Appendix

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Fundamental constants

Avogadro number	N	6.022×10^{23}
Atomic mass unit (or) Unified atomic mass	amu (or) u	1.660×10^{-27} kg
Speed of light	c	2.997×10^{8} m s^{-1}
Elementary charge (or) Charge of an electron	e	1.602×10^{-19} C
Planck's constant	h	6.626×10^{-34} Js
Mass of electron	m_e	9.109×10^{-31} kg
Mass of proton	m_p	1.672×10^{-27} kg
Mass of neutron	m_n	1.674×10^{-27} kg
Bohr's radius	a_0	0.529 Å
Rydberg constant	R_∞	1.097×10^{5} cm^{-1}
Universal gas constant	R	8.314 J K^{-1} mol^{-1} 0.082 L atm K^{-1} mol^{-1} 1.987 cal K^{-1} mol^{-1} 62.36 L mmHg K^{-1} mol^{-1} 83.14 L mbar K^{-1} mol^{-1}

Commonly used SI Prefixes

femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
f	p	n	μ	m	c	d	k	M	G
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

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Inter - Conversion of Units

1 Å	=	10^{-10} m		
1 atm	=	101.325 kPa	=	1.01325×10^5 N m^{-2}
1 atm	=	1.01325×10^5 J m^{-3}	=	760 Torr (mmHg)
1 eV	=	1.60219×10^{-19} J		
1 N	=	1 J m^{-1}	=	10^5 dyne
1 J	=	10^7 erg	=	1 Kg m^2 s^{-2}
1 cal	=	4.184 J		

Critical constants of selected gases

Gas	Critical Pressure, P_c (atm)	Critical Volume, V_c (cm^3 mol^{-1})	Critical Temperature, T_c (K)
He	2.26	57.76	5.21
Ne	26.86	41.74	44.44
Ar	48.00	75.25	150.72
Kr	54.27	92.24	209.39
Xe	58.0	118.8	289.75
H_2	12.8	64.99	33.23
N_2	33.54	90.10	126.3
O_2	50.14	78.0	154.8
Cl_2	76.1	124	417.2
Br_2	102	135	584
HCl	81.5	81.0	324.7
CO_2	72.85	94.0	304.2
H_2O	218.3	55.3	647.4
NH_3	111.3	72.5	405.5
CH_4	45.6	98.7	190.6
C_2H_4	50.50	124	283.1
C_2H_6	48.20	148	305.4
C_6H_6	48.6	260	562.7

Van der waals constants for select gases

Name	a (L^2 bar mol^{-2})	b (L mol^{-1})
Ammonia	4.225	0.0371
Benzene	18.24	0.1154
Carbon dioxide	3.64	0.04267
Carbon monoxide	1.505	0.03985
Chlorine	6.579	0.05622
Helium	0.0346	0.0238
Hexane	24.71	0.1735
Hydrogen	0.2476	0.02661
Hydrogen bromide	4.51	0.04431
Hydrogen chloride	3.716	0.04081
Hydrogen sulfide	4.49	0.04287
Mercury	8.2	0.01696
Methane	2.283	0.04278
Nitric oxide	1.358	0.02789
Nitrogen	1.37	0.0387
Nitrogen dioxide	5.354	0.04424
Nitrous oxide	3.832	0.04415
Oxygen	1.382	0.03186
Sulfur dioxide	6.803	0.05636
Water	5.536	0.03049

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Molar heat capacities of select compounds:

	$C_{v,m}$ (J K^{-1} mol^{-1})	$C_{p,m}$ (J K^{-1} mol^{-1})
Gases		
Inert gases	12.48	20.79
H_2	20.44	28.82
N_2	20.74	29.12
O_2	20.95	29.36
CO_2	28.46	37.11
Liquids		
H_2O	-	75.29
CH_3OH	-	81.6
C_2H_5OH	-	111.5
C_6H_6	-	136.1
Solids		
C (diamond)	-	6.11
Cu	-	244.4
Fe	-	25.1
SiO_2	-	44.4

Standard heat of combustion (ΔH_f^0, kJ mol^{-1})

Methane(g)	=	- 890	Ethanol(l)	=	- 1368
Ethane(g)	=	- 1560	Acetic acid (l)	=	- 875
Propane(g)	=	- 2220	Benzoic acid (s)	=	- 3227
Butane(g)	=	- 2878	Glucose (s)	=	- 2808
Benzene(l)	=	- 3268	Sucrose (s)	=	- 5645
Methanol(l)	=	- 726			

Thermodynamic data for select compounds

	ΔH_f^0 (kJ mol^{-1})	ΔG_f^0 (kJ mol^{-1})	S^0 (J K^{-1} mol^{-1})
C (s , graphite)	0	0	5.740
H_2(g)	0	0	130.684
N_2(g)	0	0	191.61
O_2(g)	0	0	205.138
Cl_2(g)	0	0	223.07
Ag(s)	0	0	42.55
Cu(s)	0	0	33.150
Au(s)	0	0	47.40
Fe(s)	0	0	27.28
Zinc(s)	0	0	41.63
C(s, diamond)	1.895	2.900	2.377
CO(g)	-110.53	-137.17	197.67
CO_2(g)	-393.51	-394.36	213.74
HCl(g)	-92.31	-95.30	186.91
H_2O(l)	-285.83	-237.13	69.91
H_2O(g)	-241.82	-228.57	188.83
NH_3(g)	-46.11	-16.45	192.45
Methane(g)	-74.81	-50.72	186.26
Ethane(g)	-84.68	-32.82	229.60
Propane(g)	-103.85	-23.49	269.91
Butane(g)	-126.15	-17.03	310.23
Benzene(l)	49.0	124.3	173.3
Methanol(l)	-238.66	-166.27	126.8
Ethanol(l)	-277.69	-174.78	160.7

Lattice Enthalpies of alkali metal halides ($-\Delta H^0$ Lattice, kJ mol^{-1})

	F	Cl	Br	I
Li	1022	846	800	744
Na	902	771	733	684
K	801	701	670	629
Rb	767	675	647	609
Cs	716	645	619	585

C_P and C_V for Mono, di and tri atomic gases

	C_V Value	C_P Value ($C_P = R + C_V$)
Monatomic gas	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic gas	$\frac{5}{2}R$	$\frac{7}{2}R$
Triatomic	$\frac{6}{2}R$	$\frac{8}{2}R$

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Unit - 1
Basic Concepts of Chemistry and Chemical Calculations

Evaluate yourself :

1. (i) **Element** - Copper wire, Silver plate

(ii) **Compound** - Sugar, distilled water, carbon dioxide, Table salt, Naphthalene balls

(iii) **Mixture** - Sea water

2. (i) C_2H_5OH : (2 x 12) + (5 x 1) + (1 x 16) + (1 x 1) = **46 g**

(ii) $KMnO_4$: (1 x 39) + (1 x 55) + (4 x 16) = **158 g**

(iii) $K_2Cr_2O_7$: (2 x 39) + (2 x 52) + (7 x 16) = **294 g**

(iv) $C_{12}H_{22}O_{11}$: (12 x 12) + (22 x 1) + (11 x 16) = **342 g**

3. (a) Molar mass of ethane, C_2H_6 = (2 x 12)+ (6 x 1) = 30 g mol^{-1}

n = mass / molar mass = 9 g / 30 g mol^{-1} = **0.3 mole**

(b) At 273 K and 1 atm pressure 1 mole of a gas occupies a volume of 22.4 L

Therefore,

number of moles of oxygen, that occupies a volume of 224 ml at 273 K and 3 atm pressure

$$= \frac{1\,\text{mole}}{273\,\text{K} \times 1\,\text{atm} \times 22.4\,\text{L}} \times 0.224\,\text{L} \times 273\,\text{K} \times 3\,\text{atm}$$

$$= 0.03\,\text{mole}$$

1 mole of oxygen contains 6.022 x 10^{23} molecules

0.03 mole of oxygen contains = 6.022 x 10^{23} x 0.03

= **1.807 x 10^{22} molecules of oxygen**

4. (a) Mass of the metal = 0.456 g

Mass of the metal chloride = 0.606 g

0.456 g of the metal combines with 0.15 g of chlorine.

Mass of the metal that combines with 35.5 g of chlorine is $\frac{0.456}{0.15} \times 35.5$

= **107.92 g eq^{-1}.**

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(b) Equivalent mass of a oxidising agent $= \dfrac{\text{molar mass}}{\text{number of moles of electrons gained by one mole of the reducing agent}}$

$= \dfrac{294.2 \text{ g mol}^{-1}}{6 \text{ eq mol}^{-1}}$

$=$ **49.0 g eq^{-1}**

5.

Element	Percentage Composition	Atomic mass	Relative no. of atoms = $\frac{\text{Percentage}}{\text{Atomic mass}}$	Simple ratio
C	54.55 %	12	54.55/12 = 4.55	4.55 / 2.27 = 2
H	9.09 %	1	9.09 / 1 = 9.09	9.09 / 2.27 = 4
O	36.36 %	16	36.36/16 = 2.27	2.27/2.27 = 1
Empirical formula (C_2H_4O)				

6.

Element	Percentage Composition	Relative no. of atoms = $\frac{\text{Percentage}}{\text{Atomic mass}}$	Atomic mass= $\frac{\text{Percentage}}{\text{Relative no. of atoms}}$	Simple ratio
X	32 %	2	16	4
Y	24 %	1	24	2
Z	44 %	0.5	88	1
Empirical formula ($X_4 Y_2 Z$)				

Calculated empirical formula mass $= (16 \times 4) + (24 \times 2) + 88$

$= 64 + 48 + 88 = 200$

$n = \dfrac{\text{molar mass}}{\text{calculated empirical formula mass}}$

$\therefore n = \dfrac{400}{200}$

$= 2$

$\therefore$ **Molecular formula $(X_4Y_2Z)_2$** $=$ **$X_8Y_4Z_2$**

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7.

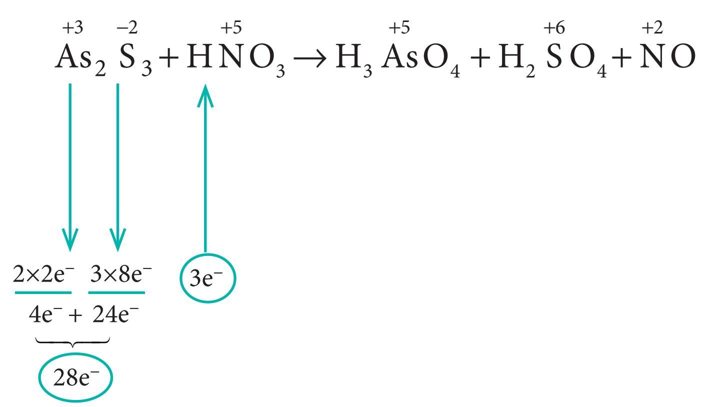
Content	Reactant		Products	
	x	y	*l*	m
Stoichiometric coefficient	2	3	4	1
No. of moles allowed to react	8	15	–	–
No. of moles of reactant reacted and product formed	8	12	16	4
No. of moles of un-reacted reactants and the product formed	–	3	16	4

Limiting reagent : **x**

Product formed : **16 moles of *l* & 4 moles of m**

Amount of excess reactant : **3 moles of y**

8.



Equate the total no. of electrons in the reactant side by cross multiplying,

⇒ $3\ As_2\ S_3 + 28\ HNO_3 \rightarrow H_3AsO_4 + H_2SO_4 + NO$

Based on reactant side, balance the products

⇒ $3\ As_2\ S_3 + 28\ HNO_3 \rightarrow 6\ H_3AsO_4 + 9\ H_2SO_4 + 28\ NO$

Product side :36 hydrogen atoms & 88 oxygen atoms

Reactant side :28 hydrogen atoms & 84 oxygen atoms

Difference is 8 hydrogen atoms & 4 oxygen atoms

∴ Add 4 H_2O molecule on the reactant side.

Balanced equation is,

$\mathbf{3\ As_2\ S_3 + 28\ HNO_3 + 4\ H_2O \rightarrow 6\ H_3AsO_4 + 9\ H_2SO_4 + 28\ NO}$

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EVALUATION

I Choose the best answer

1. (a) 40 ml of CO_2 gas
2. (d) 200 u
3. (c) assertion is true but reason is false
4. (b) oxygen
5. (a) 102 g
6. (c) 6.022×10^{20}
7. (c) 16 %
8. (c) 0.075
9. (d) 1 mole of HCl
10. (c) $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2\ HCl$
11. (b) $P_4 + 3\ NaOH + 3\ H_2O \rightarrow PH_3 + 3\ NaH_2PO_2$
12. (b) 52.7
13. (d) 6.022×10^{24} molecules of water
14. (a) NO
15. (a) 6.022×10^{23}
16. (c) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-} < SO_4^{2-}$
17. (c) molar mass of ferrous oxalate / 3
18. (d) the mass of one mole of carbon
19. (c) the ratio between the number of molecules in A to number of molecules in B is 2:1
20. (a) 3.59 g
21. (b) 44 g mol^{-1}
22. (c) both (a) & (b)
23. (a) propene
24. (a) relative atomic mass is 12 u
25. (a) $_6C^{12}$

Key to the multiple choice questions

1. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Content	CH_4	O_2	CO_2
Stoichiometric coefficient	1	2	1
Volume of reactants allowed to react	40 mL	80 mL	
Volume of reactant reacted and product formed	40 mL	80 mL	40 mL
Volume of gas after cooling to the room temperature	-	-	40 mL

Since the product was cooled to room temperature, water exists mostly as liquid. Hence, option (a) is correct

2.

$$= \frac{(200\times90)+(199\times8)+(202\times2)}{100} = 199.96$$
$$\simeq 200\ u$$

3. Correct reason: Total number of entities present in one mole of any substance is equal to 6.022×10^{23}.

4. Reaction 1 : $2C + O_2 \rightarrow 2CO$

2 × 12 g carbon combines with 32 g of oxygen. Hence,

Equivalent mass of carbon $= \frac{2\times12}{32}\times8 = 6$

Reaction 2 : $C + O_2 \rightarrow CO_2$

12 g carbon combines with 32 g of oxygen. Hence,

Equivalent mass of carbon $= \frac{12}{32}\times8 = 3$

5. Let the trivalent metal be M^{3+}

Equivalent mass	=	mass of the metal / valance factor
$9\ g\ eq^{-1}$	=	mass of the metal / 3 eq
Mass of the metal	=	27 g
Oxide formed M_2O_3;		
Mass of the oxide	=	(2 x 27) + (3 x 16)
	=	**102 g**

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6. Weight of the water drop = 0.018 g

No. of moles of water in the drop = Mass of water / molar mass

= 0.018 / 18 = 10^{-3} mole

No of water molecules present in 1 mole of water = 6.022×10^{23}

No. water molecules in one drop of water (10^{-3} mole) = $6.022 \times 10^{23} \times 10^{-3}$

= **6.022×10^{20}**

7. $MgCO_3 \rightarrow MgO + CO_2 \uparrow$

$MgCO_3$: (1 x 24) + (1 x 12) + (3 x 16) = 84 g

CO_2 : (1 x 12) + (2 x 16) = 44 g

100 % pure 84 g $MgCO_3$ on heating gives 44 g CO_2

Given that 1 g of $MgCO_3$ on heating gives 0.44 g CO_2

Therefore, 84 g $MgCO_3$ sample on heating gives 36.96 g CO_2

$$\text{Percentage of purity of the sample} = \frac{100\,\%}{44\,g\,CO_2} \times 36.96\,g\,CO_2$$
$$= 84\,\%$$

Percentage of impurity = **16 %**

8. $NaHCO_3 + CH_3COOH \rightarrow \underbrace{CH_3COONa + H_2O} + CO_2\uparrow$

6.3 g + 30 g → 33 g + x

The amount of CO_2 released, x = 3.3 g

No. of moles of CO_2 released = 3.3 / 44 = 0.075 mol

9 $H_2(g) + Cl_2(g) \rightarrow 2\ HCl\ (g)$

Content	**H_2(g)**	**Cl_2(g)**	**HCl (g)**
Stoichiometric coefficient	1	1	2
No. of moles of reactants allowed to react at 273 K and 1 atm pressure	22.4 L (1 mol)	11.2 L (0.5 mol)	-
No. of moles of reactant reacted and product formed	0.5	0.5	1
Amount of HCl formed = 1 mol			

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10. $\overset{+2}{Ba}\overset{-1}{Cl_2} + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4} \rightarrow \overset{+2}{Ba}\overset{+6}{S}\overset{-2}{O_4} + 2\,\overset{+1}{H}\overset{-1}{Cl}$

11. $\overset{0}{P_4} + 3\,NaOH + 3\,H_2O \rightarrow \overset{-3}{P}H_3 + 3\,NaH_2\overset{+1}{P}O_2$

12. The reduction reaction of the oxidising agent(MnO_4^-) involves gain of 3 electrons. Hence the equivalent mass = (Molar mass of $KMnO_4$)/3 = 158.1/3 = 52.7

13. No. of moles of water present in 180 g

= Mass of water / Molar mass of water

= 180 g / 18 g mol^{-1} = 10 moles

One mole of water contains

= 6.022 x 10^{23} water molecules

10 mole of water contains = 6.022 x 10^{23} x 10 = 6.022 x 10^{24} water molecules

14. 7.5 g of gas occupies a volume of 5.6 liters at 273 K and 1 atm pressure Therefore, the mass of gas that occupies a volume of 22.4 liters

$$= \frac{7.5\text{ g}}{5.6\text{ L}} \times 22.4\text{ L} = 30\text{ g}$$

Molar mass of NO (14+16) = 30 g

15. No. of electrons present in one ammonia (NH_3) molecule (7 + 3) = 10

$$\text{No. of moles of ammonia} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{1.7\text{ g}}{17\text{ gmol}^{-1}} = 0.1\text{ mol}$$

No. of molecules present in 0.1 mol of ammonia

$= 0.1 \times 6.022 \times 10^{23} = 6.022 \times 10^{22}$

No. of electrons present in 0.1 mol of ammonia

$= 10 \times 6.022 \times 10^{22} = 6.022 \times 10^{23}$

16. $\overset{+3}{S_2}O_4^{2-} < \overset{+4}{S}O_3^{2-} < \overset{+5}{S_2}O_6^{2-} < \overset{+6}{S}O_4^{2-}$

17. $\overset{2+}{Fe}\overset{3+}{C_2}O_4 \xrightarrow{\text{Oxidising agent}} \overset{3+}{Fe} + \overset{+4}{C}O_2$

$n = 1 + 2(1) = 3$

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18. The mass of one mole of carbon

19. No, of moles of oxygen = 8 g/32 g

= 0.25 moles of oxygen

No. of moles of sulphur dioxide = 8 g / 64 g

= 0.125 moles of sulphur dioxide

Ratio between the no. of molecules = 0.25: 0.125

= 2:1

20. $AgNO_3 + KCl \rightarrow KNO_3 + AgCl$

50 mL of 8.5 % solution contains 4.25 g of $AgNO_3$

No. of moles of AgNO3 present in 50 mL of 8.5 % $AgNO_3$ solution

= Mass / Molar mass

= 4.25 / 170

= 0.025 moles

Similarly, No of moles of KCl present in 100 mL of 1.865 % KCl solution

= 1.865 / 74.5

= 0.025 moles

So total amount of AgCl formed is 0.025 moles (based on the stoichiometry)

Amount of AgCl present in 0.025 moles of AgCl

= no. of moles x molar mass

= **0.025 x 143.5 = 3.59 g**

21. No. of moles of a gas that occupies a volume of 612.5 mL at room temperature and pressure ($25\ ^0$C and 1 atm pressure)

= 612.5×10^{-3} L / 24.5 $Lmol^{-1}$

= 0.025 moles

We know that,

Molar mass = Mass / no. of moles

= **1.1 g /0.025 mol = 44 g mol^{-1}**

22. No. of moles of carbon present in 6 g of C-12 = Mass / Molar mass

$= 6/12 = 0.5$ moles $= 0.5 \times 6.022 \times 10^{23}$ carbon atoms.

No. of moles in 8 g of methane = 8 / 16 = 0.5 moles

$= 0.5 \times 6.022 \times 10^{23}$ carbon atoms.

No. of moles in 7.5 g of ethane = 7.5 / 30 = 0.25 moles

$= 2 \times 0.25 \times 6.022 \times 10^{23}$ carbon atoms.

23. Percentage of carbon in ethylene $(C_2H_4) = \frac{\text{mass of carbon}}{\text{Molar mass}} \times 100$

$$= \frac{24}{28} \times 100 = 85.71\,\%$$

Percentage of carbon in propene $(C_3H_6) = \frac{36}{42} \times 100 = 85.71\%$

24. (a) relative atomic mass of C-12 is 12 u

25. ${}_{6}C^{12}$

II Key to brief answer questions:

32. Given :

The density of CO_2 at 273 K and 1 atm pressure = 1.965 kgm^{-3}

Molar mass of CO_2 = ?

At 273 K and 1 atm pressure, 1 mole of CO_2 occupies a volume of 22.4 L

Mass of 1 mole of $CO_2 = \frac{1.965\,\text{Kg}}{1\text{m}^3} \times 22.4\,\text{L}$

$$= \frac{1.965 \times 10^3\,\text{g} \times 22.4 \times 10^{-3}\,\cancel{\text{m}^3}}{1\,\cancel{\text{m}^3}}$$

$$= 44.01\,\text{g}$$

Molar mass of CO_2 = 44 $gmol^{-1}$

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33.

Compound	Given no. of moles	No. of oxygen atoms
Ethanol - C_2H_5OH	1	$1 \times 6.022 \times 10^{23}$
Formic acid - HCOOH	1	$2 \times 6.022 \times 10^{23}$
Water - H_2O	1	$1 \times 6.022 \times 10^{23}$
Answer : Formic acid		

34. Average atomic mass $= \dfrac{(78.99 \times 23.99) + (10 \times 24.99) + (11.01 \times 25.98)}{100}$

$= \dfrac{2430.9}{100}$

$= 24.31u$

35. Reaction : $x + y + z_2 \leftarrow xyz_2$

Question	Number of moles of reactants allowed to react			Number of moles of reactants consumed during reaction			Limiting reagent
	x	y	z_2	x	y	z_2	
(a)	200 atoms	200 atoms	50 molecules	50 atoms	50 atoms	50 molecules	z_2
(b)	1 mol	1mol	3 mol	1 mol	1 mol	1 mol	x and y
(c)	50 atom	25 atom	50 molecules	25 atom	25 atom	25 molecules	y
(d)	2.5 mol	5 mol	5 mol	2.5 mol	2.5 mol	2.5 mol	x

36. Given: mass of one atom $= 6.645 \times 10^{-23}$ g

Ψ mass of 1 mole of atom $= 6.645 \times 10^{-23}\text{ g} \times 6.022 \times 10^{23}$

$= 40$ g

Ψ number of moles of element in 0.320 kg $= \dfrac{1\text{ mole}}{40\text{ g}} \times 0.320\text{ kg}$

$= \dfrac{1\text{ mol} \times 320\text{ g}}{40\text{ g}}$

$= 8$ mol.

38.

Compound	Molecular formula	Empirical formula
Fructose	$C_6 H_{12} O_6$	CH_2O
Caffeine	$C_8 H_{10} N_4 O_2$	$C_4 H_5 N_2 O$

39. Given $2Al + Fe_2O_3 \leftarrow Al_2O_3 + 2Fe$

	Reactants		Products	
	Al	**Fe_2O_3**	**Al_2O_3**	**Fe**
Amount of reactant allowed to react	324 g	1.12 kg	-	-
Number of moles allowed to react	$\frac{324}{27} = 12$ mol	$\frac{1.12 \times 10^3}{160} = 7$ mol	-	-
Stoichiometric Co-efficient	2	1	1	2
Number of moles consumed during reaction	12 mol	6 mol	-	-
Number of moles of reactant unreacted and number of moles of product formed	-	1 mol	6 mol	12 mol

Molar mass of Al_2O_3 formed

$$= 6 \text{ mol} \times 102 \text{ g mol}^{-1} \begin{bmatrix} Al_2O_3 \\ (2 \times 27) + 3(\times 16) \\ 54 + 48 = 102 \end{bmatrix} \quad = 612 \text{ g}$$

Excess reagent = Fe_2O_3

Amount of excess reagent left at the end of the reaction = 1 mol × 160 g mol^{-1}

$$= 160 \text{ g} \begin{bmatrix} Fe_2O_3 \\ (2 \times 56) + (3 \times 16) \\ 112 + 48 = 160 \end{bmatrix} \quad = 160 \text{ g}$$

40. Balanced equation for the combustion of ethane

$$C_2H_6 + \frac{7}{2} O_2 \leftarrow 2CO_2 + 3H_2O$$

$$\Leftarrow \quad 2C_2H_6 + 7O_2 \leftarrow 4CO_2 + 6\, H_2O$$

To produce 4 moles of CO_2, 2 moles of ethane is required

Ψ To produce 1 mole (44 g) of CO_2 required

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number of moles of ethane $= \dfrac{2 \text{ mol ethane}}{4 \text{ mol } \cancel{CO_2}} \times 1 \text{ mol } \cancel{CO_2}$

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

= 0.5 mole of ethane

41.

$$\overset{-1}{H_2O_2} + Fe^{2+} \longrightarrow Fe^{3+} + \overset{-2}{H_2O}$$

H_2O_2 ↑ $(1e^- \times 2)$; Fe^{2+} ↓ $1e^-$

$1\ H_2O_2 + 2Fe^{2+} \leftarrow Fe^{3+} + H_2O$

$\Leftarrow \quad H_2O_2 + 2Fe^{2+} + 2H^+ \leftarrow 2Fe^{3+} + 2H_2O$

42.

Element	Percentage	Atomic mass	Relative number of atoms	Simple ratio	Whole no.
C	76.6	12	$\frac{76.6}{12} = 6.38$	$\frac{6.38}{1.06} = 6$	6
H	6.38	1	$\frac{6.38}{1} = 6.38$	$\frac{6.38}{1.06} = 6$	6
O	17.02	16	$\frac{17.02}{16} = 1.06$	$\frac{1.06}{1.06} = 1$	1

Empirical formula $= C_6H_6O$

$$n = \frac{\text{Molar mass}}{\text{Calculated empirical formula mass}}$$

$$= \frac{2 \times \text{vapour density}}{94} = \frac{2 \times 47}{94} = 1$$

Ψ molecular formula $(C_6H_6O) \times 1 = C_6H_6O$

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43.

Element	%	Relative no. of atoms	Simple ratio
Na	14.31	$\frac{14.31}{23} = 0.62$	$\frac{0.62}{0.31} = 2$
S	9.97	$\frac{9.97}{32} = 0.31$	$\frac{0.31}{0.31} = 1$
H	6.22	$\frac{6.22}{1} = 6.22$	$\frac{6.22}{0.31} = 20$
O	69.5	$\frac{69.5}{16} = 4.34$	$\frac{4.34}{0.31} = 14$

Ψ Empirical formula = $Na_2\,S\,H_{20}\,O_{14}$

$$n = \frac{\text{molar mass}}{\text{calculated empirical formula mass}} = \frac{322}{322} = 1$$

$$\left[\begin{array}{l} Na_2\,S\,H_{20}\,O_{14} \\ = (2 \times 23) + (1 \times 32) + (20 \times 1) + 14\,(16) \\ = 46 + 32 + 20 + 224 \\ = 322 \end{array}\right]$$

Molecular formula = $Na_2\,S\,H_{20}\,O_{14}$

Since all the hydrogen in the compound present as water

Ψ Molecular formula is $Na_2\,SO_4 \cdot 10H_2O$

44. (i)

$$K_2\overset{+6}{Cr_2}O_7 + K\overset{-1}{I} + H_2SO_4 \rightarrow K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + \overset{0}{I_2} + H_2O$$

↑ $2 \times 3e^-$ ↓ $1e^-$

$$\mathbf{K_2Cr_2O_7 + 6KI} + H_2SO_4 \rightarrow K_2SO_4 + Cr_2\,(SO_4)_3 + I_2 + H_2O$$

$$K_2Cr_2O_7 + 6KI + H_2SO_4 \rightarrow K_2SO_4 + \mathbf{Cr_2(SO_4)_3 + 3I_2} + H_2O$$

$$K_2Cr_2O_7 + 6KI + \mathbf{7H_2SO_4} \rightarrow \mathbf{4K_2SO_4} + Cr_2\,(SO_4)_3 + 3I_2 + \mathbf{7H_2O}$$

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(ii)

$$K\overset{+7}{M}nO_4 + Na_2\overset{+4}{S}O_3 \longrightarrow \overset{+4}{M}nO_2 + Na_2\overset{+6}{S}O_4 + KOH$$

$\uparrow 3e^-$ $\quad\quad$ $\downarrow 2e^-$

$$\Rightarrow \mathbf{2KMnO_4 + 3Na_2SO_3} \longrightarrow MnO_2 + Na_2SO_4 + KOH$$

$$\Rightarrow 2KMnO_4 + 3Na_2SO_3 \longrightarrow \mathbf{2MnO_2 + 3Na_2SO_4} + KOH$$

$$\Rightarrow 2KMnO_4 + 3Na_2SO_3 + \mathbf{H_2O} \longrightarrow 2MnO_2 + 3Na_2SO_4 + \mathbf{2KOH}$$

(iii)

$$\overset{0}{C}u + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{C}u(NO_3)_2 + \overset{+4}{N}o_2 + H_2O$$

$\downarrow 2e^-$ $\quad$ $\uparrow 1e^-$

$$\mathbf{Cu + 2HNO_3} \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

$$Cu + 2HNO_3 + \mathbf{2HNO_3} \longrightarrow Cu(NO_3)_2 + \mathbf{2NO_2} + 2H_2O$$

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(iv)

$$K\overset{+7}{M}nO_4 + H_2\overset{+3}{C_2}O_4 + H_2SO_4 \longrightarrow K_2SO_4 + \overset{+2}{M}nSO_4 + \overset{+4}{C}O_2 + H_2O$$

$\downarrow 5e^-$ $\quad\quad$ $\uparrow 1e^- \times 2$

$$\mathbf{2KMnO_4 + 5H_2C_2O_4} + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$$

$$2KMnO_4 + 5H_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + \mathbf{2MnSO_4 + 10CO_2} + H_2O$$

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

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45. (i) Half reaction are

$$\overset{+7}{M}nO_4^- \longrightarrow Mn^{2+} \quad \text{............. (1)}$$

and $$Sn^{2+} \longrightarrow Sn^{4+} \quad \text{............. (2)}$$

$$(1) \Rightarrow \quad MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$(2) \Rightarrow \quad Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$

$$(1) \times 2 \Leftarrow \quad 2MnO_4^- + 16H^+ + \cancel{10e^-} \longrightarrow 2Mn^{2+} + 8H_2O$$

$$(2) \times 5 \Leftarrow \quad 5\,Sn^{2+} \longrightarrow 5Sn^{4+} + \cancel{10e^-}$$

$$\Rightarrow \quad 2MnO_4^- + 5Sn^{2+} + 16H^+ \longrightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$$

(ii)

$$\overset{+3}{C_2}O_4^{2-} \longrightarrow \overset{+4}{C}O_2 \quad \text{................. (1)}$$

$$\overset{+6}{Cr_2}O_7^{2-} \longrightarrow Cr^{3+} \quad \text{................. (2)}$$

$$(1) \Rightarrow \quad C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2\,e^- \quad \text{................. (3)}$$

$$Cr_2O_7^{2-} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 7\,H_2O \quad \text{................. (4)}$$

$$(3) \times 3 \Leftarrow \quad 3\,C_2O_4^{2-} \longrightarrow 6\,CO_2 \cancel{+6\,e^-} \quad \text{................. (5)}$$

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H^2O \quad \text{................. (4)}$$

$$Cr_2O_7^{2-} + 3\,C_2O_4^{2-} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 6\,CO_2 + 7\,H_2O$$

(iii)

half reaction $\Leftarrow$

$$S_2O_3^{2-} \longrightarrow S_4O_6^{2-} \quad \text{............... (1)}$$

$$I_2 \longrightarrow I^- \quad \text{............... (2)}$$

$$(1) \Leftarrow \quad 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + \cancel{2e^-} \quad \text{............... (3)}$$

$$(2) \Leftarrow \quad I_2 + \cancel{2e^-} \longrightarrow 2I^- \quad \text{............... (4)}$$

$$(3) + (4) \Leftarrow \quad 2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

(iv) Half reactions are

$$\overset{0}{Z}n \longrightarrow Zn^{2+} \quad \text{............... (1)}$$

$$\overset{+5}{N}O_3^- \longrightarrow \overset{+2}{N}O \quad \text{............... (2)}$$

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$(1) \Rightarrow \quad Zn \longrightarrow Zn^{2+} + 2e^-$ .... (3)

$(2) \Rightarrow \quad NO_3^- + 3e^- + 4H^+ \longrightarrow NO + 2H_2O$ .... (4)

$(3) \times 3 \Rightarrow \quad 3Zn \longrightarrow 3Zn^{2+} + \cancel{6e^-}$ .... (5)

$(4) \times 2 \Rightarrow \quad 2NO_3^- + \cancel{6e^-} + 8H^+ \longrightarrow 2NO + 4H_2O$ .... (6)

$$3Zn + 2NO_3^- + 8H^+ \longrightarrow 3Zn^{2+} + 2NO + 4H_2O$$

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Unit - 2
Quantum Mechanical Model of Atom

Evaluate yourself:

1) Given: accelerated potential = 1 keV

The kinetic energy of the electron =

the energy due to accelerating potential.

$$\frac{1}{2}mv^2 = eV$$

$$mv^2 = 2eV$$

$$m^2v^2 = 2meV \Rightarrow (mv)^2 = 2meV$$

$$\Rightarrow mv = \sqrt{2meV}$$

$$\text{de Broglie wavelength } \lambda = \frac{h}{mv}$$

$$\Rightarrow \lambda = \frac{h}{\sqrt{2meV}}$$

m = mass of the electron = 9.1×10^{-31} kg

h = Planck constant = 6.626×10^{-34} Js

1 eV = 1.6×10^{-19} J

$$\lambda = \frac{6.626\times10^{-34}\,Js}{\sqrt{2\times9.1\times10^{-31}\,kg\times1keV}}$$

$$\lambda = \frac{6.626\times10^{-34}\,JS}{\sqrt{2\times9.1\times10^{-31}\times1\times10^{3}\times1.6\times10^{-19}\,kgJ}}$$

$$\lambda = 3.88\times10^{-11}\,m$$

$$[\because \frac{Js}{\sqrt{J\,kg}} = J^{1/2}kg^{-1/2}.\,s$$

$$= (kgm^2s^{-2})^{1/2}.kg^{-1/2}s$$

$$= m]$$

2. Given

$\Delta v = 5.7 \times 10^5 ms^{-1}$ Δx = ?

According to Heisenberg's uncertainty principle, $\Delta x\,.\,\Delta p \geq \frac{h}{4\pi}$

$$\frac{h}{4\pi} = \frac{6.626\times10^{-34}}{4\times3.14}kgm^2s^{-1}$$

$$\frac{h}{4\pi} = 5.28\times10^{-35}$$

$$\Delta x\,.\,\Delta p \geq 5.28\times10^{-35}$$

$$\Delta x\,.\,m.\Delta v \geq 5.28\times10^{-35}$$

$$\Rightarrow \Delta x \geq \frac{5.28\times10^{-35}\,kgm^2s^{-1}}{9.1\times10^{-31}\,kg\times5.7\times10^{5}\,ms^{-1}}$$

$$\Rightarrow \Delta x \geq 1.017\times10^{-10}\,m$$

3. n = 4

$l = 0, 1, 2, 3$

$\therefore$ 4 sub shells s, p, d & f.

$l = 0$ $m_l = 0 \Rightarrow$ one 4s orbital.

$l = 1$ $m_l = -1, 0, +1 \Rightarrow$ three 4p orbitals.

$l = 2$ $m_l = -2, -1, 0, +1, +2 \Rightarrow$ five 4d orbitals.

$l = 3$ $m_l = -3, -2, -1, 0, +1, +2, +3 \Rightarrow$ seven 4f orbitals.

Over all 16 orbitals are possible.

4.

Orbital	n	l	Radial node $n - l - 1$	Angular node l	Total node $n - 1$
3d	3	2	0	2	2
4f	4	3	0	3	3

5. $E_n = \frac{-13.6}{n^2} eV$

Second excited state

$n = 3 \qquad \therefore E_3 = \frac{-13.6}{9} eV$

$E_3 = -1.51 eV$

6. Electronic configuration of Fe^{3+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5$

Five unpaired electrons.

1	1	1	1	1

$3d^5$

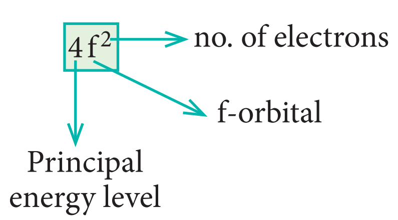
Electronic configuration of Mn^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5$

$\therefore$ **Five unpaired electrons.**

Electronic configuration of Ar: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

no unpaired electrons.

7.



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n = 4 ; f orbital $l = 3 \Rightarrow m_l = -3, -2, -1, 0, +1, +2, +3$

Out of two electrons, one electron occupies 4f orbital with $m_l = -3$ and another electron occupies 4f orbital with $m_l = -2$.

∴ All the four quantum numbers for the two electrons are

Electron	n	l	m_l	m_s
$1e^-$	4	3	−3	+1/2
$2e^-$	4	3	−2	+1/2

8.

Electronic configuration of Fe^{3+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5$

Electronic configuration of Ni^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^8$

Fe^{3+} has stable $3d^5$ half filled configuration.

EVALUATION

I Choose the best answer:

1. (c) 30
2. (c) 4.42×10^{-18} J
3. (b) $\lambda_1 = 2\lambda_2$
4. (d) Stark effect
5. (b)
6. (d) n=6 to n=5
7. (a)
8. (c) $d_{z^2}, d_{x^2-y^2}$
9. (b) Spin quantum number
10. (b) $[Xe]4f^7\ 6s^2$; $[Xe]4f^7\ 5d^1\ 6s^2$; $[Xe]4f^9\ 6s^2$
11. (c) 4l+2
12. (d) $\sqrt{6}\ h/2\pi$
13. (c) 2
14. (c)
15. (a) 9
16. (a) ns→(n-2)f→(n-1)d→np
17. (b) (ii),(iv) & (v)
18. (b) 17
19. (a) Zero
20. (c) $1/2m\ \sqrt{h/\pi}$
21. (c) 6.6×10^{-31} cm
22. (d) 0.4
23. (d) -9E
24. (a) $\hat{H}\psi = E\psi$
25. (d) $\Delta E.\Delta X \geq h/4\pi$

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Key to multiple choice questions:

1.

M^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

M : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$

Atomic number = 26

Mass number =56

No. of neutrons = 56 -26 = 30

2. E = hν = hc/λ

$$= \frac{6.626 \times 10^{-34}\ \text{J s} \times 3 \times 10^{8}\ \text{m s}^{-1}}{45 \times 10^{-9}\ \text{m}}$$

$$= 4.42 \times 10^{-18}\ \text{J}$$

3.

$$\frac{E1}{E2} = \frac{25\ \text{eV}}{50\ \text{eV}} = \frac{1}{2}$$

$$\frac{hc}{\lambda_1} \times \frac{\lambda_2}{hc} = \frac{1}{2}$$

$$2\lambda_2 = \lambda_1$$

4. Spliting of spectral lines in magnetic field is called Zeeman effect and spliting of spectral lines in electric field, is called Stark effect.

5. **Correct statement:** For n=1, the electron has more negative energy than it does for n=6 which means that the electron is **strongly** bound in the smallest allowed orbit.

6. n = 6 to n=5

$E_6 = -13.6 / 6^2$; $E_5 = -13.6 / 5^2$

$E_6 - E_5 = (-13.6 /6^2) - (-13.6/5^2)$

= 0.166 eV atom^{-1}

$E_5 - E_4 = (-13.6 /5^2) - (-13.6/4^2)$

= 0.306 eV atom^{-1}

9. Spin quantum number

For the first electron $m_s = +½$

For the second electron $m_s = -½$

10. Eu : [Xe] $4f^7$, $5d^0$, $6s^2$

Gd : [Xe] $4f^7$, $5d^1$, $6s^2$

Tb: [Xe] $4f^9$, $5d^0$, $6s^2$

11 $2(2l+1) = 4l+2$

12. Orbital angular momentum = $\sqrt{l(l+1)}\ h/2\pi$ For d orbital = $\sqrt{(2 \times 3)}\ h/2\pi = \sqrt{6}\ h/2\pi$

13 n = 3; l=1; m = -1

either $3p_x$ or $3p_y$

i.e., Maximum two electrons can be accomodated either in $3p_x$ or in $3p_y$

14 No. of radial node = n-***l***-1

No. of angular node = ***l***

for 3p orbital

No. of angular node = ***l*** = 1

No. of radial node = n-l-1 = 3-1-1 = 1

15. n = 3; l = 0; m_l = 0 - one s orbital

n = 3; l = 1; m_l = -1, 0, 1 - three p orbitals

n = 3; l = 2; m_l = -2, -1, 0, 1, 2 - five d Orbitals

Overall nine orbitals are possible.

16. n = 6

According Aufbau principle,

6s →4f →5d →6p

ns → (n-2)f →(n-1)d → np

17 (ii) l can have the values from 0 to n-1

n=2; possible 'l' values are 0, 1 hence l = 2 is not possible.

(iv) for l=0; m=-1 not possible

(v) for n=3 l = 4 and m = 3 not possible

18. n+l = 8

Electronic configuration of atom with atomic number 105 is [Rn] $5f^{14}$ $6d^3$ $7s^2$

Orbital	(n+l)	No. of electrons
5f	5+3 = 8	14
6d	6+2 = 8	3
7s	7+0 = 7	2
No of electrons = 14 + 3 = 17		

19. Option (a) - Zero **(Refer to Figure 2.9)**

20.

$$\Delta x.\Delta p \geq \frac{h}{4\pi}$$

$$\Delta p.\Delta p \geq \frac{h}{4\pi}$$

$$\Delta p^2 \geq \frac{h}{4\pi}$$

$$m^2(\Delta v)^2 \geq \frac{h}{4\pi}$$

$$(\Delta v) \geq \sqrt{\frac{h}{4\pi m^2}}$$

$$\Delta v \geq \frac{1}{2m}\sqrt{\frac{h}{\pi}}$$

21.

m = 100 g = 100 x 10^{-3} kg

v = 100 cm s^{-1} = 100 x 10^{-2} m s^{-1}

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626\times10^{34}\,Js^{-1}}{100\times10^{-3}\,kg\times100\times10^{-2}\,ms^{-1}}$$

$$= 6.626\times10^{-33}\,ms^{-1}$$

$$= 6.626\times10^{-31}\,cms^{-1}$$

23.

$$E_n = \frac{-13.6}{n^2}\,eV\ atom^{-1}$$

$$E_1 = \frac{-13.6}{(1)^2} = -13.6$$

$$E_3 = \frac{-13.6}{(3)^2} = -\frac{13.6}{9}$$

Givethat

$$E_3 = -E$$

$$-\frac{13.6}{9} = -E$$

$$-13.6 = -9E$$

$$\Rightarrow E_1 = -9E$$

II Key to brief answer question:

27. n = 4 l = 0, 1, 2, 3

four sub-shells ⇒ s, p, d, f

l = 0 m_l = 0; one 4s orbital.

l = 1 m_l = −1, 0, +1 ; three 4p orbitals.

l = 2 m_l = −2, −1, 0, +1, +2 ; five 4d orbitals.

l = 3 m_l = -3, −2, −1, 0, +1, +2 , +3; seven 4f orbitals

Over all Sixteen orbitals.

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28.

Orbital	n	l	Radial node $n-l-1$	Angular node l
2s	2	0	1	0
4p	4	1	2	1
5d	5	2	2	2
4f	4	3	0	3

30. i) ground state

1	1	1	1	1

ii) maximum exchange energy

1	1	1	1	1

32.

Orbital	n	l
$3p_x$	3	1
$4d_{x^2-y^2}$	4	2

34.

$$\Delta x . \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x . \Delta p \geq 5.28 \times 10^{-35} Kgm^2s^{-1}$$

$$\Delta x . (m\Delta v) \geq 5.28 \times 10^{-35} Kgm^2s^{-1}$$

Given Δ v = 0.1%

$v = 2.2 \times 10^6\ ms^{-1}$

$m = 9.1 \times 10^{-31}$ Kg

$$\Delta v = \frac{0.1}{100} \times 2.2 \times 10^6 ms^{-1}$$

$$= 2.2 \times 10^3 ms^{-1}$$

$$\therefore \Delta x \geq \frac{5.28 \times 10^{-35} Kgm^2s^{-1}}{9.1 \times 10^{-31} Kg \times 2.2 \times 10^3 ms^{-1}}$$

$$\Delta x \geq 2.64 \times 10^{-8} m$$

35. Electronic configuration of oxygen

$= 1s^2\ 2s^2\ 2p^4$

⥮ ⥮ ⥮ 1 1

$\therefore$ 8^{th} electron present in $2p_x$ orbital and the quantum numbers are

$n = 2, l = 1, m_l$ = either +1 or -1 and

$s = -1/2$

Electronic configuration of chlorine =

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$
⥮	⥮	⥮ ⥮ ⥮	⥮	⥮ ⥮ 1
				$3p_x\ 3p_y\ 3p_z$

15^{th} electron present in $3P_Z$ orbital and the quantum numbers are n = 3, l = 1, m_l = either +1 or -1 and m_s = +1/2

36.

$$E_n = \frac{-13.6}{n^2} eV \quad atom^{-1}$$

$$n = 3 \quad E_3 = \frac{-13.6}{3^2} = \frac{-13.6}{9} = -1.51\ eV\ atom^{-1}$$

$$n = 4 \quad E_4 = \frac{-13.6}{4^2} = \frac{-13.6}{16} = -0.85\ eV\ atom^{-1}$$

$\Delta E = (E_4 - E_3) = (-0.85) - (-1.51)$ eV atom^{-1}

$= (-0.85 + 1.51)$

$= 0.66$ eV atom^{-1}

$(1eV = 1.6 \times 10^{-19}\ J)$

$\Delta E = 0.66 \times 1.6 \times 10^{-19}$ J

$\Delta E = 1.06 \times 10^{-19}$ J

$hv = 1.06 \times 10^{-19}$ J

$$\frac{hc}{\lambda} = 1.06 \times 10^{-19} J$$

$$\therefore \lambda = \frac{hc}{1.06 \times 10^{-19} J}$$

$$= \frac{6.626 \times 10^{-34} JS \times 3 \times 10^8 ms^{-1}}{1.06 \times 10^{-19} J}$$

$$\lambda = 1.875 \times 10^{-6} m$$

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37. Given : de Broglie wavelength of the tennis ball equal to 5400 Å.

m = 54 g

v = ?

$$\lambda = \frac{h}{mV}$$

$$V = \frac{h}{m\lambda}$$

$$V = \frac{6.626\times10^{-34}\,JS}{54\times10^{-3}\,Kg\times5400\times10^{-10}\,m}$$

$$V = 2.27\times10^{-26}\,ms^{-1}$$

38.

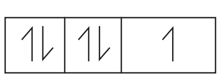
n	l	Sub Enery levels	m_l values	Number of orbitals
4	2	4d	−2, −1, 0, +1, +2	five 4d orbitals
5	3	5f	−3, −2, −1, 0, +1, +2, +3	seven 5f orbitals
7	0	7s	0	one 7s orbitals

41. no. of electrons : 35 (given)

no. of protons : 35

Electronic configuration

$1s^2\ 2s^2\ 2p^6\ 3s^2\ \ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$



$4P_x$ $4P_y$ $4P_z$

last electron present in $4P_y$ orbital

n = 4 l = 1 m_l = either +1 or -1 and s = −1/2

43. $He^+ \rightarrow He^{2+} + e^-$

$$E_n = \frac{-13.6z^2}{n^2}$$

$$E_1 = \frac{-13.6\,(2)^2}{(1)^2} = -54.4$$

$$E_\infty = \frac{-13.6(2)^2}{(\infty)^2} = 0$$

∴ Required Energy for the given process = $E_\infty - E_1$ = 0 − (− 54.4) = 54.4 ev

44.

	Atom	Uni-negative ion
number of electron	x − 1	x
number of protons	x − 1	x −1
number of neutrons	y	y

Given that, y = x + 11.1% of x

$$= \left(x + \frac{11.1}{100}x\right) = x + 0.111x$$

$$y = 1.111x$$

mass number = 37

number of protons + number of neutrons = 37

(x − 1) + 1.111x = 37

x + 1.111x = 38

2.111x = 38

$$x = \frac{38}{2.11}$$

x = 18.009 x = 18 (whole number)

∴ Atomic number = x − 1

= 18 −1 = 17

Mass number = 37

Symbol of the ion $^{37}_{17}Cl^-$

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45)

$r_n = \frac{(0.529)n^2}{z} \overset{o}{A}$ $E_n = \frac{-13.6\,(z^2)}{n^2}$ ev atom^{-1}

for Li^{2+} z = 3

Bohr raduis for the third orbit (r_3)

$= \frac{(0.529)\,(3)^2}{3}$

$= 0.529 \times 3$

= 1.587 Å

Energy of an electron in the fourth orbit (E_4) $= \frac{-13.6\,(3)^2}{(4)^2}$

= – 7.65 eV atom^{-1}

46) Given

$v = 2.85 \times 10^8$ ms^{-1}

$m_p = 1.673 \times 10^{-27}$ Kg

$\lambda = \frac{h}{mv}$

$= \frac{6.626 \times 10^{-34}\, kgm^2s^{-1}}{1.673 \times 10^{-27}\, kg \times 2.85 \times 10^8\, ms^{-1}}$

$\lambda = 1.389 \times 10^{-15} \Rightarrow \lambda = 1.389 \times 10^{-5}\, \overset{o}{A}$

$[\because 1\overset{o}{A} = 10^{-10}\, m]$

47) m = 160 g = 160×10^{-3} kg

v = 140 km hr^{-1} = $\frac{140 \times 10^3}{60 \times 60}$ms^{-1}

v = 38.88 ms^{-1}

$\lambda = \frac{h}{mv}$

$\lambda = \frac{6.626 \times 10^{-34}\, Kgm^2s^{-1}}{160 \times 10^{-3}\, Kg \times 38.88\, ms^{-1}}$

$\lambda = 1.065 \times 10^{-34}\, m$

48) Δx = 0.6 Å = 0.6×10^{-10} m

Δp = ?

$\Delta x\,.\,\Delta p \ge \frac{h}{4\pi}$

$\Delta x\,.\,\Delta p \ge 5.28 \times 10^{-35}\, kgm^2s^{-1}$

$(0.6 \times 10^{-10})\Delta p \ge 5.28 \times 10^{-35}$

$\Rightarrow \Delta p \ge \frac{5.28 \times 10^{-35}\, kgm^2s^{-1}}{0.6 \times 10^{-10}\, m}$

$\Delta p \ge 8.8 \times 10^{-25}\, kgms^{-1}$

49)

$\Delta x\,.\,\Delta p \ge \frac{h}{4\pi}$

$\lambda.(m\Delta v) \ge \frac{h}{4\pi}$

$\Delta v \ge \frac{h}{4\pi(m\lambda)}$

$\Delta v \ge \frac{h}{4\pi \times m \times \frac{h}{mv}}$ $\left[\because \lambda = \frac{h}{mv}\right]$

$\Delta v \ge \frac{v}{4\pi}$

Therefore,

minimum uncertainity in velocity $= \frac{v}{4\pi}$

50) Potential difference = 100V

$= 100 \times 1.6 \times 10^{-19}$J

$\lambda = \frac{h}{\sqrt{2mev}}$

$= \frac{6.626 \times 10^{-34}\, Kgm^2s^{-1}}{\sqrt{2 \times 9.1 \times 10^{-31}\, Kg \times 100 \times 1.6 \times 10^{-19}\, J}}$

$\lambda = 1.22 \times 10^{-10}\, m$

51)

n	*l*	m_l	sub energy level
4	**2**	0	4d
3	1	0	**3p**
5	**1**	**any one value –1, 0, +1**	5p
3	**2**	–2	3d

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Unit - 3
Periodic classification of elements

Evaluate yourself

2. Atomic number : 120

IUPAC temporary symbol : Unbinilium

IUPAC temporary symbol : Ubn

Possible electronic configuration :[Og] $8s^2$

3. Electronic Configuration : $(n-1)d^2\ ns^2$

for n = 5, the electronic configuration is,

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 4d^2\ 5s^2$ Atomic number : 40

4^{th} group 5^{th} period (d block element) = Zirconium

4. Electronic Configuration of Aluminium

$_{13}Al\ \underbrace{1s^2}_{(n-2)}\ \underbrace{2s^2\ 2p^6}_{(n-1)}\ \underbrace{3s^2\ 3p^1}_{n}$

Group	no. of electrons	Contribution of each electron to 'S' value	Contribution of a particular group
n	2	0.35	0.70
(n – 1)	8	0.85	6.80
(n – 2)	2	1	2.00
			9.50

∴ Effective nuclear charge = Z – S

= 13 – 9.5

$(Z_{eff})_{Al}$ = 3.5

Electronic Configuration of chlorine

$\underbrace{1s^2}_{n-2}\ \underbrace{2s^2\ 2p^6}_{n-1}\ \underbrace{3s^2\ 3p^5}_{n}$

Group	no. of electrons	Contribution of each electron to 'S' value	Contribution of a particular group
n	6	0.35	2.1
(n – 1)	8	0.85	6.8
(n –2)	2	1	2
		S =	10.9

∴ Effective nuclear charge = Z – S

= 17 – 10.9

$(Z_{eff})_{cl}$ = 6.1

$(Z_{eff})_{cl} > (Z_{eff})_{Al}$ and. Hence $r_{cl} < r_{Al}$.

5.

X^{3+}, Y^{2+}, Z^- are isoelectronic.

∴ Effective nuclear charge is in the order $(Z_{eff})_{Z^-} < (Z_{eff})_{Y^{2+}} < (Z_{eff})_{X^{3+}}$ and

Hence, ionic radii should be in the order

$r_{Z^-} > r_{Y^{2+}} > r_{X^{3+}}$

∴ The correct values are,

Species	Ionic radii
Z^-	136
Y^{2+}	64
X^{3+}	49

6. **Noble gases :** Ioniation energy ranging from 2372 $KJmol^{-1}$ to 1037 kJ mol^{-1}.
For element X, the IE_1, value is in the

range of noble gas, moreover for this element both IE_1 and IE_2 are higher and hence X is the noble gas.

For Y, the first ionisation energy is low and second ionisation energy is very high and hence Y is most reactive metal.

For Z, both IE_1 and IE_2 are higher and hence it is least reactive.

7. $Cl(g) + e^- \longrightarrow Cl^-(g)$ $\Delta H = 348$ kJ mol^{-1}

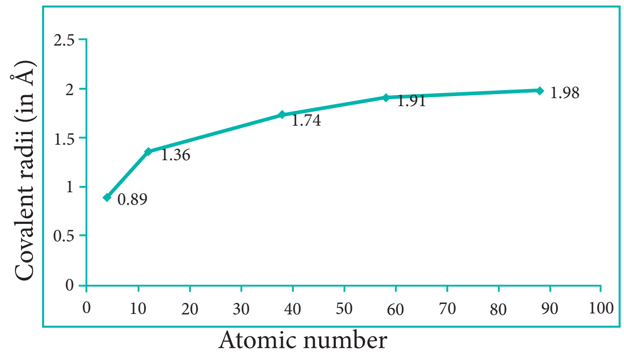
For one mole (35.5g) 348 kJ is released.

$\therefore$ For 17.75g chlorine, $\frac{348\ kJ}{35.5\ \cancel{g}} \times 17.75\ \cancel{g}$ energy leased.

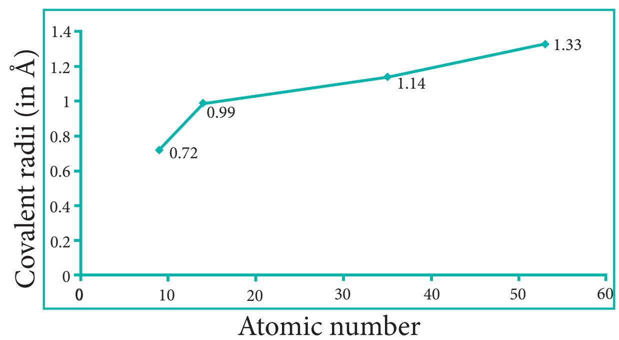
$$\therefore \text{The amount of energy released} = \frac{348}{2}$$
$$= 174\ kJ$$

Activitiy : 3.1

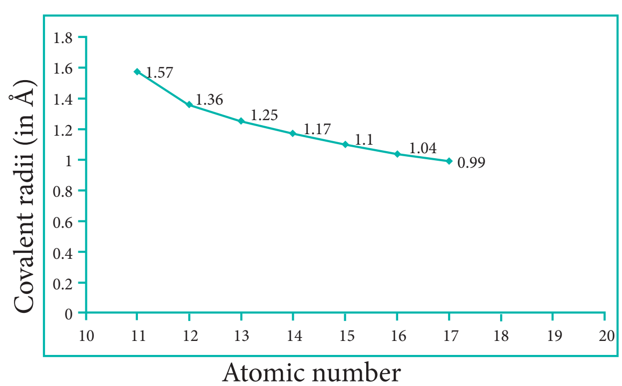
Covalent radii - 2nd group elements



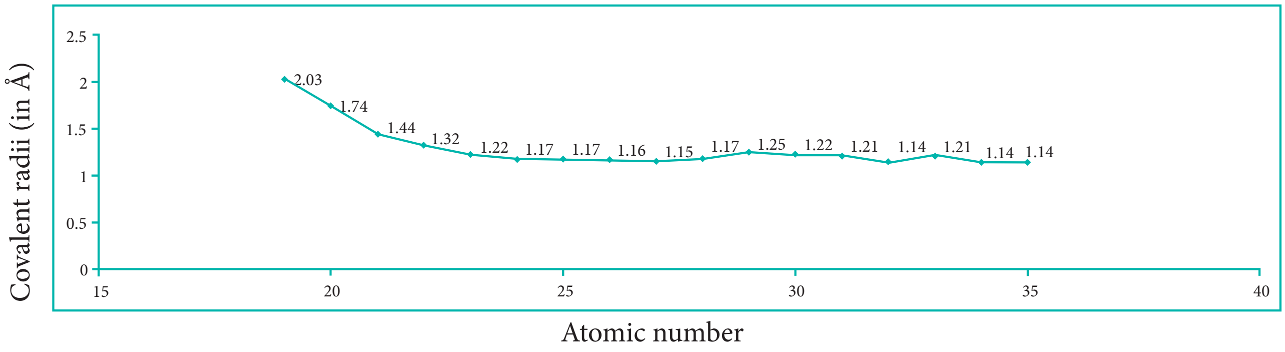
Covalent radii - 17th group elements



Covalent radii - 3rd period elements



Covalent radii - 4th period elements



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EVALUATION

I Choose the best answer:

1. (d) bibibium
2. (b) AB_2
3. (d) f-block elements
4. (a) I < Br < Cl < F (increasing electron gain enthalpy)
5. (d) fluorine
6. (c) Aluminium
7. (b) Na < Al < Mg < Si < P
8. (a)
9. (d) Ca < Al < C < O < F
10. (c) Cl > F > Br > I
11. (d) Hydrogen
12. (c) Argon
13. (a) Y > Z > X > A
14. (c)
15. (a) $1s^2, 2s^2, 2p^6, 3s^1$
16. (c) Oxygen
17. (c) +527 kcal mol^{-1}
18. (a) s > p > d > f
19. (d) None of these
20. (b) 575 kJ mol^{-1}
21. (a)
22. (a) Generally increases
23. (d) Be and Al

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EVALUATION

I Choose the best answer:

1. (c)
2. (c) $CO + H_2$
3. (b)
4. (d) group one elements
5. (c) 1p+2n
6. (a) Palladium, Vanadium
7. (a)
8. (a) 1.2 g
9. (d) EDTA
10. (c) $CaCl_2$
11. (a) sodium aluminium silicate
12. (a)
13. (c) $CrO(O_2)_2$
14. (c) 5/2
15. (d) 8.4
16. (d) sp^3 and sp^3
17. (c) monobasic acid
18. (a) tetrahedrally by 4-H atoms
19. (b) intra-molecular hydrogen bonding and inter molecular hydrogen bonding
20. (c) both (a) & (b)
21) (c) amphoteric oxide

Key for multiple choice questions:

1) Option (c)

   Correct statement : Hydrogen has three isotopes of which **protium** is the most common.

2) Option (c)

   $CO + H_2$ - Water gas

3) Option (b)

   Correct statement : Ortho isomer - one nuclear spin

   Para isomer - zero nuclear spin

4) Option (d)

   eg : Sodium hydride ($Na^+ H^-$)

5) Option (c)

   ${}_1T^3$ ($1e^-$, 1p, 2n)

7) Option (a)

   $Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2Na^+$

8) mass of deuterium = 2 × mass of protium

   If all the 1.2 g hydrogen is replaced with deuterium, the weight will become 2.4g. Hence the increase in body weight is (2.4 – 1.2 = 1.2 g)

   Option (a)

9) EDTA (option (d))

10) Permanent hardness if water is due to the presence of the chlorides, nitrates and sulphates of Ca^{2+} and Mg^{2+} ions.

    Option (c) $CaCl_2$

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11) Zeolite is sodium aluminium silicate.

($NaAlSi_2O_6 . H_2O$)

Option (a)

12) (a) 1 mL of H_2O_2 will give 100ml O_2 at STP.

13) $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \rightarrow 2CrO(O_2)_2 + 5H_2O$

Option (c)

14) $2MnO_4^- + 5H_2O_2(aq) + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

Option (c) 5/2 moles

15) Volume strength of hydrogen peroxide = Normality of hydrogen peroxide × 5.6

$= 1.5 \times 5.6$

$= 8.4$

Option (d)

$$\underset{(2 \times 34g)}{2H_2O_2} \rightarrow 2H_2O + \underset{(22.4\text{ litres})}{O_2} \uparrow$$

Volume strength of Hydrogen peroxide

$$= \frac{\text{Normality} \times \text{Equivalent weight of } H_2O_2 \times 22.4}{68}$$

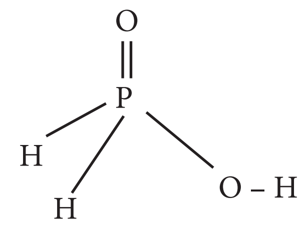
$$= \text{Normality} \times \left(\frac{17 \times 22.4}{68}\right)$$

Volume strength of hydrogen peroxide = Normality × 5.6

16) sp^3 and sp^3

Option (d)

17) Hypophosphorus acid on reaction with D_2O, only one hydrogen is replaced by deuterium and hence it is mono basic

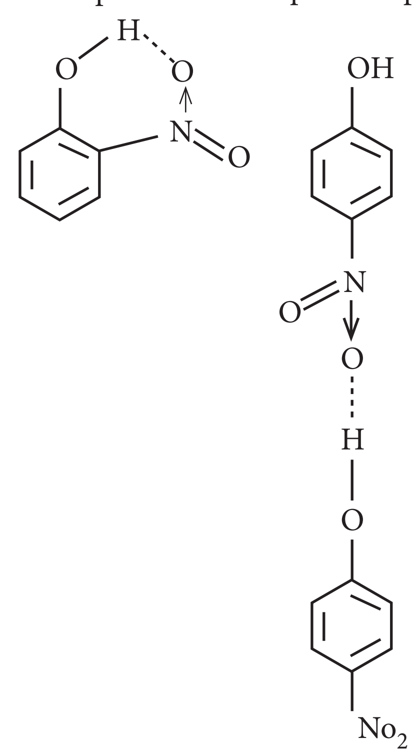


Option (c) monobasic acid

18) (a) tetrahedrally surrounded by 4 hydrogen atoms (refer 4.6 (a) Structure of ice)

19)

o-nitro phenol p - nitro phenol



Option (b)

20) Heavy water is used as moderator as well as coolant in nuclear reactions.

Option (c)

21) Water is a amphoteric oxide.

Option (c)

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EVALUATION

I Choose the best answer.

1. (c) Density: $Li < K < Na < Rb < C$
2. (a) Li^+ has minimum degree of hydration among alkali metal cations
3. (d) none of these
4. (b) Li
5. (c) kerosene
6. (a) superoxide and paramagnetic
7. (c) Potassium carbonate can be prepared by solvay process
8. (b) Magnesium
9. (b) $MI < MBr < MCl < MF$
10. (a) Castners process
11. (c) $Ca(CN)_2$
12. (a) $MgCl_2$
13. (a) p-2, q-1, r-4, s-5, t-6, u-3
14. (d) both assertion and reason are false
15. (a)
16. (b) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
17. (c) Its salts are rarely hydrolysed
18. (c) milk of lime
19. (b) $NaHCO_3$
20. (b) $Ca(OH)_2$
21. (a) Ca^{2+} ions are not important in maintaining the regular beating of the heart.
22. (b) CaF_2
23. (a) $CaSO_4.2H_2O$
24. (b) CaNCN
25. (d) Li_2CO_3

Keys to multiple choice questions:

1) Option (c)

   Potassium is lighter than sodium

   (Refer table 5.3)

   The correct order of density is

   $Li < K < Na < Rb < Cs$

   $0.54 < 0.86 < 0.97 < 1.53 < 1.90$ (in g cm^{-3})

2) Option (a)

   Li^+ has maximum degree of hydration among alkali metal cations.

   $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

3) All these compounds reacts with alkali metals to evolve hydrogen gas.

   (d) none of these.

4) hydration energy of Li^+ is more and hence Li^+ is stabilized in aqueous medium.

   (b) Li

5) (c) Kerosene

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6) RbO_2 is a super oxide which contains Rb+ and O_2^- ions. O_2^- contains one unpaired electron and hence it is paramagnetic.

Option (a)

7) Potassium carbonate cannot be prepared by solvay process. Potassium bicarbonate is fairly soluble in water and does not precipitate out.

Option (c)

8)

Li ↘ Mg	Be ↘ Al	B ↘ Si

Option (b)

9) ionic character (difference in electronegativity)

MI < MBr < MCl < MF

Option (b)

10) Castner's process

$NaOH \rightleftharpoons Na^+ + OH^-$

Cathode : $Na^+ + e^- \rightarrow Na$

Anode : $2OH^- \rightarrow H_2O + 1/2O_2 + 2e^-$

Option (a)

11) $$CaC_2 + N_2 \xrightarrow{300-350^\circ C} \underset{\text{Calciumcyanide}}{Ca(CN)_2}$$

Option (c)

12) (a) $MgCl_2$

The order of hydration energy of alkaline earth metal is

$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

13. (p) sodium –yellow (2)

(q) Calcium – Brick red (1)

(r) Barium – apple green (4)

(s) Strontium – Crimson red (5)

(t) Cesium – blue (6)

(u) Potassium – Violet (3)

Option (a)

14. (d)

Among alkali and alkaline earth metals,

K, Rb and Cs alone forms superoxides.

Superoxide O_2^- has 3 electron bond.

15. (a)

both are true and reason is the correct explanation of assertion.

16. Solubility of carbonates decreases down the group and hence the correct order of solubility is,

(b) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$

17) **Correct Statement:** Beryllium salts are easily hydrolysed

option (c)

18) Slaked lime $Ca(OH)_2$

The suspension is called milk of lime and the clear solution is called lime water.

Option (c)

19)

$$2NaHCO_3 \xrightarrow{\Delta} \underset{\text{(Soluble in water)}}{Na_2CO_3} + H_2O + CO_2 \uparrow$$

$$Na_2CO_3 \xrightarrow{2HCl} 2\,NaCl + H_2O + CO_2 \uparrow$$

Correct option (b)

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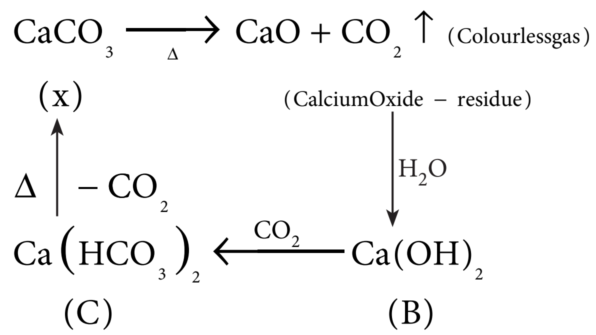
20)



Option (b)

21) Ca^{2+} ion plays an important role in maintaining regular heart beat.

Option (a)

22) 'Blue john' – CaF_2

(A variety of fluorite)

∴ Option (b)

23) $CaSO_4 . 2H_2O$ ∴ Option (a)

24) $CaC_2 + N_2 \xrightarrow[1\ atm]{} CaNCN$

nitrolium
(or)
Calcium cyanamide

∴ Option (b)

25) Li_2CO_3 is least stable.

Option (d)

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Unit - 6 Gaseous State

Evaluate yourself:

1. Volume of freon (V_1) = 1.5 dm^3

Pressure (P_1) = 0.3 atm

'T' isconstant

P_2 = 1.2 atm

V_2 = ?

Ψ $P_1V_1 = P_2V_2$

$$\Rightarrow V_2 = \frac{P_1V_1}{P_2}$$

$$= \frac{0.3\ \cancel{atm} \times 1.5\ dm^3}{1.2\ \cancel{atm}}$$

$$= 0.375\ dm^3$$

Ψ Volume decreased from 1.5 dm^3 to 0.375 dm^3

2. $V_1 = 0.375\ dm^3$ $V_2 = 0.125$

$P_1 = 1.05$ atm $P_2 = ?$

'T' - Constant

$P_1V_1 = P_2V_2$

$$\therefore P_2 = \frac{P_1V_1}{V_2} = \frac{1.05 \times 0.375}{0.125}$$

$$= 3.15\ atm$$

3. $V_1 = 3.8\ dm^3$ $T_2 = 0^0C = 273$ K

$T_1 = ?$ $V_2 = 2.27\ dm^3$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad T_1 = \left(\frac{T_2}{V_2}\right) \times V_1$$

$$= \frac{273\ K}{2.27\ \cancel{dm^3}} \times 3.8\ \cancel{dm^3}$$

$$T_1 = 457\ K$$

4. $V_1 = 7.05\ dm^3$ $V_2 = 2.35\ dm^3$

$\varepsilon_1 = 0.312$ mol $\varepsilon_2 = ?$

'P' and 'T' are constant

$$\therefore \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$\Rightarrow n_2 = \left(\frac{n_1}{V_1}\right) \times V_2$$

$$n_2 = \frac{0.312\ mol}{7.05\ \cancel{dm^3}} \times 2.35\ \cancel{dm^3}$$

$$n_2 = 0.104\ mol$$

Number of moles exhaled =

0.312 - 0.104 = 0.208 moles

5) $T_1 = 8\ ^0C = 8 + 273 = 281$ K

$P_1 = 6.4$ atm $V_1 = 2.1$ ml

$T_2 = 25^0\ C = 25 + 273 = 298$ K

$P_2 = 1$ atm $V_2 = ?$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\Rightarrow V_2 = \left(\frac{P_1V_1}{T_1}\right) \times \frac{T_2}{P_2}$$

$$= \frac{6.4\ \cancel{atm} \times 2.1\ ml}{281\ \cancel{K}} \times \frac{298\ \cancel{K}}{1\ \cancel{atm}}$$

$$V_2 = 14.25\ ml$$

6(a)

$V_{O_2} = 12\ dm^3$ $P = 1$ atm

$V_{He} = 46\ dm^3$

$V_{total} = 5\ dm^3$

$$P_{O_2} = x_{O_2} \times P_{total}$$

$$x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{He}}$$

$$= \frac{0.54}{0.54 + 2.05}$$

$$= \frac{0.54}{2.59} = 0.21$$

$$n_{O_2} = \frac{1\ mol}{22.4\ \cancel{L}} \times 12\ \cancel{L}$$

$$n_{O_2} = 0.54\ mol$$

$$n_{He} = \frac{1\ mol}{22.4\ \cancel{L}} \times 46\ \cancel{L}$$

$$n_{He} = 2.05\ mol$$

$$P_{total} \times V_{total} = 1\ atm \times 22.4\ l$$

$$\therefore P_{total} = \frac{1\ atm \times 22.4\ \cancel{l}}{5\ \cancel{l}}$$

$$P_{total} = 4.48\ atm$$

$$\therefore P_{O_2} = 0.21 \times 4.48\ atm$$

$$= 0.94\ atm$$

$$P_{He} = x_{He} \times P_{total}$$

$$x_{He} = \frac{n_{He}}{n_{O_2} + n_{He}}$$

$$= \frac{2.05}{0.54 + 2.05}$$

$$x_{He} = \frac{2.05}{2.59} = 0.79$$

$$\therefore P_{He} = 0.79 \times 4.48\ atm$$

$$P_{He} = 3.54\ atm$$

6 (b) $2KClO_{3\,(s)} \longrightarrow 2KCl_{(s)} + 3O_{2\,(g)}$

$$P_{total} = 772\ mm\ Hg$$

$$P_{H_2O} = 26.7\ mm\ Hg$$

$$P_{total} = P_{O_2} + P_{H_2O}$$

$$\therefore P_{O_2} = P_{total} - P_{H_2O}$$

$P_1 = 26.7$ mm Hg $\qquad T_2 = 295$ K

$T_1 = 300$ K $\qquad P_2 = ?$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\Rightarrow P_2 = \left(\frac{P_1}{T_1}\right) T_2 = \frac{26.7\ mm\ Hg}{300\ \cancel{K}} \times 295\ \cancel{K}$$

$$P_2 = 26.26\ mm\ Hg$$

$$\therefore P_{O_2} = 772 - 26.26$$

$$= 745.74\ mm\ Hg$$

7) $t_1 = 1.5$ minutes $\qquad (gas)_{hydro\ carbon}$

$t_2 = 4.73$ minutes $\qquad (gas)_{Bromine}$

$$\frac{\gamma_{Hydrocarbon}}{\gamma_{Bromine}} = \frac{t_{Bromine}}{t_{Hydrocarbon}}$$

(∵ Volume is constant)

$$= \frac{4.73\ minutes}{1.5\ minutes}$$

$$= 3.15$$

$$\frac{\gamma_{Hydrocarbon}}{\gamma_{Bromine}} = \sqrt{\frac{M_{Bromine}}{M_{hydrocarbon}}}$$

$$3.15 = \sqrt{\frac{159.8\ gmol^{-1}}{M_{hydro\ carbon}}}$$

Squaring on both sides and rearranging,

$$M_{hydro\ carbon} = \frac{159.8\ g\ mol^{-1}}{(3.15)^2}$$

$$M_{hydro\ carbon} = 16.1\ g\ mol^{-1}$$

$n(12) + (2n+2)\,1 = 16$ $\qquad$ [∵ general formula for hydrocarbon C_nH_{2n+2} (alkane)]

$12n + 2n + 2 = 16$

$14n = 16 - 2$

$14n = 14$

$n = 1$

Ψ The hydro carbon is $C_1H_{2(1)+2} = CH_4$

8) Critical temperature of a gas is defined as the temperature above which it cannot be liquified even at high pressures.

Ψ When cooling starts from 700 K, H_2O will liquify first, then followed by ammonia and finally carbondioxide will liquify.

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EVALUATION

I Choose the correct answer:

1. (d) at high pressure the intermolecular interactions become significant
2. (d) inversely proportional to the square root of its molecular weight
3. (c) $\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$
4. (b) exert no attractive forces on each other
5. (a) 1/3
6. (b) Boyle temperature
7. (c) diffusion
8. (b) near the hydrogen chloride bottle
9. (d) units of pressure and volume
10. (c) 8.3 J mol^{-1} K^{-1}
11. (a) Boyle's Law
12. (c) NH_3
13. (d) I, II and III
14. (c) 0.41 dm^3
15. (c) P
16. (b) 4
17. (c) 1/8
18. (b) 1/T
19. (a) P
20. (b) NH_3
21. (c) mol^{-1} L and L^2 atm mol^{-2}
22. (d) both assertion and reasons are false
23. (c) 3.41 g L^{-1}
24. (c)
25. (d) HI

Keys to multiple choice questions:

5. mass of methane

= mass of oxygen = a

number of moles of methane = $\frac{a}{16}$

number of moles of Oxygen = $\frac{a}{32}$

mole fraction of Oxygen = $\frac{\frac{a}{32}}{\frac{a}{16}+\frac{a}{32}}$

$=\frac{\frac{a}{32}}{\frac{3a}{32}}$

$=\frac{1}{3}$

Partial pressure of oxygen

= mole fraction × Total Pressure

$=\frac{1}{3}P$

6. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called Boyle temperature

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8. Rate of diffusion α $1/\sqrt{M}$

$M_{NH_3} = 17$; $M_{HCl} = 36.5$

$\gamma_{NH_3} > \gamma_{HCl}$

Hence white fumes first formed near hydrogen chloride

12. Higher the value of 'a', greater the intermolecular force of attraction, easier the liquefaction.

option (c) is correct

14.

$$\text{Compressibility factor (z)} = \frac{PV}{nRT}$$

$$V = \frac{z \times nRT}{P}$$

$$= \frac{0.8697 \times 1 \times 8.314 \times 10^{-2}\ \text{bar dm}^3\ \text{K}^{-1}\ \text{mol}^{-1} \times 400\ \text{K}}{71\ \text{bar}}$$

$$V = 0.41\ \text{dm}^3$$

Option (c)

15. T_1 $\quad T_2 = 2T_1$

V_1 $\quad V_2 = 2V_1$

P_1 $\quad P_2 = ?$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$P_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{V_2} = \frac{P_1V_1}{T_1} \times \frac{2T_1}{2V_1}$$

$$P_2 = P_1$$

Option (c)

16.

$$\frac{\gamma_{H_2}}{\gamma_{C_nH_{2n+2}}} = \sqrt{\frac{M_{C_nH_{2n+2}}}{M_{H_2}}}$$

$$3\sqrt{3} = \sqrt{\frac{M_{C_nH_{2n+2}}}{2}}$$

Squaring on both sides and rearranging

$27 \times 2 = M_{C_nH_{2n-2}}$

$54 = n(12) + (2n-2)(1)$

$54 = 12n + 2n - 2$

$54 = 14n - 2$

$n = (54+2)/14 = 56/14 = 4$

Option (b)

17.

$$\frac{\gamma_{O_2}}{\gamma_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}} = \sqrt{\frac{2}{32}} = \frac{1}{4}$$

$$\gamma_{O_2} = \frac{1}{4}\gamma_{H_2}$$

The fraction of oxygen that escapes in the time required for one half of the hydrogen to escape is 1/8

Option (c)

18.

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \text{[For an ideal gas } PV = nRT\text{]}$$

$$= \frac{1}{V}\left(\frac{\partial\left(\frac{nRT}{P}\right)}{\partial T}\right)_P$$

$$= \frac{nR}{PV}\left(\frac{\partial T}{\partial T}\right) = \frac{nR}{nRT} = \frac{1}{T}$$

Option (b)

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19. Greater the 'a' value, easier the liquefaction

21. $an^2/V^2 = atm$

$a = atm\ L^2/mol^2 = L^2\ mol^{-2}\ atm$

$nb = L$

$b = L/mol = L\ mol^{-1}$

Option (c)

22. **Correct Statement:** Critical temperature of CO_2 is 304 K. It means that CO_2 cannot be liquefied above 304 K, whatever the pressure may applied.

Pressure is inversely proportional to volume

Option (d)

23.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$= \frac{m}{\left(\frac{nRT}{P}\right)} = \left(\frac{m}{n}\right)\frac{P}{RT}$$

$$= \text{Molar mass} \times \frac{P}{RT}$$

$$= \frac{28\ g\ mol^{-1} \times 5\ atm}{0.082\ L\ atm\ K^{-1}\ mol^{-1} \times 500\ K}$$

$$= 3.41 g\ L^{-1}$$

Option (c)

24. For a fixed mass of an ideal gas V α T

P α 1/V

and PV = Constant

Option (c)

25. At a given temperature and pressure

Volume α no. of moles

Volume α Mass / Molar mass

Volume α 28 / Molar mass

i.e. if molar mass is more, volume is less. Hence HI has the least volume

Option (d)

II Key to short answer questions:

44. $T_1 = 15^0\ C + 273$ $T_2 = 38 + 273$

$T_1 = 288\ K$ $T_2 = 311\ K$

$V_1 = 2.58\ dm^3$ $V_2 = ?$

(P = 1 atom constant)

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \left(\frac{V_1}{T_1}\right) \times T_2$$

$$= \frac{2.58\ dm^3}{288\ \cancel{K}} \times 311\ \cancel{K}$$

$V_2 = 2.78\ dm^3$ i.e. volume increased from $2.58\ dm^3$ to $2.78\ dm^3$

45. $V_1 = 8.5\ dm^3$ $V_2 = 6.37\ dm^3$

$T_1 = ?$ $T_2 = 0^0\ C = 273\ K$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 \times \left(\frac{T_2}{V_2}\right) = T_1$$

$$T_1 = 8.5\ \cancel{dm^3} \times \frac{273\ K}{6.37\ \cancel{dm^3}}$$

$$T_1 = 364.28 K$$

46. $n_A = 1.5\ mol$ $n_B = ?$

$V_A = 37.6\ dm^3$ $V_B = 16.5\ dm^3$

(T = 298 K constant)

$$\frac{V_A}{n_A} = \frac{V_B}{n_B}$$

$$n_A = \left(\frac{n_A}{V_A}\right) V_B$$

$$= \frac{1.5\ \text{mol}}{37.6\ \cancel{dm^3}} \times 16.5\ \cancel{dm^3}$$

$$= 0.66\ \text{mol}$$

47. n = 1.82 mole

V = 5.43 dm^3

T = 69.5 + 273 = 342.5

P = ?

PV = nRT

$$P = \frac{nRT}{V}$$

$$P = \frac{1.82\ \text{mol} \times 0.0821\ \cancel{dm^3}\ \text{atm mol}^{-1}\ K^{-1} \times 342.5\ K}{5.43\ \cancel{dm^3}}$$

$$P = 9.425\ \text{atm}$$

48.

P_1 = 1.2 atm

T_1 = 18^0 C + 273 = 291 K

T_2 = 85^0 C + 273 = 358 K

P_2 = ?

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_2 = \left(\frac{P_1}{T_1}\right) \times T_2$$

$$= \frac{1.2\ \text{atm}}{291\ \cancel{K}} \times 358\ \cancel{K}$$

$$P_2 = 1.48\ \text{atm}$$

49. T_1 = 6 ^{0}C + 273 = 279 K

P_1 = 4 atm V_1 = 1.5 ml

T_2 = 25^0 C + 273 = 298 K

P_2 = 1 atm V_2 = ?

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{4\ \cancel{atm} \times 1.5\ \text{ml} \times 298\ \cancel{K}}{279\ \cancel{K} \times 1\ \cancel{atm}}$$

V_2 = 6.41 ml

50. Given,

V = 154.4 x 10^{-3} dm^3,

P = 742 mm of Hg

T = 298 K m = ?

$$n = \frac{PV}{RT} = \frac{742\ \text{mm Hg} \times 154.4 \times 10^{-3}\ L}{62\ \text{mm Hg L K}^{-1}\text{mol}^{-1} \times 298\ K}$$

$$= 0.006\ \text{mol}$$

$$n = \frac{\text{Mass}}{\text{Molar mass}}$$

$$\text{Mass} = n \times \text{Molar mass}$$

$$= 0.006 \times 2.016$$

$$= 0.0121\ g = 12.1\ mg$$

51.

$$\frac{\gamma_{unknown}}{\gamma_{N_2}} = \frac{t_{N_2}}{t_{unknown}} = \sqrt{\frac{M_{N_2}}{M_{unknown}}}$$

$$\frac{84\ sec}{192\ sec} = \sqrt{\frac{28\ g\ mol^{-1}}{M_{unknown}}}$$

On squaring both sides and rearranging

$$\left(\frac{84\ sec}{192\ sec}\right)^2 = \frac{28\ g\ mol^{-1}}{M_{unknown}}$$

$$M_{unknown} = 28\ g\ mol^{-1} \times \left(\frac{192\ sec}{84\ sec}\right)^2$$

$$M_{unknown} = 146.28\ g\ mol^{-1}$$

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52. $m_{O_2} = 52.5$ g $\quad P_{O_2} = ?$

$m_{CO_2} = 65.1$ g $\quad P_{CO_2} = ?$

T = 300 K $\quad$ P = 9.21 atm

$P_{O_2} = X_{O_2}$ x Total Pressure

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{CO_2}}$$

$$n_{O_2} = \frac{\text{Mass of } O_2}{\text{Molar mass of } O_2}$$

$$= \frac{52.5\text{ g}}{32\text{ g mol}^{-1}} = 1.64\text{ mol}$$

$$n_{CO_2} = \frac{\text{Mass of } CO_2}{\text{Molar mass of } CO_2}$$

$$= \frac{65.1\text{ g}}{44\text{ g mol}^{-1}} = 1.48\text{ mol}$$

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{CO_2}} = \frac{1.64}{3.12} = 0.53$$

$$X_{CO_2} = \frac{n_{CO_2}}{n_{O_2} + n_{CO_2}} = \frac{1.48}{3.12} = 0.47$$

$$P_{O_2} = X_{O_2} \times \text{Total pressure}$$

$$= 0.53 \times 9.21\text{ atm} = 4.88\text{ atm}$$

$$P_{CO_2} = X_{CO_2} \times \text{Total pressure}$$

$$= 0.47 \times 9.21\text{ atm} = 4.33\text{ atm}$$

53. Pressure of the gas in the tank at its melting point

$T_1 = 298$ K; $P_1 = 2.98$ atom; $T_2 = 1100$ K; $P_2 = ?$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\Rightarrow \quad P_2 = \frac{P_1}{T_1} \times T_2$$

$$= \frac{2.98\text{ atm}}{298\text{ K}} \times 1100\text{ K} = 11\text{ atm}$$

At 1100 K the pressure of the gas inside the tank will become 11 atm. Given that tank can withstand a maximum pressure of 12 atm, the tank will start melting first.

Unit - 7 Thermodynamics

Evaluation Yourself

1.

Solution :

Given

$\Delta H_f^0\ CO_2 = -393.5\ kJ\ mol^{-1}$

$\Delta H_f^0\ CO = -111.31\ kJ\ mol^{-1}$

$\Delta H_f^0\ (H_2O) = -242\ kJ\ mol^{-1}$

$CO_2(g) + H_2(g) \leftarrow CO(g) + H_2O(g)$

$\Delta H_r^0 = ?$

$\Delta H_r^0 = \Sigma\ (\Delta H_f^0\ )_{products}$

$\quad - \ \Sigma\ (\Delta H_f^0)_{reactants}$

$\Delta H_r^0 = [\Delta H_f^0\ (CO) + \Delta H_f^0\ (H_2O)]$

$\quad - [\Delta H_f^0\ (CO_2\ ) + \Delta H_f^0\ (H_2)]$

$\Delta H_r^0 = [-\ 111.31 + (-\ 242)]$

$\quad - [-\ 393.5 + (0)]$

$\Delta H_r^0 = [-\ 353.31] + 393.5$

$\Delta H_r^0 = 40.19$

$\Delta H_r^0 = +\ 40.19\ kJ\ mol^{-1}$

2.

Solution :

Given :

number of moles of water n

$= \frac{180\ g}{18\ g\ mol^{-1}} = 10\ mol$

molar heat capacity of water

$C_P = \quad 75.3\ J\ K^{-1}\ mol^{-1}$

$T_2 = \quad 100^0\ C = 373\ K$

$T_1 = \quad 25^0\ C = 298\ K$

AH = ?

AH = $nC_P\ (T_2 - T_1)$

AH = $10\ mol \times 75.3\ J\ mol^{-1}\ K^{-1}$

$\times\ (373 - 298)\ K$

AH = 56475 J

AH = 56.475 kJ

3.

$$C_6H_6\ (l) + \frac{7}{2}\,O_2(g) \rightarrow 6\,CO_2\ (g) + 3\,H_2O\ (l)$$

AU at 25^0 C = –3268.12 kJ

Solution :

Given

$T = 25^0\ C = 298\ K$;

AU = $-3268.12\ kJ\ mol^{-1}$

AH = ?

AH = AU + An_gRT

AH = AU + $(n_p - n_r)$ RT

$$\Delta H = -3268.12\ + \left(6 - \frac{15}{2}\right) \times 8.314 \times 10^{-3}\ x\ 298$$

AH = -3268.12

$\quad - (1.5 \times 8.314 \times 10^{-3} \times 298)$

AH = $-\ 3268.12 - 3.72$

AH = $-\ 3271.84\ kJ\ mol^{-1}$

4.

Solution :

Given :

$Mg(S) + Br_2(1) \leftarrow$

$MgBr_2(S)\ AH_f^0 = -524\ KJ\ mol^{-1}$

Sublimation :

$Mg(S) \leftarrow Mg(g)$

$AH_1^0 = +148\ KJ\ mol^{-1}$

Ionisation :

$Mg(g) \leftarrow Mg^{2+}(g) + 2e^-$

$AH_2^0 = 2188\ KJ\ mol^{-1}$

Vapourisation :

$Br_2(1) \leftarrow Br_2(g)$

$AH_3^0 = +31\ KJ\ mol^{-1}$

Dissociation :

$Br_2(g) \leftarrow 2Br(g)$

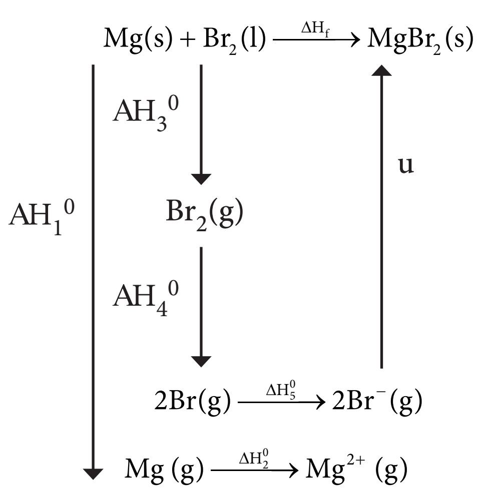
$AH_4^0 = +193\ KJ\ mol^{-1}$

Electron affinity :

$Br(g) + e^- \leftarrow Br^-(g)$

$AH_5^0 = -324.5\ KJ\ mol^{-1}$

Solution :



$AH_f = AH_1 + AH_2 + AH_3 + AH_4 + 2AH_5 + u$

$-524 = 148 + 2188 + 31 + 193 + (2 \times -324.5) + u$

$-524 = 1911 + u$

$u = -524 - 1911$

$u = -2435\ kJ\ mol^{-1}$

5.

Solution:

Given

$T_h = 127^0\ C = 127 + 273 = 400\ K$

$T_C = 47^0\ C = 47 + 273 = 320\ K$

% efficiency ε = ?

$$\eta = \left[\frac{T_h - T_C}{T_h}\right] \times 100$$

$$\eta = \left[\frac{400 - 320}{400}\right] \times 100$$

$$\eta = \left[\frac{80}{400}\right] \times 100$$

$\eta = 20\%$

6.

Solution:

Given:

$S^0\ (urea) = 173.8\ J\ mol^{-1}\ K^{-1}$

$S^0\ (H_2O) = 70\ J\ mol^{-1}\ K^{-1}$

$S^0\ (CO_2) = 213.5\ J\ mol^{-1}\ K^{-1}$

$S^0\ (NH_3) = 192.5\ J\ mol^{-1}\ K^{-1}$

$NH_2 - CO - NH_2 + H_2O \leftarrow 2NH_3 + CO_2$

$AS_r^0 = \Sigma (S^0)_{products} - \Sigma (S^0)_{reactants}$

$AS_r^0 = [2\ S^0\ (NH_3) + S^0\ (CO_2)]$

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$- [S^0 \text{ (urea)} + S^0 (H_2O)]$

$AS_r^0 = [2 \times 192.5 + 213.5]$

$- [173.8 + 70]$

$AS_r^0 = [598.5] - [243.8]$

$AS_r^0 = 354.7 \text{ J mol}^{-1} \text{ K}^{-1}$

7.

Solution:

Given:

$T_b = 351 \text{ K}$

$AH_{vap} = 39840 \text{ J mol}^{-1}$

$AS_v = ?$

$$\Delta S_v = \frac{\Delta H_{vap}}{T_b}$$

$$\Delta S_v = \frac{39840}{351}$$

$$\Delta S_v = 113.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

8.

Solution:

Given:

$AH = -10 \text{ kJ mol}^{-1} = -10000 \text{ J mol}^{-1}$

$AS = -20 \text{ J K}^{-1} \text{ mol}^{-1}$

$T = 300 \text{ K}$

$AG = ?$

$AG = AH - TAS$

$AG = -10 \text{ kJ mol}^{-1} - 300 \text{ K} \times (-20\text{x}10^{-3}) \text{ kJ K}^{-1} \text{ mol}^{-1}$

$AG = (-10+6) \text{ kJ mol}^{-1}$

$AG = -4 \text{ kJ mol}^{-1}$

At 600 K

$AG = -10 \text{ kJ mol}^{-1} - 600 \text{ K} \times (-20\text{x}10^{-3}) \text{ kJ K}^{-1} \text{ mol}^{-1}$

$AG = (-10 + 12) \text{ kJ mol}^{-1}$

$AG = +2 \text{ kJ mol}^{-1}$

The value of ΔG is negative at 300K and the reaction is spontaneous, but at 600K the value ΔG becomes positive and the reaction is non spontaneous.

EVALUATION

I Choose the best answer:

1. (b) AH
2. (d) decrease in free energy
3. (b) $q = 0$
4. (d) $= 0$
5. (a) $w = -AU$
6. (d) $\frac{\text{mass}}{\text{volume}}$
7. (a) – 900 J
8. (b) negative
9. (b) – 67.6 kcal
10. (a) graphite is more stable than diamond
11. (d) – 462 kJ
12. (d) frictional energy
13. (d) AH < AU
14. (c) + 3 kJ
15. (a) – 2.48 kJ
16. (b) – 500 R
17. (d) $\frac{b-2a}{2}$

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18. (d) – 635.66 kJ

19. (c) 80 kJ mol^{-1}

20. (a) AH < 0 and AS > 0

21. (c) adiabatic expansion

22. (d) (–, –, +)

23. (b) 27 ^{0}C

24. (d) $CaCO_3(S) \leftarrow CaO(S) + CO_2(g)$

25. (a) 300K

Keys to multiple choice questions:

7.

w = – P A V

w = – (1 × 10^5 Nm^{-2})

(1 × 10^{-2} m^3 – 1 × 10^{-3} m^3)

w = –10^5 (10^{-2} – 10^{-3}) Nm

w = – 10^5 (10 – 1) 10^{-3}) J

w = – 10^5 (9 × 10^{-3}) J

w = –9 × 10^2 J

w = –900 J

9.

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

AH_C^0 (CO) = AH_f (CO_2) – AH_f(CO) + AH_f (O_2)]

AH_C^0 (CO) = – 94 KCal – [– 26.4 KCal + 0]

AH_C^0 (CO) = – 94 KCal + 26.4 KCal

AH_C^0 (CO) = – 67.6 KCal

11.

$2Al + Cr_2O_3 \leftarrow 2Cr + Al_2O_3$

AH_r^0 = [2AH_f (Cr) + AH_f (Al_2O_3)]

– [2AH_f (Al) + AH_f (Cr_2O_3)]

AH_r^0 = [0 + (– 1596 kJ)]

– [0 + (– 1134)]

AH_r^0 = – 1596 kJ + 1134 kJ

AH_r^0 = – 462 kJ

14.

AU = q + w

AU = – 1 kJ + 4 kJ

AU = + 3kJ

15.

$Fe + 2HCl \leftarrow FeCl_2 + H_2$

1 mole of Iron liberates 1 mole of Hydrogen gas

55.85 g Iron = 1 mole Iron

Ψ n = 1

T = 25^0 C = 298 K

w = – P A□V

$$w = -P\left(\frac{nRT}{P}\right)$$

w = – nRT

w = –1 × 8.314 × 298 J

w = – 2477.57 J

w = – 2.48 kJ

16.

T_i = 125^0 C = 398 K

T_f = 25^0 C = 298 K

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$AH = nC_p (T_f - T_i)$

$$\Delta H = 2 \times \frac{5}{2} R (298 - 398)$$

$AH = - 500 R$

17.

$C + O_2 \leftarrow CO_2$ $AH^0 = - a KJ$ .... (i)

$2CO + O_2 2CO_2$ $AH^0 = -b kJ$ .... (ii)

$$C + \frac{1}{2} O_2 \rightarrow CO \ \Delta H^0 = ?$$

(i) × 2

$2C + 2O_2 \leftarrow 2CO_2$ $AH^0 = - 2a kJ$ .... (iii)

Reverse of equation (ii) will be

$2CO_2 \leftarrow 2CO + O_2$ $AH^0 = + b kJ$ .... (iv)

(iii) + (iv)

$2C + O_2 \leftarrow 2CO \ AH^0 = b - 2a kJ$ .... (v)

(v) ∂2

$$C + \frac{1}{2} O_2 \rightarrow CO \quad \Delta H^0 = \frac{(b - 2a)}{2} kJ$$

18.

Given :

$AH_C (CH_4)$ $= - 890 \text{ kJ mol}^{-1}$

$AH_C (C_3H_8)$ $= - 2220 \text{ kJ mol}^{-1}$

Let the mixture contain lit of and lit of propane.

$CH_4 + 2O_2 \leftarrow CO_2 + 2H_2O$

x 2x

$C_3H_8 + 5O_2 \leftarrow 3CO_2 + 4H_2O$

(15.68 – x) 5 (15.68 – x)

Volume of oxygen consumed = 2x + 5 (15.68 – x) = 32 lit

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$2x + 78.4 - 5x = 32\ l$

$78.4 - 3x = 32$

$3x = 46.4\ l$

$x = 15.47\ l$

Given mixture contains 15.47 lit of methane and 0.213 lit of propane, hence

$$\Delta H_C = \left[\left(\frac{\Delta H_C\ (CH_4)}{22.4\ lit}\right) x\ lit\right] + \left[\left(\frac{\Delta H_C\ (C_3H_8)}{22.4\ lit}\right)(15.68 - x)\ lit\right]$$

$$\Delta H_C = \left[\left(\frac{-890\ kJ\ mol^{-1}}{22.4\ lit}\right) 15.47\ \ lit\right] + \left[\left(\frac{-2220}{22.4\ lit}\right) 0.21\ \ lit\right]$$

$$\Delta H_C = \left[-611.87\ \ kJ\ mol^{-1}\right] + \left[-20.81\ \ kJ\ mol^{-1}\right]$$

$$\Delta H_C = -632.68\ KJ\ mol^{-1}$$

19.

$4E_{C-H} = 360\ kJ\ mol^{-1}$

$E_{C-H} = 90\ kJ\ mol^{-1}$

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

$E_{C-C} + 6 \times 90 = 620\ kJ\ mol^{-1}$

$E_{C-C} + 540 = 620\ kJ\ mol^{-1}$

$E_{C-C} = 80\ kJ\ mol^{-1}$

22. During compression, energy of the system increases, in isothermal condition, to maintain temperature constant, heat is liberated from the system. Hence q is negative.

During compression entropy decreases.

During compression work is done on the system, hence w is positive

23.

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$T_b = \frac{\Delta H_V}{\Delta S_V} = \frac{4800\ J\ mol^{-1}}{16\ J\ mol^{-1}\ K^{-1}} = 300\ K = 27^0 C$$

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24. In $CaCO_3(S) \leftarrow CaO(S) + CO_2(g)$, entropy change is positive. **in option d, A solid reactant gives a gaseous product. Hence the entropy change is expected to be maximum for this process.**

25.

AG = AH – T A□$

At 300K

AG = 30000 J mol^{-1} – 300 K

× 100 J K^{-1} mol^{-1}

AG = 0

above 300 K ; ΔG will be negative and reaction becomes spontaneous.

I Keys to the short answer questions:

53.

SOLUTION :

Given :

n = 2 moles

V_i = 500 ml = 0.5 lit

V_f = 2 lit

T = 25^0C = 298 K

$w = -2.303\ nRT\log\left(\frac{V_f}{V_i}\right)$

$w = -2.303 \times 2 \times 8.314 \times 298$

$\times \log\left(\frac{2}{0.5}\right)$

$w = -2.303 \times 2 \times 8.314$

$\times 298 \times \log(4)$

$w = -2.303 \times 2 \times 8.314$

$\times 298 \times 0.6021$

w = −6871 J

w = −6.871 kJ

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54.

SOLUTION :

Given :

$T_i = 298$ K

$T_f = 298.45$ K

$k = 2.5$ kJ K^{-1}

m = 3.5g

$M_m = 28$

heat evolved = k ΔT

$= k(T_f - T_i)$

$= 2.5$ kJ K^{-1} (298.45–298)K

= 1.125kJ

$\Delta H_c = \frac{1.125}{3.5} \times 28$ kJ mol^{-1}

$\Delta H_c = 9$ kJ mol^{-1}

55.

SOLUTION :

Given :

$T_{sys} = 77^0C = (77 + 273) = 350$ K

$T_{surr} = 33^0$ C = (33 + 273) = 306 K

q = 245 J

$\Delta S_{sys} = \frac{q}{T_{sys}} = \frac{-245}{350} = -0.7$ JK^{-1}

$\Delta S_{surr} = \frac{q}{T_{sys}} = \frac{+245}{306} = +0.8$ JK^{-1}

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

$\Delta S_{univ} = -0.7$ JK^{-1} + 0.8 JK^{-1}

$\Delta S_{univ} = 0.1$ JK^{-1}

56.

SOLUTION :

Given :

n = 1mole

P = 4.1 atm

V=2 Lit

T = ?

q=3710 J

$\Delta S = \frac{q}{T}$

$\Delta S = \frac{q}{\left(\frac{PV}{nR}\right)}$

$\Delta S = \frac{nRq}{PV}$

$$\Delta S = \frac{1 \times 0.082 \text{ lit atm } K^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}}$$

$$\Delta S = \frac{1 \times 0.082 \text{ lit atm } K^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}}$$

$\Delta S = 37.10$ JK^{-1}

57.

SOLUTION:

Given :

ΔH_f(NaCl) = 30.4 kJ = 30400 J mol^{-1}

ΔS_f(NaCl) = 28.4 JK^{-1} mol^{-1}

$T_f = ?$

$\Delta S_f = \frac{\Delta H_f}{T_f}$

$T_f = \frac{\Delta H_f}{\Delta S_f}$

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$$T_f = \frac{30400\ J\ mol^{-1}}{28.4\ J\ K^{-1}\ mol^{-1}}$$

$T_f = 1070.4\ K$

58.

SOLUTION :

Given

$C_3H_8 + 5O_2 \leftarrow 3CO_2 + 4H_2O$

$\Delta H^0_C = -2220.2\ kJ\ mol^{-1}$ ------(1)

$C + O_2 \leftarrow CO_2$

$\Delta H^0_f = -393.5\ kJ\ mol^{-1}$ ------(2)

$H_2 + \frac{1}{2} O_2 \leftarrow H_2O$

$\Delta H^0_f = -285.8\ kJ\ mol^{-1}$ ------ (3)

$3C + 4H_2 \leftarrow C_3H_8$

$\Delta H^0_C = ?$

$(2) \times 3 \Rightarrow 3C + 3O_2 \leftarrow 3CO_2$

$\Delta H^0_f = -1180.5\ kJ$ ------(4)

$(3) \times 4 \Rightarrow 4\ H_2 + 2O_2 \leftarrow 4H_2O$

$\Delta H^0_f = -1143.2\ kJ$ ------(5)

$(4) + (5) - (1) \Rightarrow 3C + 3O_2 + 4H_2 + 2O_2 + 3CO_2 + 4H_2O \leftarrow 3CO_2 + 4H_2O + C_3H_8 + 5O_2$

$\Delta H^0_f = -1180.5 - 1143.2$

$- (-2220.2)\ kJ$

$3C + 4\ H_2 \leftarrow C_3H_8$

$\Delta H^0_f = -103.5\ kJ$

Standard heat of formation of propane is $\Delta H^0_f (C_3H_8) = -103.5\ kJ$

59.

S. No	Liquid	Boiling points (^{0}C)	ΔH (kJ mol^{-1})
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

SOLUTION :

For ethanol :

Given :

$T_b = 78.4^0\ C = (78.4 + 273)$

$= 351.4\ K$

$\Delta H_V(\text{ethanol}) = +\ 42.4\ kJ\ mol^{-1}$

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{+\ 42.4\ kJ\ mol^{-1}}{351.4\ K}$$

$$\Delta S_V = \frac{+\ 42400\ J\ mol^{-1}}{351.4\ K}$$

$\Delta S_V = +120.66\ J\ K^{-1}\ mol^{-1}$

For Toluene :

Given :

$T_b = 110.6^0\ C = (110.6+273)$

$= 383.6\ K$

$\Delta H_V\ (\text{toluene}) = +\ 35.2\ kJ\ mol^{-1}$

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{+\ 35.2\ kJ\ mol^{-1}}{383.6\ K}$$

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$$\Delta S_V = \frac{+35200 \text{ J mol}^{-1}}{383.6 \text{ K}}$$

ΔS_V = + 91.76 J K^{-1} mol^{-1}

60.

Solution :

Given :

ΔH = 30.56 kJ mol^{-1}

= 30560 J mol^{-1}

ΔS = 6.66 × 10^{-3} $kJK^{-1}mol^{-1}$

T = ? at which ΔG=0

$\Delta G = \Delta H - T\Delta S$

$0 = \Delta H - T\Delta S$

$$T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{30.56 \text{kJmol}^{-1}}{6.66 \times 10^{-3} \text{kJK}^{-1} \text{mol}^{-1}}$$

T = 4589 K

(i) At 4589K ; ΔG = 0 the reaction is in equilibrium.

(ii) at temperature below 4598 K , $\Delta H > T \Delta S$

$\Delta G = \Delta H - T \Delta S > 0$, the reaction in the forward direction, is non spontaneous. In other words the reaction occurs in the backward direction.

61.

Solution :

Given

T = 400K ; ΔH^0 = 77.2 kJ mol^{-1}=77200 J mol^{-1} ; ΔS^0 = 122 JK^{-1} mol^{-1}

$\Delta G^0 = -2.303 \text{ RT} \log K_{eq}$

$$\log K_{eq} = \frac{-\Delta G^0}{2.303 \text{ RT}}$$

$$\log K_{eq} = -\frac{(\Delta H^0 - T\Delta S^0)}{2.303 \text{ RT}}$$

$$\log K_{eq} = -\left(\frac{77200 - 400 \times 122}{2.303 \times 8.314 \times 400}\right)$$

$$\log K_{eq} = -\left(\frac{28400}{7659}\right)$$

$\log K_{eq}$ = – 3.7080

K_{eq} = antilog (–3.7080)

K_{eq}= 1.95 × 10^{-4}

62.

Solution :

Given

T = 298K ; ΔU = – 742.4 kJ mol^{-1}

ΔH = ?

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

$\Delta H = \Delta U + (n_p - n_r) RT$

$$\Delta H = -742.4 + \left(2 - \frac{3}{2}\right) \times 8.314 \times 10^{-3} \times 298$$

= – 742.4 + (0.5 × 8.314 × 10^{-3} × 298)

= – 742.4 + 1.24

= – 741.16 kJ mol^{-1}

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63.

Solution :

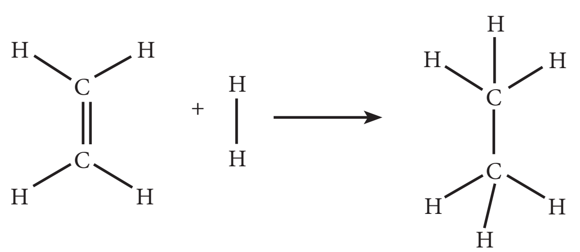
Given :

$E_{C-H} = 414 \text{ kJ mol}^{-1}$

$E_{C-C} = 347 \text{ kJ mol}^{-1}$

$E_{C=C} = 618 \text{ kJ mol}^{-1}$

$E_{H-H} = 435 \text{ kJ mol}^{-1}$



Ethylene Ethane

$\Delta H_r = \Sigma \text{ (Bond energy)}_r - \Sigma \text{ (Bond energy)}_p$

$\Delta H_r = (E_{C=C} + 4E_{C-H} + E_{H-H}) - (E_{C-C} + 6E_{C-H})$

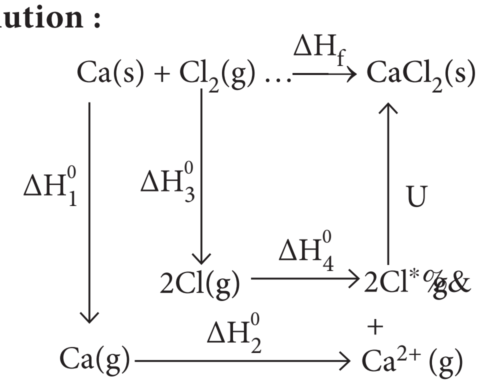
$\Delta H_r = (618 + (4 \times 414) + 435) - (347 + (6 \times 414))$

$\Delta H_r = 2709 - 2831$

$\Delta H_r = -122 \text{ kJ mol}^{-1}$

64.

Solution :



$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + 2\,\Delta H_4 + u$

$-795 = 121 + 2422 + 242.8 + (2 \times -355) + u$

$-795 = 2785.8 - 710 + u$

$-795 = 2075.8 + u$

$u = -795 - 2075.8$

$u = -2870.8 \text{ kJ mol}^{-1}$

65.

Solution :

Given :

$\Delta H_f (Fe_2O_3) = -741 \text{ kJ mol}^{-1}$

$\Delta H_f (CO) = -137 \text{ kJ mol}^{-1}$

$\Delta H_f (CO_2) = -394.5 \text{ kJ mol}^{-1}$

$Fe_2O_3 + 3CO \leftarrow 2Fe + 3CO_2$

$\Delta Hr = ?$

$\Delta Hr = \Sigma(\Delta H_f)_{products} - \Sigma (\Delta H_f)_{reactants}$

$\Delta Hr = [2\,\Delta H_f (Fe) + 3\Delta H_f (CO_2)] - [\Delta H_f (Fe_2O_3) + 3\Delta H_f (CO)]$

$\Delta Hr = [0 + 3(-394.5)] - [-741 + 3(-137)]$

$\Delta Hr = [-1183.5] - [-1152]$

$\Delta Hr = -1183.5 + 1152$

$\Delta Hr = -31.5 \text{ kJ mol}^{-1}$

66.

Solution:

Given :

$T = 175^0 C = 175 + 273 = 448K$

Concentration of 1-pentyne

$[A] = 1.3\%$

Concentration of 2-pentyne
$[B] = 95.2\%$

Concentration of 1, 2-pentadiene
$[C] = 3.5\%$

At equilibrium

$B \rightleftharpoons A$

95.2% 1.3% $\Leftarrow$

$$K_1 = \frac{1.3}{95.2} = 0.0136$$

$B \rightleftharpoons C$

95.2% 3.5% $\Leftarrow$

$$K_2 = \frac{3.5}{95.2} = 0.0367$$

$\Leftarrow \Delta G_1^0 = -2.303\ RTlogK_1$

$\Delta G_1^0 = -2.303 \times 8.314 \times 448 \times \log 0.0136$

$\Delta G_1^0 = +16010\ J$

$\Delta G_1^0 = +16\ kJ$

$\Leftarrow \Delta G_2^0 = -2.303\ RT \log K_2$

$\Delta G_2^0 = -2.303 \times 8.314 \times 448 \times \log 0.0367$

$\Delta G_2^0 = +12312\ J$

$\Delta G_2^0 = +12.312\ kJ$

67.

Solution:

Given :

$T = 33K$

$N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial no of moles	100		0
Number of moles dissociated	50		-
No of moles remaining	50		100
Total no of moles	150 moles		
$P_{N_2O_4} = \frac{n_{N_2O_4}}{n_{N_2O_4} + n_{NO_2}} .P$ $P_{N_2O_4} = \frac{50\ mol}{150\ mol} .1\ atm$ $P_{N_2O_4} = 0.333\ atm$ $P_{NO_2} = \frac{n_{NO_2}}{n_{N_2O_4} + n_{NO_2}} .P$ $P_{NO_2} = \frac{100\ mol}{150\ mol} .1\ atm$ $P_{NO_2} = 0.667\ atm$	$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}}$ $K_P = \frac{(0.667)^2\ atm^2}{0.333\ atm}$ $K_P = 1.336\ atm$ $\Delta G^0 = -2.303\ RT \log K_P$ ΔG^0 $= -2.303\ X\ 8.314\ X\ 33\ X\ \log 1.336$ $\Delta G^0 = -79.49\ J\ mol^{-1}$		

68.

Solution :

Given :

$\Delta H_f^0\ (SO_2) = -297\ kJ\ mol^{-1}$

$\Delta H_f^0\ (SO_3) = -396\ kJ\ mol^{-1}$

$SO_2 + \frac{1}{2} O_2 \leftarrow SO_3 \quad \Delta H_r^0 = ?$

$\Delta H_r^0 = (\Delta H_f^0)_{compound} - \Sigma (\Delta H_f)_{elements}$

$$\Delta H_r^0 = \Delta H_f^0 (SO_3) - \left(\Delta H_f^0 (SO_2) + \frac{1}{2} \Delta H_f^0 (O_2) \right)$$

$\Delta H_r^0 = -396\ kJ\ mol^{-1} - (-297\ kJ\ mol^{-1} + 0)$

$\Delta H_r^0 = -396\ kJ\ mol^{-1} + 297$

$\Delta H_r^0 = -99\ kJ\ mol^{-1}$

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69.

Solution:

Given :

T = 298 K

$\Delta H = 400 \text{ KJ mol}^{-1}$

$\Delta S = 0.2 \text{ KJ K}^{-1} \text{ mol}^{-1}$

$\Delta G = \Delta H - T\Delta S$

if T = 2000 K

$\Delta G = 400 - (0.2 \times 2000) = 0$

$\Delta H = 400 \text{ KJ mol}^{-1}$ if T > 2000 K

ΔG will be negative.

The reaction would be spontaneous only beyond 2000K

70.

Solution :

Given :

T = 298K

$\Delta G_r^0 = -13.6 \text{ kJ mol}^{-1}$

$= -13600 \text{ J mol}^{-1}$

$\Delta G^0 = -2.303 \text{ RT} \log K_{eq}$

$$\log K_{eq} = \frac{-\Delta G^0}{2.303 \text{ RT}} \quad \log K_{eq} = \frac{13.6 \text{kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3} \text{JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$$

$\log K_{eq} = 2.38$

$K_{eq} = \text{antilog } (2.38)$

$K_{eq} = 239.88$

71.

Solution :

Given :

$\Delta H_C (CH_4) = -890 \text{ kJ mol}^{-1}$

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$\Delta H_C (C_2H_4) \quad = -1423 \text{ kJ mol}^{-1}$

Let the mixture contain x lit of CH_4 and (3.67 – x) lit of ethylene.

$CH_4 + 2O_2 \leftarrow CO_2 + 2H_2O$

x lit x lit

$C_2H_4 + 3O_2 \leftarrow 2CO_2 + 2H_2O$

(3.67–x)lit 2 (3.67 – x) lit

Volume of Carbondioxide formed = x + 2 (3.67–x) = 6.11 lit

x + 7.34 – 2x = 6.11

7.34 – x = 6.11

x = 1.23 lit

Given mixture contains 1.23 lit of methane and 2.44 lit of ethylene, hence

$$\Delta H_C = \left[\frac{\Delta H_C (CH_4)}{22.4 \text{ lit}} \times (x) \text{ lit}\right]$$

$$+ \left[\frac{\Delta H_C (C_2H_4)}{22.4 \text{ lit}} \times (3.67 - x) \text{ lit}\right]$$

$$\Delta H_C = \left[\frac{-890 \text{ kJ mol}^{-1}}{22.4 \text{ lit}} \times 1.23 \text{ lit}\right]$$

$$+ \left[\frac{-1423}{22.4 \text{ lit}} \times (3.67 - 1.23) \text{ lit}\right]$$

$\Delta H_C = [-48.87 \text{ kJ mol}^{-1}]$

$+ [-155 \text{kJ mol}^{-1}]$

$\Delta H_C = -203.87 \text{ kJ mol}^{-1}$

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