0.02]^1} = k$$

$$k = 37.5 \text{ mol}^{-1} \text{L s}^{-1}$$

23 Solution:

We know that, $t_{1/2} = 0.693/k$

$$t_{1/2} = 0.693/1.54 \times 10^{-3} \text{ s}^{-1} = 450 \text{ s}$$

24. Solution:

We know that, $k = 0.693/t_{1/2}$

$$k = 0.693/8.0 \text{ minutes} = 0.087 \text{ minutes}^{-1}$$

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]}$$

$$t = \frac{2.303}{0.087 \text{ min}^{-1}} \log \left(\frac{100}{1} \right)$$

$$t = 52.93 \text{ min}$$

25 Solution:

i) Order of a reaction = 1; $t_{1/2} = 60$; seconds, $k = ?$

$$\text{We know that, } k = \frac{0.6932}{t_{1/2}}$$

$$k = \frac{2.303}{60} = 0.01155 \text{ s}^{-1}$$

ii) $[A_0] = 100\%$ $t = 180 \text{ s}$, $k = 0.01155 \text{ seconds}^{-1}$, $[A] = ?$

For the first order reaction

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$0.01155 = \frac{2.303}{180} \log \left(\frac{100}{[A]} \right)$$

$$\frac{0.01155 \times 180}{2.303} = \log \left(\frac{100}{[A]} \right)$$

$$0.9207 = \log 100 - \log [A]$$

$$\log [A] = \log 100 - 0.9207$$

$$\log [A] = 2 - 0.9207$$

$$\log [A] = 1.0973$$

$$[A] = \text{antilog of } (1.0973)$$

$$[A] = 12.5\%$$

26 Solution:

i) Let $A = 100\text{M}$, $[A_0] - [A] = 20\text{M}$,

For the zero order reaction

$$k = \left(\frac{[A_0] - [A]}{t} \right)$$

$$k = \left(\frac{20M}{20\text{min}} \right) = 1 \text{ Mmin}^{-1}$$

Rate constant for a reaction = 1 Mmin^{-1}

ii) To calculate the time for 80% of completion

$$k = 1 \text{ Mmin}^{-1}, [A_0] = 100M, [A_0] - [A] = 80M, t = ?$$

Therefore,

$$t = \left(\frac{[A_0] - [A]}{k} \right) = \left(\frac{80M}{1 \text{ Mmin}^{-1}} \right) = 80 \text{ min}$$

27 Solution:

Here, we are given that

$$E_a = 22.5 \text{ kcal mol}^{-1} = 22500 \text{ cal mol}^{-1}$$

$$T = 40^\circ\text{C} = 40 + 273 = 313 \text{ K}$$

$$k = 1.8 \times 10^{-5} \text{ sec}^{-1}$$

Substituting the values in the equation

$$\log A = \log k + \left(\frac{E_a}{2.303RT} \right)$$

$$\log A = \log(1.8 \times 10^{-5}) + \left(\frac{22500}{2.303 \times 1.987 \times 313} \right)$$

$$\log A = \log(1.8) - 5 + (15.7089)$$

$$\log A = 10.9642$$

$$A = \text{antilog}(10.9642)$$

$$A = 9.208 \times 10^{10} \text{ collisions s}^{-1}$$

28.Solution:

For a first order reaction

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

In the present case, $V_\infty = 58.3 \text{ ml}$.

The value of k at different time can be calculated as follows:

$t \text{ (min)}$	V_t	$V_\infty - V_t$	$\frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$
6	19.3	$58.3 - 19.3 = 39.0$	$k = \frac{2.303}{6} \log \left(\frac{58.3}{39} \right) = 0.0670 \text{ min}^{-1}$
12	32.6	$58.3 - 32.6 = 25.7$	$k = \frac{2.303}{12} \log \left(\frac{58.3}{25.7} \right) = 0.0683 \text{ min}^{-1}$
18	41.3	$58.3 - 41.3 = 17.0$	$k = \frac{2.303}{18} \log \left(\frac{58.3}{17} \right) = 0.0685 \text{ min}^{-1}$
24	46.5	$58.3 - 46.5 = 11.8$	$k = \frac{2.303}{24} \log \left(\frac{58.3}{11.8} \right) = 0.0666 \text{ min}^{-1}$

Since the value of k comes out to be nearly constant, the given reaction is of the first order. The mean value of $k = 0.0676 \text{ min}^{-1}$

29. Solution:

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$k = \left(\frac{2.303}{t} \right) \log \left(\frac{V_0}{V_t} \right)$$

In the present case, $V_0 = 46.1 \text{ ml}$.

The value of k at each instant can be calculated as follows:

$t \text{ (min)}$	V_t	$k = \left(\frac{2.303}{t} \right) \log \left(\frac{V_0}{V_t} \right)$
10	29.8	$k = \frac{2.303}{10} \log \left(\frac{46.1}{29.8} \right) = 0.0436 \text{ min}^{-1}$
20	19.3	$k = \frac{2.303}{20} \log \left(\frac{46.1}{19.3} \right) = 0.0435 \text{ min}^{-1}$

Thus, the value of k comes out to be nearly constant. Hence it is a reaction of the first order.

30. Solution:

i) For the first order reaction $k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$

Assume, $[A_0] = 100 \%$, $t = 50 \text{ minutes}$

Therefore, $[A] = 100 - 40 = 60$

$$k = (2.303 / 50) \log (100 / 60)$$

$$k = 0.010216 \text{ min}^{-1}$$

Hence the value of the rate constant is $0.010216 \text{ min}^{-1}$

ii) $t = ?$, when the reaction is 80% completed,

$$[A] = 100 - 80 = 20 \%$$

From above, $k = 0.010216 \text{ min}^{-1}$

$$t = (2.303 / 0.010216) \log (100 / 20)$$

$$t = 157.58 \text{ min}$$

The time at which the reaction will be 80% complete is 157.58 min.