① Answer key for chemistry - Paper-I - FYBSc.
Sem.I - NOV-2018 code No. 00056903

Q.1 A] i] a) open system. (2 m)

ii] a) U + PV

iii] b) $\left(\frac{\partial H}{\partial t}\right)_P$

iv] a) inexact differential.

v] a) diluted solution

vi] b) mole fraction

vii] a) Two

viii] c) l

ix] a) lead.

x] b) Noble

xi] a) 3.70

xii] c) both a & b

B] ~~True or false.~~

xiii] b) 2-Nitrocyclopentanol.

xiv] b) sp^2

xv] b) Nucleophile.

xvi] c) oxo

xvii] a) + I effect.

xviii] c) sp^3

B] state true or false. (03 m)

i] True

ii] False

iii] True

iv] True

v] False

vi] True

Q.1 c]   Match the following

i]   Extensive property   → c] volume

ii]   Physical unit of concentration → e] weight of solute / volume of solution.

iii] k, L, M, N   ⟶ d) Main energy levels.

iv] Mullikens method ⟶ g) Electronegativity

v] $CH_3 \rightarrow \overset{O}{\underset{}{C}}{-}OH$ → b) Inductive effect.

Vi] sp^2-hybridization → a) $120°$

Set- IV

2A	A	Derive Kirchhoff's equation. Give its applications.	05
		Consider a general reaction,	04

Consider a general reaction,

$aA + bB = cC + dD$

The change in enthalpy is given by,

$\Delta H(\text{reaction}) = \Sigma H_{(product)} - \Sigma H_{(Reactants)}$

$= (cH_C + dH_D) - (aH_A + bH_B)$

Where,

H_A and H_B = molar enthalpies of the reactants A and B and

H_C and H_D = molar enthalpies of the products C and D.

Differentiating the above equation with respect to temperature at constant pressure, we get,

$$\left(\frac{\delta(\Delta H)}{\delta T}\right)_P = \left[c\left(\frac{\delta H_c}{\delta T}\right)_p + d\left(\frac{\delta H_D}{\delta T}\right)_p\right] - \left[a\left(\frac{\delta H_A}{\delta T}\right)_P + b\left(\frac{\delta H_B}{\delta T}\right)_p\right]$$

By definition of heat capacity at constant pressure,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$\left(\frac{\delta(\Delta H)}{\delta T}\right)_p = [cC_{PC} + dC_{PD}] - [aC_{PA} + bC_{PB}]$$

$$\left(\frac{\delta(\Delta H)}{\delta T}\right)_P = \Sigma C_{p(product)} - \Sigma C_{p(reactant)} = \Delta C_p$$

$d(\Delta H) = \Delta Cp\ dT$

integrating the above equation,

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta c_p\, dT = \Delta C_P \int_{T_1}^{T_2} dT$$

The heat capacity is taken to be independent of temperature for small range of temperature.

$\Delta H_2 - \Delta H_1 = \Delta Cp\ (T_2 - T_1)$ ....1.

ΔC_p = Difference in heat capacities of product and reactants at constant pressure

This is equation is known as Kirchhoff's equation.

Applications: 01

1) Kirchhoff's equation is used to calculate the heat of reaction at different temperature.

It can also be used to calculate the change in molar heat capacity at constant of Pressure.

	B	Explain the term enthalpy of combustion and give its applications.	05
		Enthalpy of combustion is defined as enthalpy change accompanying the complete combustion of one mole of substance in standard state.	02

e.g. The combustion of ethane under standard conditions to form carbon dioxide and water is,

$$C_2H_{6(g)} + 7/2\ O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O(l),\ \Delta H^\circ_{298} = -1560.1\ kJ$$

Enthalpy of combustion of most of the reaction is negative; this indicates that the reaction is exothermic except for some substances like N_2 and F_2.

Applications:

i) **Calculations of enthalpy of formation:** — 01

It is difficult to determine the enthalpy of formation of organic compound but easy to determine heat of combustion. Hence, heat of combustion is used to calculate the heat of formation in such cases.

ii) **Heat of formation of allotropic forms:** — 01

Allotrope of carbon i.e. diamond and graphite has different values of heat of combustion. By knowing these values, the respective values of heat of formation can be calculated.

iii) **The calorific values of fuels:**

The efficiencies of fuel can be compared by determining their standard heats of combustion. — 01

	C	One mole of an ideal gas at 2 atmospheres and 28 °C is compressed isothermally to one half its volume by an external pressure of 3 atmosphere. Calculate the work done. ($R = 0.082$ atm dm^3 K^{-1}mol^{-1}, 1 atm dm^3 = 101.32 J)	05

Solution : $n = 1$, $P = 2\ atm$, $T = 28 + 273 = 301\ K$.

$$P_{ext.} = 3\ atm.\quad w = ?$$

Work done, $W = -P_{ext}(V_2 - V_1) \cdots\cdots$ ①

$$\therefore V_1 = \frac{nRT}{P} = \frac{1 \times 0.082 \times 301}{2}$$

$$V_1 = 12.341\ dm^3.$$

$$V_2 = \frac{V_1}{2} = \frac{12.341}{2}$$

$$V_2 = 6.1705\ dm^3.$$

$$\therefore\ W = -3 \times (6.1705 - 12.341)$$

$$= -3 \times (-6.1705)$$

$$W = 18.5115\ atm.dm^3$$

$$W = 18.5115 \times 101.32 = 1875.58\ J.$$

(5)

	D	i) Explain Zeroth law of thermodynamics ii) Define the thermodynamic terms system and surrounding.	
		i) **Zeroth law of thermodynamics:** Consider a two closed systems A and B in which temperature of A (T_A) is greater than temperature of B (T_B). When these two systems are brought closer to one another an exchange of energy takes place between A and B until $T_A = T_B$. At this point, the two systems are said to be in thermal equilibrium. The transfer of energy from one system to another due to temperature difference is called heat. Further, if a third system C with temperature Tc is in thermal equilibrium with system A, then Tc = T_A and system C must be in thermal equilibrium with system B also. This idea is summed up by a statement called Zeroth law of thermodynamics.	02

A ———Thermal equilibrium———→ C

B ———Thermal equilibrium———→ C

A ———Thermal equilibrium———→ B

Statement:
Of the three systems A, B, C, if A and B are separately in thermal equilibrium with C, then A and B are also in thermal equilibrium with one another.   01

ii) System:
A part of the universe which is under thermodynamics study is known as system.   01
E.g. water in beaker, gas in a cylinder, etc.

Surrounding:
Everything in the universe which is not the part of system is called surrounding.   01

(6)

Q2 E:

1 Parts per million : It is the number of parts of one component in 1 million parts of a solution.

$$ppm = \frac{wt\ of\ solute}{wt\ of\ solvent\ X\ wt.of\ solute} \times 10^6$$ 1 Mark

ii Parts per billion : It is the number of parts of one component in 10^9 parts of a solution.

$$ppm = \frac{wt\ of\ solute}{wt\ of\ solvent\ X\ wt.of\ solute} \times 10^9$$ 1 Mark

iii Milli moles : It is defined as one thousandth of a mole.

No.of mmol = V (mL) x Molarity   1 Mark

iv Milli Equivalents : It is defined as one thousandth of a equivalent.

$$meq = \frac{mass\ of\ solute\ in\ mg}{Eq.wt\ of\ solvent\ (\frac{mg}{meq})} \times 10^9$$ 1 Mark

v Acidity = It is defined as no.of replaceable hydroxyl groups present in one molecule or ion of base.   1 Mark

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Q2. F.

$$M = \frac{wt.of\ solute\ in\ g\ \times\ 1000}{Mol.wt\ \times\ vol.}$$ 2 Marks

$$Wt\ of\ solute\ in\ g = \frac{0.25\ x\ 40\ x\ 700}{1000}$$ 2 Marks

$$= 7.0\ g$$ 1 Mark

Questions should be —
WRITTEN IN LEGIBLE HANDWRITING IN BLACK INK.
SIGNS, SKETCHES OR FIGURES IF ANY BE DRAWN IN NEAT BLACK INK,
so as to avoid mistakes in the printed question papers.

Duration .... Hours.   Total Marks assigned to the paper ....

Q. No.		Marks
	N.B. :	
Q-3 A)	Discuss the limitations of Bohr's Atomic Model.	
	1) It could not explain the spectral line in hydrogen atom.	01 01
	2) Not explain Fine spectrum.	
	3) Does not explain zeeman effect.	01.
	Does not explain stark effect.	01
	4) It is not correct to regard the electron in atom as discrete particles.	01.

Q. No.		Marks

B) What is penetration of orbital ?
   Discuss the consequences of
   orbital penetration.
The extent to which an orbital of a shell **01.**
interact with the lower quantum shell
orbital is termed as penetration of
orbitals.
eg. the energy of the 4S orbital is
lower than that of the 3d orbitals so that **01½**
filling of the 4s orbital commences
even before the third shell has been
completely filled up. This is referred
to as penetration of the 3d orbital by
the 4S orbitals. **01.**
   $s > p > d > f$. shell numbers n'es.
   5S orbital penetrates both 4f and
   4d orbitals. intensity of maxima **01½**
in orbital at a radial distance of
low orbital is in the order as given above
order of shielding of any orbital is
   $s > p > d > f$

8

Q. No.		Marks
c)	Describe hydrogenic energy levels. Each wave function obtained by Schrodinger equation for hydrogen atom is labelled by set of three integer n, l, m.	01.

Each quantum number specifies a physical properties of electron n: specifies energy.

Angular momentum l specifies Magnitude of orbital orientation A angular momentum.

The value of l indicates shape   01.
m indicates orientation of lobes.

$$E_n = -hcRZ^2/n^2 \quad n = 1, 2, 3.$$

$$R = 1.097 \times 10^7 \, m^{-1}$$

The zero of energy (at $n = \infty$) corresponds to the electron and   02 nucleus being widely separated and stationary. Positive values of the energy correspond to unbound state of electron in which it travel with velocity hence posses energy.
If negative shows electron in the   01 bound state lower than widely separated
$\therefore$ the energy proportional to $1/n^2$ the energy levels converges as the energy neg the value of l specifies the magnitude A the orbital angular momentum through $\{l(l+1)\}^{1/2} \hbar$. $l = 0, 1, 2 \ldots$ rate at which electron circulate around the nucleus m_l specifies orientation, clockwise or anticlockwise.

(10)

Page No............

Q. No.		Marks

23 D) periodic trends in electron gain enthalpy —

__In periods__ :— EG enthalpy increases from left **1M**
to right in a period. For halogens ns^2, np^5 **1M**
has -ve electron gain enthalpy. Halogen form
stable anion with $ns^2 np^6$ by gaining e^-. **½**

__In groups__ :— Electron gain enthalpy decreases
from top to bottom, as effective nuclear
charge decreases due to shielding effect **2½**
of inner electrons

 Exception — Fluorine has less electron
gain enthalpy than Chlorine

E) Isoelectronic species :— Atoms or ions
are those which have the same number **1M**
of electrons.
 As at. no. increases, nuclear charge increases
& therefore size decreases **1M**
eg. nuclear charge increases from Na^+ to
Si^{4+} but the no. of e^-s remains the same in
each ion. Hence size decreases from Na^+ to Si^{4+} **1M**

e^-s	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}	
	10	10	10	10	**2M.**
Nuclear Charge (At·No)	11	12	13	14	

F) Effective nuclear charge— The actual charge
or nuclear attraction which is felt by
the outermost electron is an atom **1M**
is called effective nuclear charge z^*.
 Eff. nuclear charge z^* is less than

(11)

IV

Q. No.		Marks
	nuclear charge z by an amount s ie shielding constant.	
	$z^* = z - s$	1M 1M
	$s = 0$. for each e^- in a group	1M
	$s = 0.35$ for each e^- in same group	
	$s = 0.85$ for each e^- in n-1 group	1M
	$s = 1.00$ for # —— in closer n-1 groups	

(11)

12

Q4

Q. No.		Marks

a) i) 3-oxobutanoic acid   ii) 3-ethoxy cyclopentanol

iii) 2-bromo methyl propanoate   iv) N,N-dimethyl propanamine

v) 4-methyl-2-pentene

     Each correct name (1m) × 5   5m

b) sp^3 hybridisation (1m)

tetrahedral structure, bond angle 109°28' (1m)   5m

Diagram showing type of orbitals and overlap (3m)

[No diagram, only description cut 1m]

c) Types of hybridization — sp^3 & sp^2 (1m)   5m
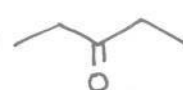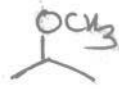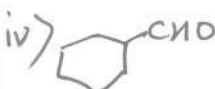
Effect on any 4 bond properties (4m)

d) i) Stronger acid HCOOH (1m)   3m

Reason for strength +I effect of CH_3 gp in

CH_3COOH makes H^+ release difficult, hence weaker

acid And destabilization of conjugate base (2m)

ii) Type of overlap (2m)   2m

e) i) $ClCH_2-CH_2-CH-CH_2-CH_3$ ii)   iii)   5m

                  OH

iv) ... CHO   v) ... COOH

f) Structures of primary, secondary and tertiary   5m

carbocations (3m)

3° > 2° > 1° (1m)

Any 1 reason (2m)

(inductive effect or hyperconjugation)

⟨13⟩

IV

Q5	A	State first law of thermodynamics in any three forms. Give any two limitations of it?	05
		Statements of first law of thermodynamics: 1) Energy can neither be created nor destroyed but can be converted from one form to another. 2) The energy of isolated system remains constant. 3) Whenever one kind of energy is produced, an exactly equivalent amount of another kind of energy must disappear. 4) Energy of the universe is constant. 5) It is impossible to construct a perpetual motion machine which could produce work without consuming energy. **Limitations:** 1) The law fails to tell us the source of heat and direction of flow of heat. 2) It does not define the ease or extent of convertibility of one form of energy into another. 3) It fails to explain why natural processes are unidirectional. 4) This law cannot explain why all naturally occurring processes always tend to change spontaneously in the direction which leads to equilibrium. 5) It does not say whether heat change is endothermic or exothermic. 6) Work can be completely transformed into heat, but heat cannot be completely converted into work without causing permanent change in the system or surrounding. This observation could not be explained by this law. 7) According to this law, it is not possible to have 100% efficiency for heat engine. However, experience tells that, such engines are not possible in practice. 8) From the point of view of this law, difference between spontaneous and non-spontaneous process is of no significance.	03 02

(14)

Q5 b

Definition   1 Mark

It is defined as number of moles of solute associated with 1 Kg or 1000 g of the solvent.

$$\text{Molality} = \frac{weight\ of\ solute\ X\ 1000}{Mol.wt\ X\ weight\ of\ solvent\ in\ gm}$$

$$\text{Molality} = \frac{weight\ of\ solute\ X\ 1000}{Mol.wt\ of\ solute\ X\ weight\ of\ solvent\ in\ gm} \qquad \text{2 Marks}$$

$$= \frac{18\ X\ 1000}{180\ X\ 500} \qquad \text{2 Mark}$$

$$= 0.2m \qquad \text{1 Mark}$$

Q. No.

Marks

Q5-C | Calculate zeff for 4S electron
in Iron atom

$Z = 26$

$1S^2, 2S^2, 2p^6, 3S^2, 3p^6, 3d^6, 4S^2$ 01

$(1S^2) ; (2S^2, 2p^6) (3S^2, 3p^6) (3d^6) (4S^2)$ 01
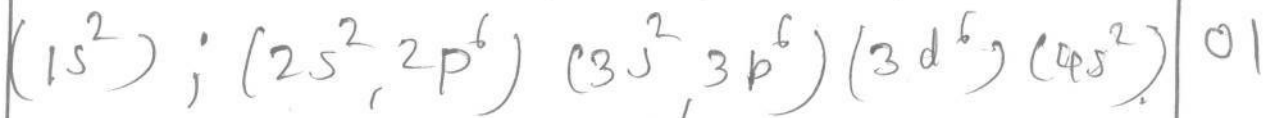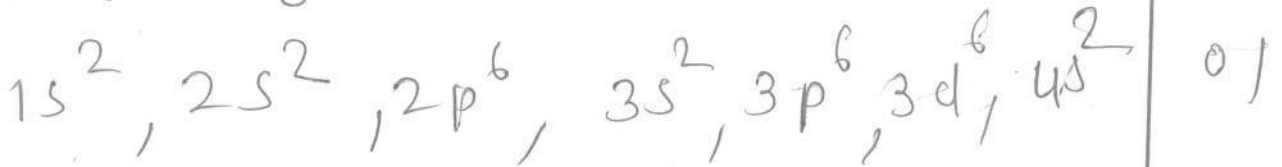
$S = (10 \times 1.0) + (14 \times 0.85) + (1 \times 0.35)$ 01

$S = 22.25$

$\therefore 2\,eff = Z - S$ 01

$= 26 - 22.25$

3.75 01

(16)

Q. No.		Marks

5 D   Atomic & ionic radii :— Magnitude of radius of atom or ion represent the size of atom or ion. The absolute size of an atom or ion Can not be defined because ① exact position of electron cannot be defined. ② Probability of finding the e^- around the nucleus is influenced by presence of other atoms. As a result size of atom changes.

1M

1M.

     The internuclear dist. in a diatomic molecule of an element is called as covalent bond length. Half of covalent bond length is the covalent radius. eg. two chlorine atom in chlorine molecule, the bond length is 19.8×10^{-2} nm. & the covalent radius is 9.9×10^{-2} nm.

1M

     CF — bond length — 14.9×10^{-2} nm
& Covalent radius — 7.7×10^{-2} nm.
→ 9.9×10^{-2} nm   Van-der waal radii larger than
→ 19.9×10^{-2} nm.   the covalent radii

1M

→ The atom lose e^- to form cation & cations are considerably smaller than resp. atom.

1M.

eg. $r_{Na} = 15.4 \times 10^{-2}$ nm   while $r_{Na^+} = 9.7 \times 10^{-2}$ nm

     $r_{Cl} = 9.9 \times 10^{-2}$ nm $r_{Cl^-} = 18.7 \times 10^{-2}$ nm

(17)

Q.5 E] 5 points of distinction (5m).

[shift / transfer of bonding pair of e's,

mobility via σ / π bonds

development of partial / complete charges

transmission via σ / π conjugated bonds

permanaut polarisation / polarisability under the

influence of attacking reageut]

F] i] Explanation of sp-hybridisation with shape and (3m)

bond angle.

ii] Any suitable elimination and substitution reaction. (2m).

1-m each