DPP - Daily Practice Problems

Chapter-wise Sheets

Date : 		**Start Time :** 		**End Time :**

CHEMISTRY

CC26

SYLLABUS : Polymers

Max. Marks : 74 		**Time : 60 min.**

GENERAL INSTRUCTIONS

- The Daily Practice Problem Sheet contains 20 Questions divided into 5 sections.
  Section I has **14** MCQs with ONLY 1 Correct Option, **3** marks for each correct answer and **–1** for each incorrect answer.
  Section II has **8** MCQs with ONE or MORE THAN ONE Correct options.
  For each question, marks will be awarded in one of the following categories:
  Full marks: **+4** If only the bubble(s) corresponding to all the correct option(s) is (are) darkened.
  Partial marks: **+1** For darkening a bubble corresponding to each correct option provided NO INCORRECT option is darkened.
  Zero marks: If none of the bubbles is darkened.
  Negative marks: **–2** In all other cases.

Section I - Straight Objective Type

This section contains 14 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which **ONLY ONE** is correct.

1. Which one of the following statement is *not true*?

(a) In vulcanization the formation of sulphur bridges between different chains make rubber harder and stronger.

(b) Natural rubber has the *trans* -configuration at every double bond.

(c) Buna-S is a copolymer of butadiene and styrene.

(d) Natural rubber is a 1, 4 - polymer of isoprene.

2. The condensation of hexamethylenediamine with sebacoyl chloride at 525 K gives

(a) nylon-6,20 		(b) nylon-6,01

(c) nylon-6,10 		(d) None of these

3. The polymer used in orthopaedic devices and in controlled drug release is

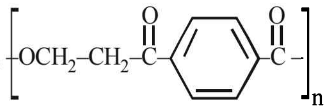
(a) Orlon 		(b) PTFE

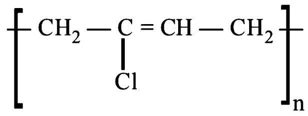
(c) SBR 		(d) PHBV

RESPONSE GRID 1. ⓐⓑⓒⓓ 2. ⓐⓑⓒⓓ 3. ⓐⓑⓒⓓ

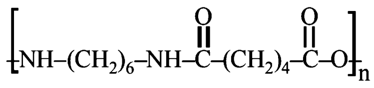
Space for Rough Work

4. Which of the following is not correctly matched?

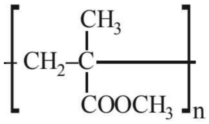
(a) Terylene 

(b) Neoprene 

$$\left[-CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2-\right]_n$$

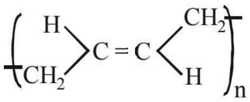
(c) Nylon-66 

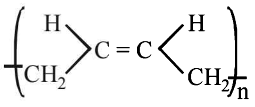
$$\left[-NH-(CH_2)_6-NH-\overset{\overset{O}{||}}{C}-(CH_2)_4-\overset{\overset{O}{||}}{C}-O-\right]_n$$

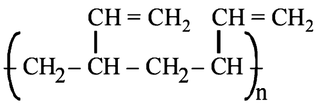
(d) PMMA 

$$\left[-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{COOCH_3}{|}}{C}}-\right]_n$$

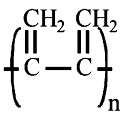
5. Mark out the most unlike form of polymerization of $CH_2=CH-CH=CH_2$

(a) 

(b) 

(c) 

$$\left(-CH_2-\underset{|}{\overset{CH=CH_2}{CH}}-CH_2-\underset{|}{\overset{CH=CH_2}{CH}}-\right)_n$$

(d) 

$$\left(-\overset{\overset{CH_2}{||}}{C}-\overset{\overset{CH_2}{||}}{C}-\right)_n$$

6. Ebonite is

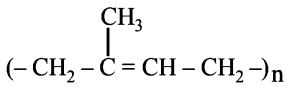
(a) Natural rubber

(b) Synthetic rubber

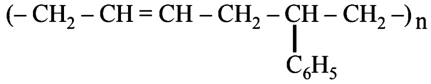
(c) Highly vulcanized rubber

(d) Polypropene

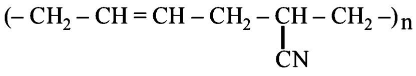
7. Structure of some important polymers are given. Which one represents Buna-S?

(a) 

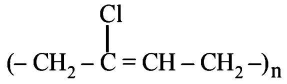
$$(-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-)_n$$

(b) 

$$(-CH_2-CH=CH-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-CH_2-)_n$$

(c) 

$$(-CH_2-CH=CH-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2-)_n$$

(d) 

$$(-CH_2-\overset{\overset{Cl}{|}}{C}=CH-CH_2-)_n$$

8. What is the percentage of sulphur used in vulcanization of rubber

(a) 05% to 30%
(b) 03% to 25%
(c) 10% to 20%
(d) 05% to 25%

9. Which one of the following is not a condensation polymer?

(a) Melamine
(b) Glyptal
(c) Dacron
(d) Neoprene

10. Which of the following is not an example of addition polymer ?

(a) Polystyrene
(b) Nylon
(c) PVC
(d) Polypropylene

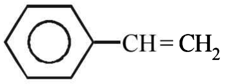
RESPONSE GRID	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ
	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ			

11. Which one of the following sets forms the biodegradable polymer?

(a) $CH_2=CH-CN$ and $CH_2=CH-CH=CH_2$

(b) H_2N-CH_2-COOH and $H_2N-(CH_2)_5-COOH$

(c) $HO-CH_2-CH_2-OH$ and

(d) 

and $CH_2=CH-CH=CH_2$

12. Among the following a natural polymer is

(a) cellulose (b) PVC

(c) teflon (d) polyethylene

13. Which of the following polymer is a polyamide ?

(a) Terylene (b) Nylon

(b) Rubber (d) Vulcanised rubber

14. Which of the following polymers do not involve cross linkages?

(a) Melmac (b) Bakelite

(c) Polythene (d) Vulcanised rubber

Section II - Multiple Correct Answer Type

This section contains 8 multiple correct answer(s) type questions. Each question has 4 choices (a), (b), (c) and (d), out of which **ONE OR MORE** is/are correct.

15. Which of the following polymers can be made by free radical addition polymerisation mechanism?

(a) PE (b) HDPE

(c) LDPE (d) Teflon

16. Which of the following polymers can be made by condensation polymerisation reaction?

(a) Dacron (b) Nylon-6, 6

(c) Bakelite (d) PE

17. Nylon-5, 10 can be prepared by:

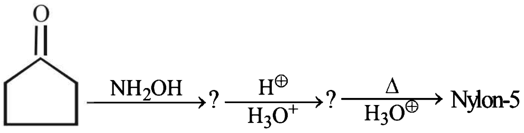
(a) $H_2N(CH_2)_5NH_2$ + Decanoic acid (Sebacic acid)

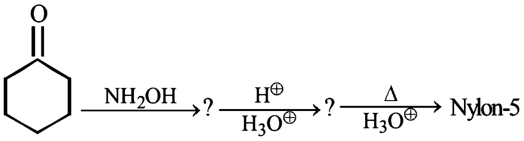
(b) $HOOC(CH_2)_3COOH + H_2N(CH_2)_{10}NH_2$

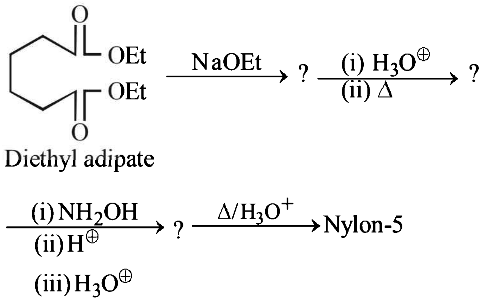
(c) $H_2N(CH_2)_6NH_2 + HOOC(CH_2)_8COOH$

(d) $H_2N(CH_2)_{10}NH_2 + HOOC(CH_2)_4COOH$

18. By which of the following reaction sequence can nylon-5 be prepared?

(a) 

(b) 

(c) 

(d) All

RESPONSE GRID				
	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ
	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ

Space for Rough Work

19. Which of the following fibres are made of polyamides?

(a) Wool (b) Natural silk

(c) Rayon (d) Nylon

20. Which of the following polymers contain 1, 3-butadiene as one of the monomers?

(a) Butyl rubber (b) Nitrile rubber

(c) ABS plastic (d) SBR

21. Which one of the following statement is/are *true*?

(a) In vulcanization the formation of sulphur bridges between different chains make rubber harder and stronger.

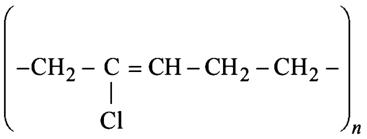
(b) Natural rubber has the *trans* -configuration at every double bond

(c) Buna-S is a copolymer of butadiene and styrene

(d) Natural rubber is a 1, 4 - polymer of isoprene

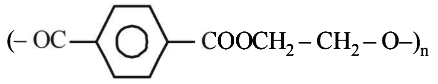
22. Structures of some common polymers are given. Which one is correctly presented?

(a) Neoprene;



$$\left(-CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2-CH_2-\right)_n$$

(b) Terylene;



(c) Nylon 6, 6;

$[-NH(CH_2)_6NHCO(CH_2)_4CO-]_n$

(d) Teflon; $(-CF_2-CF_2-)_n$

RESPONSE GRID				
	19.ⓐⓑⓒⓓ	20.ⓐⓑⓒⓓ	21.ⓐⓑⓒⓓ	22.ⓐⓑⓒⓓ

DAILY PRACTICE PROBLEM DPP CHAPTERWISE 26 - CHEMISTRY			
Total Questions	22	Total Marks	74
Attempted		Correct	
Incorrect		Net Score	
Cut-off Score	30	Qualifying Score	48
Success Gap = Net Score – Qualifying Score			
Net Score = (Correct × 4) – (Incorrect × 1)			

Space for Rough Work

1. **(a)** $$\frac{E+\text{Eq.mass of } Cl^-}{\text{Eq. mass of } Ag+\text{Eq. mass of } Cl^-}=\frac{E+35.5}{108+35.5}$$

$$=\frac{0.2}{0.5}\Rightarrow E=21.90$$

2. **(b)** $H_2SO_4+2NaOH \longrightarrow Na_2SO_4+2H_2O$;

Mol. of H_2SO_4 required for 1 mol of NaOH $=\frac{1}{2}=0.5$

$H_3PO_4+3NaOH \longrightarrow Na_3PO_4+3H_2O$;

Mol. of H_3PO_4 required for 1 mol of NaOH $=\frac{1}{3}$

Hence, mass of H_2SO_4 : mass of H_3PO_4 $=\frac{1}{2}:\frac{1}{3}$

$=3:2 \quad (M_{H_2SO_4}=M_{H_3PO_4}=98)$

3. **(a)** $Cu+2H_2SO_4(aq) \longrightarrow CuSO_4(aq)+2H_2O+SO_2(g)$
1 mole 2 mole 1 mole

From the above equation we find that 1 mole of Cu reacts with 2 mole of H_2SO_4. Since we have only 1 mole of H_2SO_4 so it is the limiting reagent.

Now

Since 2 moles of H_2SO_4 react with Cu to produce SO_2 = 1 mole

$\therefore$ 1 mole of H_2SO_4 reacts with Cu to produce SO_2

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

Now one mole of $SO_2 = 6.023 \times 10^{23}$ molecules of SO_2

$\therefore \frac{1}{2}$ mole of $SO_2=\frac{6.023\times10^{23}}{2}$ molecules of SO_2

$= 3 \times 10^{23}$ molecules of SO_2

4. **(a)** No. of molecules in different cases

(a) $\because$ 22.4 litre of H_2 at STP contains
$= 6.023 \times 10^{23}$ molecules of H_2

$\therefore$ 15 litre of H_2 at STP contains $=\frac{15}{22.4}\times 6.023\times10^{23}$

$= 4.03 \times 10^{23}$ molecules of H_2

(b) $\because$ 22.4 litre of N_2 gas at STP contains
$= 6.023\times10^{23}$ molecules of N_2

$\therefore$ 5 litre of N_2 gas at STP contains

$=\frac{5}{22.4}\times 6.023\times10^{23}$

$= 1.344 \times 10^{23}$ molecules of N_2

(c) $\because$ 2 g of $H_2 = 6.023\times10^{23}$ molecules of H_2

$\therefore$ 0.5 g of $H_2=\frac{0.5}{2}\times 6.023\times10^{23}$

$= 1.505 \times 10^{23}$ molecules of H_2

(d) Similarly 10 g of O_2 gas

$=\frac{10}{32}\times 6.023\times10^{23}$ molecules of O_2

$= 1.88 \times 10^{23}$ molecules of O_2

5. **(d)**

Element	Percentage	Atomic mass	Relative no. of atoms	Simplest ratio
C	20%	12	1.66	1
H	6.7%	1	6.7	4
N	46.7%	14	3.33	2
O	26.6%	16	1.66	1

Empirical formula = Molecular formula
$= CH_4N_2O$ or NH_2CONH_2

$$H_2NCONH_2+H_2NCONH_2 \xrightarrow{\Delta}$$

$$\underset{\text{biuret,}}{H_2NCONHCONH_2}+NH_3$$

When an aqueous solution of biuret is treated with dilute sodium hydroxide and a drop of copper sulphate, a violet colour is produced. This test is known as biuret test, is characteristic of compounds having the group –CONH.

6. **(b,c,d)** $2Na_3PO_4(aq)+3Ba(NO_3)_2(aq)$
$\longrightarrow Ba_3(PO_4)_2(s)+6NaNO_2(aq)$

Na_3PO_4 is the limiting reactant and is completely consumed.

Mol of $Ba_3(PO_4)_2$ formed $=\frac{0.2}{2}=0.1$;

mol of $Ba(NO_3)_2$ reacted $=\frac{3}{2}\times0.2=0.3$

Mol of unreacted $Ba(NO_3)_2 = 0.5 - 0.3 = 0.2$ = moL of Ba^{2+} ion

Mol of Na^+ in solution $= 0.2 \times 3 = 0.6$;

Mol of NO_3^- in solution $= 0.5 \times 2 = 1$

7. **(a,b,d)** $2CO+O_2 \rightarrow 2CO_2$ The residual gas is CO.

Volume of CO oxidised $= 2 \times 30 = 60$ mL ;

Volume of CO $= 60 + 10 = 70$ mL

hence the volume of CO remains

unreacted $= 70 - 60 = 10$ mL

Volume of CO_2 initially present in the mixture $= 100 - 70 = 30$ mL

Volume of CO_2 formed = 60 mL; Volume of CO_2 absorbed by KOH = 30 + 60 = 90 mL

As per reaction O_2 is completely consumed.

8. **(a,b,c)** Volume strength of an H_2O_2 solution is the volume of O_2 in litres at NTP produced by 1 L of the solution.

$$\underset{68\text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22.4\text{ L at NTP}}{O_2}$$

∴ Volume produced by 17g H_2O_2 (present in 1 L solution) $= \frac{22.4}{68} \times 17 = 5.6$ L at NTP

So the volume strength is 5.6.

The volume of O_2 given out at NTP by 1 L of solution $= 5.6$ L

∴ Volume of O_2 given out at NTP by 1 mL of solution $= 5.6$ mL

Converting this volume to volume at 2 atmosphere pressure and 273 K temperature, we get

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ or volume } = \frac{5.6}{2} = 2.8 \text{ mL}$$

Moles of H_2O_2 present in 1 L solution $= \frac{17}{34}$

$= 0.5$ moles

[Mol wt = 34]

∵ Volume strength = N × 5.6

∴ N = 5.6 / 5.6 = 1 N.

9. **(c)** Let the hydrocarbon be C_xH_y. The reaction that occurs can be represented as

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow x\,CO_2 + \frac{y}{2}\, H_2O$$

10 mL 10(x + y/4) mL 10x mL

1 mole of hydrocarbon reacts with $(x + y/4)$ moles of O_2(g) to produce x mole of CO_2 and $y/2$ moles of H_2O.

Volume of CO_2 produced from 10 mL of hydrocarbon $= 10x$ mL

Volume of O_2 consumed by 10 mL of hydrocarbon $= 10x(x + y/4)$ mL

At a pressure of 1 atm and room temperature water vapour is condensed to liquid state. The residual gases are CO_2 and unreacted O_2.

Hence, volume of CO_2 and left out O_2 = 180 mL

On passing the mixture of gases through aqueous KOH, CO_2 is absorbed leaving behind O_2.

Hence volume of unreacted O_2 = 100 mL (given)

Volume of O_2 reacted = 200 – 100 = 100 mL

Volume of CO_2 produced = 180 – 100 = 80 mL

Then, we have

$10x = 80$ or $x = 8$

And $10 \times (x + y/4) = 100$

or $8 + y/4 = 10 \Rightarrow y = 8$

Thus the hydrocarbon is C_8H_8

10. **4.**

Let a and b cm^3 be the volumes of CO and CH_4 respectively in the mixture.

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

1 vol 1/2vol 1 vol

a cm^3 $a/2$ cm^3 a cm^3

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

1 vol 2 vol 1 vol

b cm^3 $2b$ cm^3 b cm^3

Reactions show that volume contraction after the reaction is due only to the consumption of oxygen.

Volume contraction after reaction, $\frac{a}{2} + 2b = 13$ .... (i)

When treated with aqueous KOH, CO_2 is absorbed. Hence $a + b = 14$ ....(ii)

Solving equation (i) and (ii), $a = 10$, $b = 4$

% of CO = 50; % of CH_4 = **20**; % of He = 30;

According to question

$5x$ = % of CH_4 = 20

$x = 4$

11. **4.**

$$\underset{a\text{ moles}}{HCOOH} \xrightarrow{H_2SO_4} H_2O + \underset{a\text{ moles}}{CO}$$

$$\underset{b\text{ moles}}{H_2C_2O_4} \xrightarrow{H_2SO_4} H_2O + \underset{b\text{ moles}}{CO} + \underset{b\text{ moles}}{CO_2}$$

Total number of moles of gases formed = $a + 2b$

Moles of gas (CO_2) absorbed by KOH = b

Hence, $b = \frac{1}{6}(a + 2b)$ [Volume ∝ moles)

$a/b = 4$

12. **2.** Equivalents of A oxidised = Equivalents of A reduced. Since in acidic medium, A^{n+} is oxidised to AO_3^-, the change in oxidation state from

$(+5)$ to $(+n) = 5 - n$ [∵ O.S. of A in AO_3^- = +5]

∴ Total number of electrons that have been given out during oxidation of 2.68×10^{-3} moles of A^{n+}

$= 2.68 \times 10^{-3} \times (5 - n)$

Thus the number of electrons added to reduce 1.61×10^{-3} moles of MnO_4^- to Mn^{2+}, *i.e.*

$(+7)$ to $(+2) = 1.61 \times 10^{-3} \times 5$

[Number of electrons involved = + 7 – (+2) = 5]

∴ $1.61 \times 10^{-3} \times 5 = 2.68 \times 10^{-3} \times (5 - n)$

$$5 - n = \frac{1.61 \times 5}{2.68} \text{ or } n = 5 - \frac{8.05}{2.68} \approx \mathbf{2}$$

13. **6.**

Mass of Fe_2O_3 in the sample $= \frac{55.2}{100} \times 1 = 0.552$ g

Number of moles of $Fe_2O_3 = \dfrac{0.552}{159.8} = 3.454 \times 10^{-3}$

Number of moles of Fe^{3+} ions $= 2 \times 3.454 \times 10^{-3}$
$= 6.9 \times 10^{-3}$ mol $= 6.90$ mmol

Since its only 1 electron is exchanged in the conversion of Fe^{3+} to Fe^{2+}, the molecular mass is the same as equivalent mass.

$\therefore$ Amount of Fe^{2+} ion in 100 mL. of sol. = 6.90 meq

Volume of oxidant used for 100 mL of Fe^{2+} sol.
$= 17 \times 4 = 68$ mL.

Amount of oxidant used $= 68 \times 0.0167$ mmol
$= 1.1356$ mmol

Let the number of electrons taken by the oxidant = n

$\therefore$ No. of meq. of oxidant used $= 1.1356 \times n$

Thus $1.1356 \times n = 6.90$

$$n = \frac{6.90}{1.1356} = \mathbf{6}$$

14. 7

$d = \dfrac{\text{mass}}{V} \Rightarrow 10.5$ g/cc means in 1 cc

$\Rightarrow$ 10.5 g of Ag is present.

Number of atoms of Ag in 1 cc $\Rightarrow \dfrac{10.5}{108} \times N_A$

In 1 cm, number of atoms of Ag $= \sqrt[3]{\dfrac{10.5}{108} N_A}$

In 1 cm^2, number of atoms of Ag $= \left(\dfrac{10.5}{108} N_A\right)^{2/3}$

In 10^{-12} m^2 or 10^{-8} cm^2, number of atoms of Ag

$$\left(\frac{10.5}{108} N_A\right)^{2/3} \times 10^{-8}$$

$$= \left(\frac{10.5 \times 6.022 \times 10^{23}}{108}\right)^{2/3} \times 10^{-8} = 1.5 \times 10^{7}$$

Hence $x =$ **7**

15. (c) Molarity $= \dfrac{9.8 \times 10 \times 1.8}{98} = 1.8$ M

$$\because \ d = M\left(\frac{\text{Mol.wt.}}{1000} + \frac{1}{m}\right)$$

$$1.8 = 1.8\left(\frac{98}{1000} + \frac{1}{m}\right)$$

$\therefore m = 1.10$

H_2SO_4 is a dibasic acid i.e. it has two replaceable H^+. Hence n-factor for this is 2.

16. (b) $1.8\,N_A$ molecules = 1.8 mol of HCl in 500 mL = 1.8 Equiv., n-factor for HCl = 1 (only one replaceable H^+)

17. (a) Molarity $= \dfrac{9.8 \times 10 \times 1.2}{98} = 1.2$ M

n-factor for $H_3PO_4 = 3$

18. (b) In one mole of CO_2 the number of C atom = 1 mole

In one mole of H_2O the number of H atoms = 2 mole

Since the mole ratio of CO_2 and H_2O is 1 : 1

$\therefore$ C : H ratio is 1 : 2

19. (c) It will consists of CO_2, H_2O and hydrocarbon.

Since the hydrocarbon is C_2H_4 (the atomic ratio C : H is 1 : 2 and and so the hydrocarbon is C_2H_4)

$$\underset{1\text{ mole}}{C_2H_4} + \underset{3\text{ mole}}{3O_2} \longrightarrow \underset{(28\text{ g})}{2CO_2} + 2H_2O$$

Since the mole of O_2 required is three times the mole of hydrocarbon so in a mixture containing equal number of moles of hydrocarbon and oxygen, hydrocarbon will be in excess and some of it will remain unreacted while whole of O_2 will be consumed. Thus the mixture in vessel after the completion of reaction will consist of products (i.e., CO_2 and H_2O) and excess of hydrocarbon that has remained unreacted.

20. A - p, q; B - p; C - p, q, r; D - s

1. 5 mole of CO_2 (g) $= 1.5 \times 22400$ mL at NTP
$= 33600$ mL at NTP

Total number of atoms in one molecule of $CO_2 = 1 + 2 = 3$

Total number of atoms in 1.5 mole of $CO_2 = 1.5 \times 3 \times N_A$
$= 4.5 \times N_A$

3.0 g of $H_2 = \dfrac{3}{2} \times 22400$ mL of H_2 at NTP = 33600 mL at NTP

Number of mole of H_2 in 3.0 g $H_2 = \dfrac{3}{2}$ or 1.5 moles

Number of atoms in 1 molecule of $H_2 = 2$

Number of atoms in 1.5 mole $H_2 = 2 \times 1.5 \times N_A$
$= 3.0 \times N_A$

Volume of 1.5 moles of ozone at NTP $= 22400 \times 1.5$ mL
$= 33600$ mL

Number of atoms in one molecule of $O_3 = 3$

Total number of atoms in 1.5 mole of $O_3 = 3 \times 1.5 \times N_A$
$= 4.5 \times N_A$

Weight of 1 mole of $O_3 = 48$ g

Weight of 1.5 mole of $O_3 = 48 \times 1.5$ g $= 72$ g

Weight of 1 mole of oxygen $(O_2) = 32$ g

DAILY PRACTICE
PROBLEMS

CHEMISTRY SOLUTIONS

DPP/CC02

1. (b) de – Broglie wavelength is given by :

$$\lambda = \frac{h}{mv} \qquad \text{... (i)}$$

$$\text{K.E.} = \frac{1}{2}mv^2$$

$$v^2 = \frac{2KE}{m}$$

$$v = \sqrt{\frac{2KE}{m}}$$

Substituting this in equation (i)

$$\lambda = \frac{h}{m}\sqrt{\frac{m}{2KE}}$$

$$\lambda = h\sqrt{\frac{1}{2m(K.E.)}}$$

i.e. $\lambda \propto \frac{1}{\sqrt{KE}}$

∴ when KE become 4 times wavelength become 1/2.

2. (d) From the expression of Bohr's theory, we know that

$$m_e v_1 r_1 = n_1 \frac{h}{2\pi}$$

$$\& \; m_e v_2 r_2 = n_2 \frac{h}{2\pi}$$

$$\frac{m_e v_1 r_1}{m_e v_2 r_2} = \frac{n_1}{n_2}\frac{h}{2\pi} \times \frac{2\pi}{h}$$

Given, $r_1 = 5r_2, n_1 = 5, n_2 = 4$

$$\frac{m_e \times v_1 \times 5r_2}{m_e \times v_2 \times r_2} = \frac{5}{4}$$

$$\Rightarrow \frac{v_1}{v_2} = \frac{5}{4 \times 5} = \frac{1}{4} = 1:4$$

3. (d) $\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

To calculate shortest wavelength take $n_2 = \infty$ and longest wavelength take nearest value of n_2.

For H-atom,

$$\frac{1}{\lambda_{\text{shortest}}} \quad n_2 = \infty, Z = 1, n_1 = 1$$

$$\therefore \frac{1}{x} = R_H \text{ (Lyman series)}$$

For $\frac{1}{\lambda_{\text{longest}}}$ for $Li^{2+}, Z = 3, n_1 = 2, n_2 = 3$ (Balmer series)

$$\frac{1}{\lambda_{\text{longest}}} = \frac{1}{x} \times 3^2\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5}{4x}$$

$$\therefore \lambda_{\text{longest}} = \frac{4x}{5}$$

4. (d) Using the relation, $\lambda \propto \frac{1}{\text{K.E.}}$, we get

$\lambda_1 = \lambda$ and $\text{K.E.}_1 = E$ (initial)

$\lambda_2 = 0.9\lambda$

$[10\%$ decrease from $\lambda_1, \lambda_2 = \lambda - \frac{10}{100}\lambda$

$= \lambda(1 - 0.1) = 0.9\lambda]$

We are required to find $\text{K.E.}_2 = ?$

$$\therefore \text{K.E.}_2 = \frac{\lambda_1^2}{\lambda_2^2} \times \text{K.E.}_1 = \frac{\lambda^2}{(.9\lambda)^2} \times \text{K.E.}_1$$

$$= \frac{\lambda^2 \times 100}{81\lambda^2} \times E \quad [\text{K.E}_1 = E]$$

$$= \frac{100}{81}E \quad [\text{more than K.E.}_1 \text{ i.e., increase}]$$

Now increase in $\text{K.E.} = \text{K.E.}_2 - \text{K.E.}_1 = \frac{100}{81}E - E$

$$\% \text{ increase of K.E.} = \frac{\frac{100}{81}E - E}{E} \times 100$$

$$= \frac{19}{81} \times 100 = 23.4\%$$

5. (d) Lyman series, $n_1 = 1$

For third line of Lyman series, $n_2 = 4$

For hydrogen, $Z = 1$

$$\upsilon_H = \frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= R_H (1)^2 \left(\frac{1}{1} - \frac{1}{(4)^2}\right) = \frac{15}{16}R_H \qquad \text{...(i)}$$

For lithium, $Z = 3$

For first line of Balmer series, $n_1 = 2, n_2 = 3$

$$\upsilon_{Li} = R_H(3)^2\left(\frac{1}{(2)^2}-\frac{1}{(3)^2}\right) = R_H \times 9 \times \frac{5}{56}$$

$$= \frac{5}{4}R_H \qquad \ldots \text{(ii)}$$

on dividing equation (i) by (ii), we get

$$\frac{\upsilon_H}{\upsilon_{Li}} = \frac{(15/16)R_H}{(5/4)R_H} = \frac{15}{16}\times\frac{4}{5} = \frac{3}{4}$$

6. **(a,b,c,d)** $E_n = -13.6\frac{Z^2}{n^2}$; for He^+, $Z = 2$

$$\text{K.E.} = -E_n = 13.6\frac{Z^2}{n^2};$$

$$v_n = 2.19 \times 10^6 Z/n \text{ ms}^{-1}$$

7. **(b)** A – $1s^2 2s^2 2p^6 3s^2 3p^5$ – Cl (17), 11 p electrons
B – $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$, (Sc - 21), $l = 2$ and $m_l = 2$ for $3d$-electron.
C – $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ (Ti - 22), $n = 3$ and $l = 2$ for $3d^2$ electrons.

8. **(a, c)** $\bar{v} = RZ^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$

$$x = R\left(\frac{1}{2^2}-\frac{1}{3^2}\right) = \frac{5R}{36}$$

$$\bar{v}_1 = R \times 2^2\left(1-\frac{1}{2^2}\right) = 3R = \frac{36}{5}x \times 3 = \frac{108x}{5}$$

For H atom 2nd lyman

$$\frac{1}{\lambda_2} = R\left(1-\frac{1}{9}\right) = \frac{8}{9}\times\frac{36x}{5} = \frac{32x}{5} \Rightarrow \lambda_2 = \frac{5}{32x}$$

9. **(b, c)** Statements (a) and (d) are incorrect.
   (a) The excited electron has a tendency to return back to lower energy state.
   (d) Angular momentum $= \frac{nh}{2\pi}$

10. **(6)** As the α-particle travelling with velocity, 'u', stops at a distance 10^{-13} m, its K.E. becomes zero and gets converted into P.E.

$$\therefore \frac{1}{2}mu^2 = \frac{1}{4\pi\varepsilon_0} \times \frac{2Ze^2}{r} \quad \text{or } u^2 = \frac{Ze^2}{\pi\varepsilon_0 .m.r}$$

Here, $Z = 29$ for Cu atom

$$\Rightarrow u^2 = \frac{29 \times (1.6 \times 10^{-19})^2}{3.14 \times 8.85 \times 10^{-12} \times (4 \times 1.672 \times 10^{-27}) \times 10^{-13}}$$

$\therefore$ u **= 6.3 × 10^6 m sec^{-1}**

According to question,

$x \times 10^y = 6.3 \times 10^6$

thus, $y = 6$

11. **(2)** $\Delta v = \frac{0.001}{100} \times 30{,}000 = 0.3 \text{ cm sec}^{-1}$

According to uncertainty principle,

$$\Delta x.\Delta p \approx \frac{h}{4\pi}; \quad \Delta x.\Delta v \approx \frac{h}{4\pi m}$$

$$\Delta x \times 9.1 \times 10^{-28} \times 0.3 \approx \frac{6.625 \times 10^{-27} \times 7}{4 \times 22}$$

$$\Delta x \approx 1.93 \text{ cm.} \approx 2$$

12. **(2)** Energy of photon, $E = h\nu = \frac{hc}{\lambda}$

Here, $c = 3.0 \times 10^8 \text{ ms}^{-1}$

In first case, $\lambda = 800 \text{ nm} = 800 \times 10^{-9}$ m

$$\therefore E_1 = \frac{(6.626 \times 10^{-34} \text{Js}) \times (3 \times 10^8 \text{ms}^{-1})}{800 \times 10^{-9} \text{m}}$$

$$= 2.48 \times 10^{-19} \text{ J}$$

In second case, $\lambda = 400 \text{ nm} = 400 \times 10^{-9}$ m

$$\therefore E_2 = \frac{(6.626 \times 10^{-34} \text{Js}) \times (3 \times 10^8 \text{ms}^{-1})}{400 \times 10^{-9} \text{m}}$$

$$= 4.91 \times 10^{-19} \text{ J}$$

Ratio of energy of first and second radiations,

$$\frac{E_1}{E_2} = \frac{2.48 \times 10^{-19} \text{J}}{4.97 \times 10^{-19} \text{J}} = \frac{1}{2}$$

$E_1 : E_2 = 1 : 2$ or $E_2 = 2E_1$

Thus, energy of the radiation with wavelength 400 nm is twice that of the radiation of wavelength 800 nm.

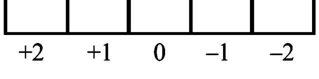
13. **(4)** Energy associated with the incident photon $= \frac{hc}{\lambda}$

$$i.e., E = \frac{(6.6 \times 10^{-34} \text{Js})(3 \times 10^8 \text{ms}^{-1})}{(300 \times 10^{-9} \text{m})}$$

$$= 6.6 \times 10^{-19} \text{ J} = \frac{6.6 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} = 4.12 \text{ eV}$$

$\therefore$ Metals showing photoelectric effect will be Li, Na, K and Mg only i.e., 4 metals (which have work function less than 4.12 eV).

14. **(1)** $n = 3, l = 2$ means $3d$ orbital



i.e. in an atom only one orbital can have the value $m_l = +2$

15. **(c)** radius $(r_n) = \frac{n^2h^2}{4\pi^2 mZe^2} = \frac{n^2}{Z} \times 0.529\text{Å}$

$$= \frac{n^2}{Z} = 0.0529 \text{ nm}$$

16. (b) $V_n = \frac{2\pi Ze^2}{nh} = \left(\frac{Ze^2}{rm}\right)^{1/2}$

17. (d) $E_n = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2} = -\frac{Z^2}{n^2} \times 313.6\,\text{kcal}$

18. (d) Given : subsidiary quantum number (l) = 4

∴ number of degenerate orbitals $= 2l + 1 = 2 \times 4 + 1$
$= 8 + 1 = 9$

For this maximum total spins (s) $= 9 \times \frac{1}{2}$

For this minimum total spins (s) $= 1 \times \frac{1}{2}$

∴ Maximum total multiplicity $= 2s + 1 = 2 \times \frac{9}{2} + 1 = 10$

Minimum total multiplicity $= 2 \times \frac{1}{2} + 1 = 2$

19. (c) Fe(Z = 26), Fe^{2+}; $3d^6$, number of d-electrons in $Fe^{2+} = 6$

In Fe, $3d^6 4s^2$, so number of d-electron = 6

In Ne(Z = 10); $1s^2\, 2s^2\, 2p^6$; number of p-electrons = 6

In Cl (Z = 17); $1s^2 2s^2 p^6 3s^2 p^5$, so number of p-electrons $= 6 + 5 = 11$

In Mg(Z = 12), $1s^2 2s^2 2p^6 3s^2$, so number of s-electrons $= 2 + 2 + 2 = 6$

Thus number of p-electrons in Cl is not equal to number of d-electrons in Fe^{2+}.

20. A-r, B-s, C-q, D-p

Wave number $\bar{v} = \frac{1}{\lambda} = kZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

For shortest wavelength ($\bar{\upsilon}_{\text{max}}$) in Lyman series

$n_1 = 1$, $n_2 = \infty$ and $Z = 1$ (for H-atom)

Hence, $\frac{1}{\lambda} = \frac{1}{x} = kZ^2 = \left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] \Rightarrow k = \frac{1}{x}$

(A) For shortest wavelength in Lyman series of Li^{2+}
$n = 1$, $n = \infty$, $Z = 3$

Hence $\frac{1}{\lambda} = \frac{1}{x} \times 3^2\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] = \frac{9}{x} \Rightarrow \lambda = \frac{x}{9}$

(B) For longest wavelength in Lyman series, $n_1 = 1$, $n_2 = 2$

$\frac{1}{\lambda} = \frac{1}{x} \times 3^2\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{27}{4x} \Rightarrow \lambda = \frac{4x}{27}$

(C) For shortest wavelength in Balmer series,
$n_1 = 2$, $n_2 = \infty$

Hence, $\frac{1}{\lambda} = \frac{1}{x} \times 3^2\left[\frac{1}{2^2} - \frac{1}{\infty^2}\right] \Rightarrow \lambda = \frac{4x}{9}$

(D) For longest wavelength in Balmer series,
$n_1 = 2$, $n_2 = 3$

Hence, $\frac{1}{\lambda} = \frac{1}{x} \times 3^2 \times \left[\frac{1}{2^2} - \frac{1}{3^2}\right] \Rightarrow \lambda = \frac{4x}{5}$

DAILY PRACTICE PROBLEMS

CHEMISTRY SOLUTIONS

DPP/CC03

1. **(b)** On moving along the period, ionization enthalpy increases.

In second period, the order of ionization enthalpy should be as follows :

$F > O > N$.

But N has half-filled structure, therefore, it is more stable than O. That is why its ionization enthalpy is higher than O. Thus, the correct order of IE is

$F > N > O$.

2. **(c)** As we move along the period, the atomic size decreases due to increase in nuclear charge. Therefore, it is more difficult to remove electron from an atom. Hence the sequence of first ionization enthalpy in decreasing order is

$$F > N > C > B > Be$$

But ionization enthalpy of boron is less as compared to beryllium because first electron in boron is to be removed from *p*-orbital while in beryllium, is to be removed from *s*-orbital.

As *s*-orbital is closer to nucleus in comparison to *p*-orbital thus energy required to remove an electron from *s*-orbital is greater.

3. **(d)** Greater the effective nuclear charge, more is the attraction of nucleus towards the electron and hence higher will be the value of E.A.

Greater the atomic radius of the atom, less will be the attraction of the nucleus to the electron to be added and hence lower will be the value of E.A.

4. **(b)** The alkali metals are highly reactive because their first ionisation potential is very low and hence they have great tendency to lose electrons to form unipositive ions. On moving down a group from Li to Cs ionisation enthalpy decreases hence the reactivity increases.

The halogens are most reactive elements due to their low bond dissociation energy, high electron affinity and high enthalpy of hydration of halide ion however their reactivity decreases with increase in atomic number. As the size increases, the attraction for an additional electron by the nucleus becomes less. Thus reactivity decreases.

5. **(d)** $O(g) + 2e^- \rightarrow O^{2-}(g), \Delta H = 603\,\text{kJ mol}^{-1}$ ......(i);

$O(g) + e^- \rightarrow O^-(g), \Delta H = -141\ \text{kJ mol}^{-1}$ ......(ii)

(i) - (ii) gives :

$O^- + e^- \rightarrow O^{2-}, \Delta H = 603 - (-141) = 744\,\text{kJ mol}^{-1}$

6. **(b)** van der Waals radii decrease as we move from left to right in a period. It is due to increasing nuclear charge. The given elements belong to second period (except Cl). The van der Waals radius of Cl will be largest.

7. **(a, b, c)** For no consideration of Aufbau principle and Hund's rule, the electronic configurations will be as:

$Ca(20):[Ar]3d^2; Zn(30):[Ar]3d^{10}4s^2$ (filling of 4*s* subshell after 3*d* subshell); Ti (22): [Ar] $3d^2$ (both electrons paired up)

$Fe^{3+}[23] = [Ar]3d^3 4s^2$

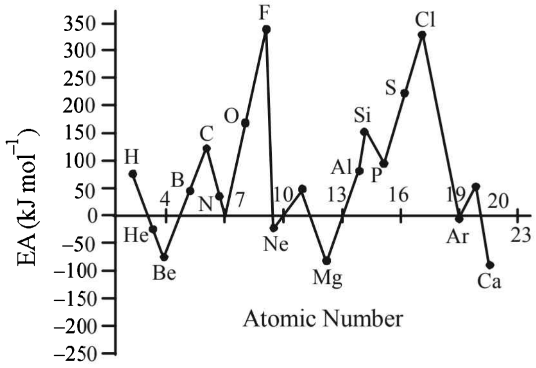
i.e., –3 unpaired electrons

8. **(a,b)** Group oxidation number (i.e., maximum oxidation state in a group) need not necessarily be the most common or most stable oxidation state for a particular element, so option (c) is **incorrect.**

In fact some elements may have no compounds at all in the group oxidation number state e.g. in case of flourine, so (d) option is incorrect.

9. **(b,c,d)** Electron affinity increases as we move from left to right in a period and decreases on moving down a group. However there are many exceptions. The periodic trends are less well defined than those for I.E. partly because of lack of reliable data.

The following graph shows the plot of E.A. values against atomic number for some elements.



From the graphs we can see that (b), (c), (d) are correct, (a) is incorrect. E.A. of $S > O$

10. **(a,c)** In option (a), (b) and (c) all the species are isoelectronic 10, 10, 18 electrons in each. In isoelectronic species the ionic radii decrease with increase in atomic number so (a) is correct, (b) is incorrect and (c) is correct.

The size of anion is larger than that of neutral atom and that of cation is smaller than the neutral atom, so $H^- > H^+$. He is a noble gas its ionic radii cannot be measured as the ionic radii are obtained from internuclear distances in ionic compounds. Thus (d) is incorrect.

11. **(7)** Long form of periodic table contains 18 groups and 7 periods.

12. **(3)** Group I B contain Cu, Ag and Au.

13. **(8)** Third period contains total 8 elements

14. **(2)** Two elements sodium and calcium are electropositive metals.

15. **(b)** The electronegativity like ionisation energy increases steadily on moving from left to right in a period.

16. **(c)** Electronegativities increase steadily on moving across a period (N > C) and generally decrease on descending a group (P > Si).

17. **(a)** Both for positive ion and negative ions the lattice energy decreases (and not increases) with increase in the size of the ion, thus statements (b) and (c) are incorrect.

For large positive ion, the magnitude of lattice energy is mainly determined by the size of the positive ion (and not of anion) thus statement (d) is also incorrect.

18. **(b)** The lattice energies of difluorides of first row transition metals increase along the period as would be expected from decrease in ionic radii. However, there is a slight decrease at manganese which is due to d^5 configuration of Mn, which reduces the effective nuclear charge and decreases the lattice energy. Due to this the correct order is (b) and not (a).

The values of the lattice energy for these are

Compound	**Lattice energy (kJ mol^{-1})**
TiF_2	2749
VF_2	2810
CrF_2	2879
MnF_2	2770
FeF_2	2912

i.e., for MnF_2 it is less than VF_2 but more than TiF_2.

19. **A - q; B - p, r; C - p, s; D - p**

(A) At. No. 47 : $[Kr]4d^9 5s^2$; group : 9 + 2 = 11th ; period : 5th

(B) For lowest At. No. having $(n-1)d^{10}ns^2np^3$ configuration, $n - 1 = 3 \Rightarrow n = 4$
Hence, group : 10 + 5 = 15th ; period : 4th

(C) At. No. 34 : [Ar] $3d^{10}4s^2 4p^4$; Group : 10 + 6 = 16th; period = 4th

(D) For lowest At. No. having $(n-1)d^{10}ns^1$ configuration, $n - 1 = 3 \Rightarrow n = 4$
Group = 10 + 1 = 11th; Period = 4th

20. **A - r; B - p; C - s; D - q**

(A) IE_1 and IE_2 are very high. The element must be inert gas.

(B) IE_1 has low value and IE_2 has very high value. The element must belong to first group (ns^1), hence it is reactive.

(C) IE_1 and IE_2 do not have very high values. The element must belong to 2nd group (ns^2) and must form halide of formula AX_2.

(D) IE_1 and IE_2 values suggest the element to be a non-metal which is not inert.

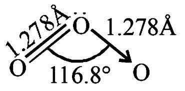
DAILY PRACTICE PROBLEMS

CHEMISTRY SOLUTIONS

DPP/CC04

1. **(a)**

(a) $\left.\begin{array}{l}\text{ONCl} = 8+7+17 = 32e^- \\ \text{ONO}^- = 8+7+8+1 = 24e^-\end{array}\right\}$ not isoelectronic

(b) 

The central atom is sp^2 hybridized with one lone pair.

(c) It is a pale blue gas. At – 249.7°, it forms violet black crystals.

(d) It is diamagnetic in nature due to absence of unpaired electrons.

2. **(c)** The molecular orbital configuration of the given molecules is

$H_2 = \sigma 1s^2$ (no electron anti-bonding)

$Li_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2$(two anti-bonding electrons)

$B_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \left\{\pi 2p_x^1 = \pi 2p_y^1\right\}$

(4 anti-bonding electrons)

Though the bond order of all the species are same (B.O = 1) but stability is different. This is due to the difference in the presence of no. of anti-bonding electron.

Higher the no. of anti-bonding electron lower is the stability hence the correct order is $H_2 > Li_2 > B_2$

3. **(c)** If x is the dipole moment of chlorobenzene, then its value for m-dichlorobenzene

$= \sqrt{x^2 + x^2 + 2x \times x \cos 120°} = 1.5\ D.\ \ x \Rightarrow 1.5\ D$ (given).

Dipole moment for o-dichlorobenzene

$= \sqrt{1.5^2 + 1.5^2 + 2 \times 1.5^2 \cos 60°}\ , = 2.60D$

4. **(b)** On changing N_2 to N_2^+, B.O. decreases from 3 to 2.5 whereas on changing O_2 to O_2^+, B.O. increases from 2 to 2.5. In former case, the bond dissociation energy decreases and in the latter case, it increases.

5. **(c)** (a) The S-atom in the excited state $(3s^2 3p^3 3d^1)$ has sp^3 hybridization- $(sp^3)^2 (sp^3)^1 (sp^3)^1 (sp^3)^1 3d^1$. The three hybrid orbitals form three (S-O) σ -bonds and the $3d$ pure orbital gives (S-O) π -bond.

(b) In PO_4^{3-}, P-atom in its excited state $(3s^1 3p^3 3d^1)$ is sp^3 hybridized. Four hybrid orbitals forms (P-O) σ -bonds whereas $3d^1$ gives (P-O) π -bond.

(c) In NO_3^-, N-atom is sp^2 hybridized as $(sp^2)^2 (sp^2)^1 (sp^2)^1 2p_z^1$

Completely filled sp^2 hybrid orbital on N-atom donates an electron pair to the vacant $2p$ orbital of O atom to form dative bond. Other two hybrid orbitals form (N-O) σ -bonds. The pure $2p_z^1$ orbital forms (N-O) π -bond.

(d) In $XeOF_4$, Xe-atom in its excited state $(5s^2 5p^3 5d^3)$ is sp^3d^2 hybridized. The singly filled five hybrid orbitals form σ -bonds with 4F atoms and O atom. The pure $5d$ orbital forms π -bond with $2p$ orbital of O-atom.

6. **(a, d)** (a) sp^3 to sp^3 (b) sp^2 to sp^3

(c) sp^2 to sp (d) sp^3 to sp^3

7. **(a, b, c)** $NO\,(11) : (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x{}^2 = \pi 2p_y)^2 (\pi^* 2p_x)^1$

$NO^+\,(10) : (\sigma 2s)^2 (\sigma^* 2s)^2\ (\pi 2p_x{}^2 = \pi 2p_y)^2; (\sigma 2p_z)^2$ B.O. = 3

$O^+{}_2\,(11)$: B.O. = 2.5

$OF^+\,(12) : (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x{}^2 = \pi 2p_y)^2 (\pi^* 2p_x)^1 (\pi^* 2p_y)^1$;

$Ne_2^+\,(15) : (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x{}^2 = \pi 2p_y)^2 (\pi^* 2p_x)^2 (\pi^* 2p_y)^2 (\sigma^* 2p_z)^1$

In a π bond the electron density is concentrated in the region perpendicular to the bond axis.

8. **(a, c)** Bond order of various species are

$$\underset{6+7+1=14}{CN^-} \text{ or } \frac{N_b - N_a}{2} = \frac{10-4}{2} = 3$$

$$\underset{8+8+1=17}{O_2^-} \text{ or } \frac{10-7}{2} = 1.5$$

$$\underset{7+8-1=14}{NO^+} \text{ or } \frac{10-4}{2} = 3$$

$$\underset{6+7-1=12}{CN^+} \text{ or } \frac{8-4}{2} = 2$$

Thus CN^- and NO^+ have identical bond order.

9. **(b, d)** (a) Na^+ ion is solvated by ion-dipole interaction while $NH^+{}_4$ ion is solvated by H-bonding which is a stronger force of attraction.

(b) Sn^{4+} has greater charge and smaller size than Sn^{2+}. Hence due to greater charge density, it distorts the Cl^- ion electron cloud to greater extent. So $SnCl_4$ is covalent.

(c) NH_3 has greater dipole moment than BF_3.

(d) I^- ion, being much bigger in size than F^- ion, is distorted to greater extent.

10. (5) For 100% ionic character of H–X, dipole moment $= 4.8 \times 10^{-10} \times 0.1 \times 10^{-9} \times 10^2 = 4.8\,D$

Hence, % ionic character of H–X bond

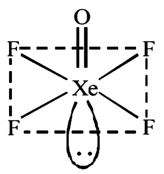
$$= \frac{1.2}{4.8} \times 100 = 25$$

According to question

$5x = 25$

$x = 5$

11. (1) sp^3d^2 hybridisation of Xe-atom in the excited state- $(sp^3d^2)^2$, $(sp^3d^2)^2$ $(sp^3d^2)^1$ $(sp^3d^2)^1$ $(sp^3d^2)^1$ $(sp^3)^1$



12. (5) Using the relation, charge $= \dfrac{\text{Dipole moment}}{\text{bond length}}$

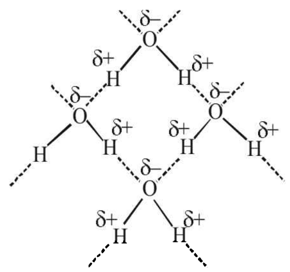
$$= \frac{0.38 \times 10^{-18}\,\text{esu} - \text{cm}}{1.61 \times 10^{-8}\,\text{cm}}$$

$= 2.44 \times 10^{-11}$ esu

$$\therefore \quad \text{Percentage of charge} = \frac{2.4 \times 10^{-11}\,\text{esu}}{4.8 \times 10^{-10}\,\text{esu}} \times 100$$

$= 5\%$

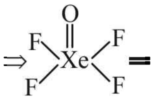
13. (4) One water molecule is bonded with 4 other water molecules as shown below.



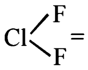
14. (5) (i) $BrF_5 = 10\,e^-$'s

(ii) $SF_6 = 12\,e^-$'s

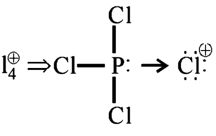
(iii) $IF_7 = 14\,e^-$'s

(iv) $XeOF_4 \Rightarrow$


$= O = 12\,e^-$'s

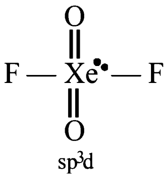
(v) $ClF_2 \Rightarrow$


$= 4\,e^-$'s

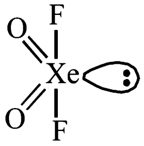
(vi) $PCl_4^{\oplus} \Rightarrow$

$Cl—\overset{Cl}{\underset{Cl}{P}}: \rightarrow \ddot{Cl}^{\oplus} = 8\,e^-$'s

Hence (i) to (v) violate octet rule.

15. (d) Xenon dioxydifluoride (XeO_2F_2)

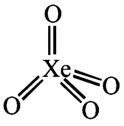


Trigonal bipyramidal



See-saw shape due to presence of one lone pair of electron

16. (d) XeO_4



sp^3, {Geometry, shape} Tetrahedral

17. (c) $XeF_6 - sp^3d^3$

Geometry – pentagonal bipyramidal

shape – monocapped octahedral

Thus, option (c) is incorrect.

18. (d) Number of hybrid orbitals, H in ClF_3

$$= \frac{1}{2}\,(\text{valence electrons of Cl} + 3 \times \text{valence electrons of F} - 3 \times 3 \text{ F-atoms})$$

$$= \frac{1}{2}(7 + 3 \times 7) - 9 = 14 - 9 = 5$$

Number of bond pairs (n) = 3

Total number of lone pairs (m) = H – n = 5 – 3 = 2

Hence, VSEPR notation of ClF_3 is AX_3E_2.

19. (a) $CO_2 : H = \frac{1}{2}(4 + 2 \times 6) - 3 \times 2 = 2$;

$n = 2$; $m = H - n = 2 - 2 = 0$

$SO_2 : H = \frac{1}{2}(6 + 2 \times 6) - 3 \times 2 = 3$;

n = 2; m = 3 – 2 = 1

$H_2O : H = \frac{1}{2}(2 \times 1 + 6) - 3 \times 0 = 4$;

n = 2; m = 4 – 2 = 2

The dipole moment of molecule α m CO_2 (m = 0), SO_2 (m = 1) and H_2O (m = 2)

Hence order is $CO_2 < SO_2 < H_2O$

20. **A → p; B → q, r, s; C → p, s; D → q, s**

Dipole-Dipole forces depend on temperature. Various forces involved in solution of HBr in carbon tetrachloride are :

HBr – HBr ; dipole-dipole

HBr – CCl_4; dipole-induced dipole

CCl_4 – CCl_4; dispersion forces

Dipole-dipole types of forces are found in molecules having dipole moment. In HBr, these is +δ on H atom and – δ on Br atom so HBr has dipole moment. There is thus a small dipole-dipole force of attraction between adjacent HBr molecules.

Dipole-induced dipole type of forces are observed in between non-polar molecule and a molecule having dipole moment. e.g. between CCl_4 (non-polar) and HBr (molecule having dipole moment)

Induced dipole-Induced dipole type of forces are found in between molecules having no dipole moment. These are also known as **London** dispersion forces.

DAILY PRACTICE PROBLEMS

CHEMISTRY SOLUTIONS

DPP/CC05

1. **(d)** $R=\dfrac{PV}{T}$

At critical point $V=V_c$

and $(V-V_c)^3=0$

Expanding this equation, we have

$$V^3-3V_c.V^2+3V_c^2.V-V_c^3=0 \qquad ..(i)$$

The vander waals equation in critical point is

$$V^3-\left(b+\frac{RT_c}{P_c}\right)V^2+\left(\frac{a}{P_c}\right)V-\frac{ab}{P_c}=0 \qquad ...(ii)$$

Comparing (i) and (ii), we get

$$V_c=3b, P_c=\frac{a}{27b^2}, T_c=\frac{8a}{27Rb}$$

Eliminating constants a and b from the values of critical constants, we obtain

$$R=\frac{8P_cV_c}{3T_c}$$

2. **(b)** At the same conditions of T and P, $V \alpha n$

$$n_{N_2}=\frac{14}{28}=\frac{1}{2};\ V_{N_2}\alpha\frac{1}{2} \qquad n_{O_3}=\frac{36}{48}=\frac{3}{4};\ V_{O_3}\alpha\frac{3}{4}$$

Hence, $V_{N_2}/V_{O_3}=\dfrac{2}{3},\ 3V_{N_2}=2V_{O_3}$

3. **(c)** $PV^{\frac{3}{2}}$ = constant.

Again $P=\dfrac{nRT}{V}$

$\therefore\quad \dfrac{nRT}{V}\times V^{\frac{3}{2}}$ = constant (K)

or, $TV^{\frac{1}{2}}=\dfrac{K}{nR}$ = K' (constant)

For two states, $T_1V_1^{\frac{1}{2}}=T_2V_2^{\frac{1}{2}}$

$$T_2=T_1\left(\frac{V_1}{V_2}\right)^{\frac{1}{2}}$$

But $V_2=\dfrac{V_1}{2}$ (given)

$$\therefore\quad T_2=T_1\left(\frac{V_1}{\frac{V_1}{2}}\right)^{\frac{1}{2}}=T_1\sqrt{2}$$

4. **(a)** $CO_2+C\longrightarrow 2CO$

Stoichiometry ratio is 1 : 2

AT STP, P = 1 atm, T = 273 K, R = 0.0821

Initial moles of CO_2; $n(CO_2\text{initial})=\dfrac{PV}{RT}$

$=\dfrac{1\times 0.5}{0.0821\times 273}$ = 0.022 mole

In final mixture no. of moles; $n(CO_2/CO \text{ mixture})$

$=\dfrac{1\times 0.7}{0.0821\times 273}$ = 0.031

Increase in volume is by = 0.031 – 0.022

= 0.009 mole of gas

Final no. of moles of CO i.e. $n_{(CO\ final)}$

$n_{(CO\ final)}=2n_{(CO2\ initial)}-n_{(CO2\ final)}$

$=2(0.022-n_{(CO2\ final)})$ ...(i)

$n_{(CO\ final)}=0.044-2n_{(CO2\ final)}$ ...(ii)

$\therefore$ Now, $n_{(CO\ final)}+n_{(CO2\ final)}=0.031$

$n_{(CO2\ final)}=0.031-n_{(CO\ final)}$ ...(ii)

Substituting (ii) in eq. (i)

$n_{(CO\ final)}=0.044-2[0.031-n_{(CO\ final)]}$

$n_{(CO\ final)}=0.044-0.062+2n_{(CO\ final)}$

$n_{(CO\ final)}=0.018$ mol.

Volume of $CO=V=\dfrac{nRT}{P}=\dfrac{0.018\times 0.0821\times 273}{1}$

= 0.40 Litre

and volume of CO_2 = 0.7 litre – 0.4 litre

= 0.3 litre

$\therefore$ CO_2 = 300 mL, CO = 400 mL

5. **(a)** Most probable velocity $=\sqrt{\dfrac{2RT}{M}}$

Average velocity $=\sqrt{\dfrac{8RT}{\pi M}}$

Root mean square velocity $=\sqrt{\dfrac{3RT}{M}}$

$\therefore$ Most probable velocity : Average velocity : Root mean square velocity

$$=\sqrt{\frac{2RT}{M}}:\sqrt{\frac{8RT}{\pi M}}:\sqrt{\frac{3RT}{M}}=\sqrt{2}:\sqrt{\frac{8}{\pi}}:\sqrt{3}$$

6. **(b)** The van der Waals equation is

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \quad \text{(For one mole)}$$

$$\text{or}\left(P+\frac{a}{V^2}\right)=\frac{RT}{(V-b)}$$

$$\text{or } P=\frac{RT}{V-b}-\frac{a}{V^2}$$

Multiplying throughout by molar volume (V) and dividing by RT, we have

$$\frac{PV}{RT}=\frac{V}{V-b}-\frac{a}{RTV} \text{ or } \frac{PV}{RT}=\left(\frac{V-b}{V}\right)^{-1}-\frac{a}{RTV}$$

$$\text{or } \frac{PV}{RT}=\left(1-\frac{b}{V}\right)^{-1}-\frac{a}{RTV}$$

$$\text{or } \frac{PV}{RT}=1+\frac{b}{V}+\frac{b^2}{V^2}+\frac{b^2}{V^3}-\frac{a}{RTV}$$

$$\text{or } \frac{PV}{RT}=1+\left(b-\frac{a}{RT}\right)\times\frac{1}{V}+\frac{b^2}{V^2}+\frac{b^3}{V^3}$$

Comparing this with virial equation we get

$$B=b-\frac{a}{RT}$$

7. **(b, c)** Given $V=10$ litre, $P=3$ atm, $T=290$ K
After driving $V=10$ litre $\quad P=?$

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2} \quad \therefore V_1=V_2=10 \text{ lit},$$

$$\therefore \frac{P_1}{T_1}=\frac{P_2}{T_2} \text{ or } P_2=\frac{P_1}{T_1}\times T_2$$

$$\text{or } P_2=3\times\frac{320}{290}=3.3103 \text{ atm.}$$

$\therefore$ Pressure of the gas in the tyre at 47°C = 3.3103 atm.
At pressure 3.103 atm, the volume of tyre is 10 lit.
$\therefore$ Volume of tyre at 3 atm pressure

$$=\frac{3.3103\times10}{3}=11.03433 \text{ lit.}$$

$\therefore$ The volume which is to be reduced at 3 atm pressure
$= 11.03433 - 10 = 1.03433$ lit.
$\therefore$ The volume which is to be reduced at 1 atm pressure

$$=\frac{1.03433\times3}{1}=3.1029 \text{ lit.}$$

$\therefore$ 3.1029 lit of air should be let out at 1 atm to restore the tyre to 3 atm at 47°C.

8. **(a,c,d)** The critical pressure,

$$P_C=\frac{a}{27b^2}=\frac{371.843\times10^3}{27\times(40.8)^2\times10^{-6}}$$

$$=\frac{371.843\times10^9}{27\times(40.8)^2}=8.273\times10^6 \text{ Pa}=8.273 \text{ MPa}$$

The critical temperature, $T_C=\frac{8a}{27Rb}$

$R = 8.314$ KPa dm^3 K^{-1} mol^{-1}

$$T_C=\frac{8a}{27Rb}=\frac{8.371.843}{8.314\times27\times40.8\times10^{-3}}$$

$= 324.79 = 324.8$ K.

The critical volume, $V_C = 3b = 3 \times 40.8 = 122.4$ cm^3

9. **(a, c)** van der Waal's equation is

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT \quad \text{[For n moles of a gas)}$$

a, b are van der Waal's constants
The ideal gas equation is $PV = nRT$ [For n moles of a gas] where P is pressure excerted by ideal gas and V is volume occupied by ideal gas.

In van der Waal's equation the term $\left(P+\frac{n^2a}{V^2}\right)$ represents the pressure exerted by the gas and ($V - nb$) the volume occupied by the gas. At low pressure, when the gas occoupies large volume the intermolecular distance between gaseous moleculas is quite large and in such case there is no significant role played by intermolecular forces and thus the gas behaves like an ideal gas thus (a) is correct

NOTE : Under high pressure the intermolecular distance decreases and the intermolecular forces play a significant role and the gas shows a devation from ideal behaviour. Thus (b) is *not* correct.

a, b i.e. the van der Waal's coefficients defined on the nature of gas and are independent of temperature so (c) is correct.

The pressure $\left(P+\frac{n^2a}{V}\right)$ is not lower than P so (d) is not correct.

Hence the correct answer is (a, c).

10. **(b,c,d)** (a) An ideal gas cannot be liquefied at any temperature for any pressure. It is due to the absence of intermolecular forces.
(b) Helium, a real gas, can be liquefied by cooling it to critical temperature or below and applying high pressure.
(c) The inversion temperature of helium is much below the room temperature. Hence, it shows heating effect during Joule-Thompson porous plug streaming of the gas at ordinary temperatures.
(d) Compressibility factor $\left(Z=\frac{PV}{RT}\right)$ of hydrogen is greater than unity

11. **(5)** Given, $P = 1.56$ atm; $V = 10$ L
$T = 317$ K; $R = 0.082$

$$\text{Total moles } (n)=\frac{PV}{RT}=\frac{1.56\times10}{0.082\times317}=0.6 \text{ mol}$$

Let C_xH_8 be a mol, therefore moles of $C_xH_{12} = (0.6 - a)$ mol; mass of C in a mol of $C_xH_{12} = 12ax$ g; mass of C in $(0.6 - a)$ mol of $C_xH_{12} = 12 \times (0.6 - a)$ g

$\therefore$ Total mass of C in mixture $= 12ax + 12x\,(0.6 - a)$ g $= 41.4$ g

$$\%\text{ of } C \text{ in mixture} = \frac{7.2x}{41.4} \times 100$$

Given % of C = 87%

$$\text{or } \frac{720x}{41.4} = 87 \text{ or } x = 5$$

12. **(5)** $r_g = \frac{1}{5} . r_{H_2}$

$$\frac{M_g}{M_{H_2}} = \left[\frac{r_{H_2}}{r_g}\right]^2 = (5)^2 = 25; M_g = 2 \times 25 = 50$$

$10\,y = 50 \Rightarrow y = 5$

13. **(8)** $\frac{r_{CH_4}}{r_x} = 2 = \sqrt{\frac{M_x}{M_{CH_4}}} = \sqrt{\frac{M_x}{16}}$, or $M_x = 64$

$8\,y = 64 \Rightarrow y = 8$

14. **(4)** v_{rms} of $X = \sqrt{\frac{3RT_x}{M_x}}$; v_{mp} of $Y = \sqrt{\frac{2RT_y}{M_y}}$

Given $v_{rms} = v_{mp}$

$$\Rightarrow \sqrt{\frac{3RT_x}{M_x}} = \sqrt{\frac{2RT_y}{M_y}}$$

$$\Rightarrow M_y = \frac{2RT_yM_x}{3RT_x} = \frac{2 \times 60 \times 40}{3 \times 400} = 4$$

15. **(c)** The curve representing the gas-liquid equilibrium ends at the *dark* point, the critical point. Above the temperature corresponding to this point, CO_2 can not be liquefied for any value of pressure. Temperature and pressure corresponding to the *dark* point are T_c and P_c.

16. **(b)** At point B, liquefaction of CO_2 commences and is complete at the point C. Along the line BC the proportion of gas phase of CO_2 decreases and that of liquid phase increases, and hence the volume of the system decreases along the line BC.

17. **(b)** For one mole of real gas, we have

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Under conditions of high pressure

$$P + \frac{a}{V^2} \approx P$$

$\therefore$ The above equation becomes

$P(V - b) = RT$

or $PV - Pb = RT$

or $PV = RT + Pb$

18. **(d)** Since the value of $b = 0$ in case of molecules to be point masses

$\therefore$ The van der Waals' equation will become

$$\left(P + \frac{an^2}{V^2}\right)(V - 0) = nRT \quad (\because b = 0, \text{ so } nb = 0)$$

$$\text{or} \quad \left(P + \frac{an^2}{V^2}\right)V = nRT$$

$$\text{or} \quad PV + \frac{an^2}{V} = nRT \quad \text{or} \quad PV = nRT - \frac{an^2}{V}$$

19. **A-q; B-p, C-s; D-r**

(A) At temperature $< T_i$, $\mu_{JT} = \left[\left(\frac{dT}{dP}\right)_H\right]$ becomes positive, i.e. cooling effect takes place in streaming process. It suggests that the forces between the gas molecules are attractive in nature.

(B) At temperature $> T_i$, μ_{JT} is negative which suggests the existance of repulsive forces between the gas molecules.

(C) At Boyle's temperature and above, a real gas obeys gas laws over a wide range of pressure.

(D) In ideal gas the intermolecular forces do not exist. Hence Joule-Thompson effect is zero.

20. **A-r; B-s; C-q; D-p**

(A) Pressure correction $= \frac{an^2}{V^2}$

$$= \frac{3.6(L^2 atm\, mol^{-2})}{10^2(L^2)} \times \left(\frac{200}{40}\right)^2 (mol^2) = 0.9 \text{L atm}$$

(B) Free space $= V - nb = 10 - 5 \times 0.05 = 9.75L$

(C) Actual volume of gas molecules

$$= \frac{nb}{4} = \frac{5 \times 0.05}{4} = 0.06L$$

(D) Effective volume of gas molecules

$= nb = 5 \times 0.05 = 0.25L$

DAILY PRACTICE PROBLEMS

CHEMISTRY SOLUTIONS

DPP/CC06

1. **(b)** $\Delta H = \Sigma\left[\Delta H_f^\circ \text{ products}\right] - \Sigma\left[\Delta H_f^\circ \text{ reactants}\right]$

$\Delta H^\circ = [\Delta H_f^\circ(CO)(g) + \Delta H_f^\circ(H_2O)(g)] -$

$[\Delta H_f^\circ(CO_2)(g) + \Delta H_f^\circ(H_2)(g)]$

$= [-110.5 + (-241.8)] - [-393.5 + 0] = 41.2$

2. **(a)** In $PH_3(g)$, energy required to break 3 P–H bonds $= 954\ kJ\ mol^{-1}$

$\therefore$ Energy required to break 1 P – H bond

$= \frac{954}{3} = 318\ kJ\ mol^{-1}$

In $P_2H_4(g)$, energy of 1 P – P bond + 4 P – H bonds $= 1485\ kJ\ mol^{-1}$

$\because$ Energy of 1 P – H bond $= 318\ kJ\ mol^{-1}$

$\therefore$ Energy of 4 P – H bond $= 318 \times 4$

$= 1272\ kJ\ mol^{-1}$

Thus, the P – P bond energy $= 1485 - 1272$

$= 213\ kJ\ mol^{-1}$

3. **(d)** For isothermal reversible expansion

$w = q = nRT \times 2.303 \log \frac{V_2}{V_1}$

$= 2RT \times 2.303 \log \frac{20}{2}$

$= 2 \times 2 \times T \times 2.303 \times 1 = 9.2\ T$

Entropy change, $\Delta S = \frac{q}{T} = \frac{9.2T}{T} = 9.2$ cal.

4. **(b)** Given, $C_p = 10$ cals at 1000 K

$T_1 = 1000$ K. $T_2 = 100$ K

$m = 32$ g

$\Delta S = ?$

at constant pressure

$\Delta S = C_p \ln \frac{T_2}{T_1}$

$= 2.303 \times C_p \log \frac{T_2}{T_1}$

$= 2.303 \times 10 \log \frac{100}{1000}$

$= -23.03\ cal\ deg^{-1}$

5. **(c)** Given

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$;

$\Delta H^\circ = -285.9\ kJ\ mol^{-1}$ ...(1)

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$;

$\Delta H^\circ = -241.8\ kJ\ mol^{-1}$ ...(2)

We have to calculate

$H_2O(l) \longrightarrow H_2O(g)$; $\Delta H^\circ = ?$

On substracting eqn. (2) from eqn. (1) we get

$H_2O(l) \longrightarrow H_2O(g)$;

$\Delta H^\circ = -241.8 - (-285.9)$

$= 44.1\ kJ\ mol^{-1}$

6. **(b)** $C_2H_5OH(l) + 3O_2(g)$

$\rightarrow 2CO_2(g) + 3H_2O(l)$

$\Delta n_g = 2 - 3 = -1$

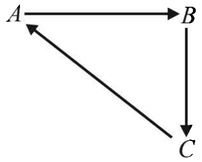
$\Delta U = \Delta H - \Delta n_g RT$

$= -1366.5 - (-1)RT$

$= -1366.5 - (1) \times \frac{8.314}{10^3} \times 300$

$= -1366.5 + 0.8314 \times 3 = -1364\ kJ$

7. **(a, d)** The over all process can be depicted as



Thus it is a cyclic process.

Hence, $\Delta E = 0$, $\Delta H = 0$, $\Delta S = 0$ (cyclic process)

and $\Delta E = q + W$ (Ist law)

$\therefore \quad 0 = q + W$

or $\quad q = -W$

Total work done $= W_{A\rightarrow B} + W_{B\rightarrow C} + W_{C\rightarrow A}$

$\therefore \quad W = -P(V_B - V_A) + 0 + 2.303\ nRT \log \frac{V_C}{V_A}$

$= -(40 - 20) + 0 + 2.303 \times 1 \times 0.082 \times \log \frac{V_C}{V_A}$

$= -6.13$ litre-atmosphere

$= -620.77\ J$

8. **(a, b, d)** For such a process,

$W = -nRT \ln \frac{P_1}{P_2}$

9. **(b)** $C_2H_6(g) \longrightarrow 2C(g) + 6H(g)$

$\Delta H_{C-C} + 6\Delta H_{C-H} = 620\ kJ\ mol^{-1}$

$C_3H_8(g) \longrightarrow 3C(g) + 8H(g)$;

$$2\Delta H_{C-C} + 8\Delta H_{C-H} = 880 \text{ kJ mol}^{-1}$$

Hence, $\Delta H_{C-C} = 80 \text{ kJ mol}^{-1}$;

$\Delta H_{C-H} = 90 \text{ kJ mol}^{-1}$

10. **(8)** $2MgCl \rightarrow Mg + MgCl_2 \qquad \Delta H = ?$

$Mg(s) + 1/2Cl_2(g) \rightarrow MgCl \qquad \Delta H_1 = -125 \text{ kJ mol}^{-1}$

$Mg(s) + Cl_2(g) \rightarrow MgCl_2 \qquad \Delta H_2 = -642 \text{ kJ mol}^{-1}$

$\Delta H = \Delta H_2 - 2\Delta H_1 = -642 - (2 \times -125) = -392 \text{ kJ mol}^{-1}$

$\therefore -49x = -392$

$x = 8$

11. **(6)** $KCl(s) \longrightarrow K^+(g) + Cl^-(g), \Delta H_1 = 181 \text{ kcal mol}^{-1}$

$KCl(s) + H_2O(l) \longrightarrow K^+(aq) + Cl^-(aq),$

$\Delta H_2 = 1.0 \text{ kcal mol}^{-1}$

Let the enthalpy of hydration of K^+ is 2a kcal mol^{-1}

$K^+(g) + H_2O(l) \longrightarrow K^+(aq), \Delta H_3 = 2a$

$Cl^-(g) + H_2O(l) \longrightarrow Cl^-(aq), \qquad \Delta H_4 = a$

$\therefore \Delta H_3 = -\Delta H_1 + \Delta H_2 - \Delta H_4$

$2a = -181 + 1 - a$

$3a = -180, a = -60$

$\therefore \Delta_{hyd}H^- \text{ of } K^+ = 2a = -60 \times 2 = -120$

$\therefore -20x = -120$

$x = 6$

12. **(5)** $\therefore \Delta_{sys}S = \frac{q_{sys}}{T_{sys}} = -\frac{300}{273+127}$

$$= \frac{-300}{400} = \frac{-3}{4} JK^{-1}$$

$$\Delta_{surr}S = \frac{-q_{sys}}{T_{surr}} = -\frac{300}{273+27}$$

$$= \frac{300}{300} = +1 \text{ JK}^{-1}$$

$\Delta_{total}S$ or $\Delta_{universe}S = \Delta_{sys}S + \Delta_{surr}S$

$$= \frac{-3}{4} + 1 = \frac{1}{4} = 0.25 \text{J K}^{-1}$$

$\therefore 0.05x = 0.25$

$x = 5$

13. **(4)** $Fe_2O_3 \quad + \quad 2Al \quad \rightarrow 2Fe + Al_2O_3$

$2 \times 56 + 48 = 160 \quad 2 \times 27 = 54$

Heat of reaction = 399 – 199 = 200 kcal [Al and Fe are in their standard states]

Total weight of reactants = 160 + 54 = 214 g

$\therefore$ Fuel value/gram $= \frac{200}{214} = 0.9346$ kcal/g

Volume of Al $= \frac{54}{2.7} = 20$ cc

Volume of $Fe_2O_3 = \frac{160}{5.2} = 30.77$ cc

Total volume = 20 + 30.77 = 50.77 cc

$\therefore$ Fuel value per cc $= \frac{200}{50.77} = 3.94 \simeq 4$ kcal/cc

14. **(8)** For adiabatic process, $W = P(V_2 - V_1)$

Here $P_1 = 1$ bar, $P_2 = 100$ bar, $V_1 = 100$ mL, $V_2 = 99$ mL;

For adiabatic process, $q = 0$ \ $\Delta U = w$

$\Delta U = q + W$

$= q - P(V_2 - V_1)$ since $W = -P(V_2 - V_1)$

$= 0 - 100(99 - 100) = 100$ bar mL

$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2V_2 - P_1V_1)$

$= 100 + [(100 \times 99) - (1 \times 100)]$

$= 100 + (9900 - 100) = 9900$ bar mL

$\Delta U + \Delta H = 100 + 9900 = 10000$

$\therefore$ the value of $\frac{\Delta U + \Delta H}{1000} - 2 = \frac{10000}{1000} - 2 = 8$

15. **(b)** Path A - reversible isothermal expansion.

According to first law of thermodynamics

$\Delta U = q - w$

$q = w$

Isothermal process $\Delta U = 0$

$$= \left(nRT_1, \ln\frac{V_2}{V_1}\right)$$

16. **(d)** Path B + C - reversible adiabatic expansion followed by reversible heating at constant volume q = 0

$$\Delta S = \frac{q_{rev}}{T}, \; q_{rev} = T\Delta S$$

$$\therefore \quad q_{rev} = nR\ln\frac{V_2}{V_1}$$

17. **(c)** D + E - Reversible expansion at constant pressure followed by a reversible cooling at constant volume.

$$w = q = P_1(V_2 - V_1)$$

18. **(a)** At constant volume,

$$\Delta S = nC_v ln\frac{T_2}{T_1}$$

Given n = 14 g of nitrogen

$$= \frac{14}{28} \text{ mole or } 0.5 \text{ mole}$$

$$\therefore \quad \Delta S = 0.5 \times 4.94 \times 2.303 \log\frac{400}{300}$$

$$\left[ln\frac{T_2}{T_1} = 2.303\log\frac{T_2}{T_1}\right]$$

$= 0.70 \text{ cal K}^{-1}$

At constant pressure

$$\Delta S = nC_p ln\frac{T_2}{T_1}$$

Since $C_p = C_v + R$

$\therefore \quad C_p = 4.94 + 2.0 = 6.94$ cal/mole

$$\therefore \quad \Delta S = \frac{1}{2} \times 6.94 \times 2.303 \log\frac{400}{300} \; [\because \; n = \frac{1}{2}]$$

$= 0.99 \text{ cal K}^{-1}$

19. **(c)** Using the relation, $\Delta S = nC_p \ln\frac{T_2}{T_1}$

We get,

$$\Delta S = 2 \times \frac{5}{2} Rln\frac{600}{300} = 5\,Rln2$$

20. **A-q; B-q, r, s; C-r; D-p, q, r**

(A) For a reversible process, $\Delta S_{\text{system}} = -\Delta S_{\text{surr}}$.

or $\Delta S_{\text{system}} + \Delta S_{\text{surr}} = \Delta S_{\text{Total}} = 0$

(B) From first law, $dE = \delta q_{\text{rev}} + W = \delta q_{\text{rev}} - PdV$

$$\delta q_{\text{rev}} = TdS = dE + PdV = CvdT + PdV$$

$$dS = C_v\frac{dT}{T} + \frac{PdV}{T} = C_v\frac{dT}{T} + R\frac{dV}{V} = R\frac{dV}{V}$$

($dT = 0$ for isothermal process)

$$dS = \int_1^2 R\frac{dV}{T}$$

Integrating $\int_1^2 dS = S_2 - S_1 = \Delta S = \int_1^2 R\frac{dV}{V} = R\ln\frac{V_2}{V_1}$

(C) In perfect gas intermolecular forces do not exit.

Hence, $\left(\frac{dP}{dT}\right)_H = \mu_{\text{J.T.}} = 0$

(D) For adiabatic and reversible process,

$$\delta q_{\text{rev}} = 0 = dE + PdV = CvdT + RT\frac{dV}{V}$$

(for ideal gas)

$$\frac{dT}{T} = -\frac{R}{C_v} \times \frac{dV}{V} = -\frac{Cp - C_v}{C_v} \times \frac{dV}{V} = -(\gamma - 1)\frac{dV}{V}$$

Integrating, $\int_1^2 \frac{dT}{T} = \ln\frac{T_2}{T_1}$

$$= -\int_1^2 (\gamma - 1)\frac{dV}{V} = -(\gamma - 1)\ln\frac{V_2}{V_1} = (\gamma - 1)\ln\frac{V_1}{V_2}$$

$$= \ln\left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$ for ideal gas $\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1}$

Hence, $\frac{P_2V_2}{P_1V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$ $\quad P_1V_1^{\gamma} = P_2V_2^{\gamma} = \text{a constant}$