1)

Answer key

Q.P. Code :- 56902

Q1 (A) (i) b) Closed System

(ii) a) Concentration

(iii) a) $\left(\frac{\partial u}{dT}\right)_V$

(iv) b) always negative

(v) R) Decinormal

(vi) b) Homogeneous mixture

(vii) b) 2 P

(viii) a) Positive

(ix) a) $\lambda = h/p$

(x) c) 8

(xi) a) normal

(xii) a) greater

(xiii) a) sp^3

(xiv) a) electron rich

(xv) b) Two

(xvi) a) Debye

(xvii) a) Pyramidal

(xviii) c) Substitution.

Q2

(B) (i) True

(ii) False

(iii) False

(iv) False

(v) False

(vi) True

(C) (i) e) U+PV

(ii) d) Parts per billion

(iii) e) 6

(iv) f) 19.8×10^{-2} nm

(v) a) R-CO-X

(vi) b) H^+

Set III

Q2	A	Explain the concept of heat and work in thermodynamics along with its sign conventions.	05
		Heat: Heat is a form of energy that is contained in a system. It can be transferred from hotter body to colder body. Its symbol is 'q'. It is not the property of the system; it is present in the body as thermal energy.	01
		Characteristics of heat: Heat stimulates random motion of atoms or molecules. Heat appears only during a change in the state of the system. Heat always flows from higher temperature to lower temperature. Its SI unit is joule J.	01
		Work: Work is mode of energy transfer between system and surrounding.	01
		Characteristics of heat: Work appears only during a change in state of the system. Work is an algebraic quantity. It has magnitude as well as sign. The SI unit of work is Joule 'J'.	01
		a) **Sign convention of heat:** If heat flows from surrounding into system, the energy of the system is raised. So it is considered as positive, +q. If heat flows from system into surrounding, the energy of the system is lowered. So it is considered as negative, -q.	01
		b) sign conventions for work: If work is done on the system, the energy of the system is increased so it is considered as positive, +w. if the work is done by the system, energy of the system decreases. So it is considered as negative, -w.	
	B	i) Distinguish between endothermic and exothermic reactions. ii) Explain the term path function.	03

i) Distinguish between endothermic and exothermic reactions

	Endothermic reactions		Exothermic reactions
1	The energy is absorbed by the system from its surrounding, hence energy of the system increases.	1	The energy is given out by the system to its surrounding, hence energy of the system decreases.
2	The internal energy of the product is greater than that of reactant i.e. $U_2 > U_1$	2	The internal energy of the reactant is greater than that of product i.e. $U_1 > U_2$
3	The change in internal energy of the system, $\Delta U = U_2 - U_1$ is positive	3	The change in internal energy of the system, $\Delta U = U_2 - U_1$ is negative

04

		ii) **Path function:** If the change in value of any function depends upon the path followed by the system from initial to final state, then that function is called path function. The heat absorbed 'q' and the work done 'w' by the system are not the state functions but are path functions, because their values depends upon the path by which process is carried out. The differential equations for heat 'δq' or work 'δw' are inexact differential and they depend on the path followed by the system.	02
	C	Calculate change in internal energy and change in enthalpy of a system when 96 g of oxygen is heated from 0°C to 95 °C. (Given: $C_v = 20.92\ J\ K^{-1}\ mol^{-1}$, $C_p = 29.29\ J\ K^{-1}\ mol^{-1}$, O = 16)	
		Solution: $\Delta U = ?, \Delta H = ?$ $n = \frac{96}{32} = 3$ moles. $T_1 = 0 + 273 = 273\ K$, $T_2 = 95 + 273 = 368\ K$. a) $\Delta U = n C_V dT$ $= n C_V (T_2 - T_1)$ $= 3 \times 20.92 \times (368 - 273)$ $= 5962.2\ J$ b) $\Delta H = n C_p dT$ $= n C_p (T_2 - T_1)$ $= 3 \times 29.29 \times (368 - 273)$ $= 3 \times 29.29 \times 95$ $\Delta H = 8347.65\ J$.	05
	D	Derive Kirchhoff's equation. Give its applications.	04
		Consider a general reaction, $aA + bB = cC + dD$ The change in enthalpy is given by, $\Delta H(\text{reaction}) = \Sigma H_{(\text{product})} - \Sigma H_{(\text{Reactants})}$ $= (cH_C + dH_D) - (aH_A + bH_B)$ 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.	

05

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:

1) Kirchhoff's equation is used to calculate the heat of reaction at different temperature.
2) It can also be used to calculate the change in molar heat capacity at constant of pressure.

01

06

Q2 e **Definition**

Equivalent weight of any substance is defined as that weight of the substance which provides the Avogadro's number of reacting units. **1 Mark**

4 Marks

Explanation

Redox Reaction:

The Reacting unit in this case is electron.The equivalent of an oxidising or reducing agent is related to the number of electrons that a single molecule or an ion can can lose or gain.

Equivalent weight of an oxidising agent =

$$\frac{Molar\ mass}{no.of\ electron\ accepted\ by\ a\ single\ molecule\ or\ ion}$$

Equivalent weight of an reducing agent =

$$\frac{Molar\ mass}{no.of\ electron\ lost\ by\ a\ single\ molecule\ or\ ion}$$

Example:

$2\ Fe^{3+}_{(aq)} + \ Sn^{2+}_{(aq)} \ = \ Sn^{4+}_{(aq)} + \ 2Fe^{2+}_{(aq)}$

The Oxidation reaction is

$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

The Reduction reaction is

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

The Equivalent weight of Fe^{3+} = Molar mass/ 1

The Equivalent weight of Sn^{2+} = Molar mass/ 2

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

Wt of solute in g $= \frac{0.12 \times 98 \times 250}{1000}$ 2 Marks

$= 2.94$ g 1 Mark

07.

M.U.P./J.Exam.2069-40,000×8pp.-2-14.

Page No. 01

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
Q.3 A)	N.B. : Slater Rules for calculating Shielding constant	05
	$Z_{eff} = Z - S$.	01
	effective Nuclear charge Z_{eff}	
	Z = Nuclear charge	
	S = Shielding constant	01.
1)	electronic Configuration	
	(1s) (2s, 2p) (3s 3p) --- so on.	
2)	electron considered in a group of s, p electrons the shielding constant (s) is sum of the following contributions.	
	a) No contribution for electron in group beyond the one considered	01
	b) 0.35 each other electron in group. 1s — 0.30. is used	01
	c) 0.85 for each electron in the next inner shell (n-1).	
	d) 1.00 for each inner shell.	01.
	for d or f. rule 2a and 2b.	
3)	1.00 for d and f left group.	

Q. No. | Marks

B) shells:- The term shells mean the sphere around the nucleus in which the electrons of the same energy level exist. In wave mechanics the term shell is substituted by electron sphere. A electron atmosphere. Most probable position of the electron from the nucleus. The quantum no 'n' is restricted to have any positive integral n: 1, 2, 3, 4 --- ∞ and referred to K, L, M, N — 1½ — ½

2) Subshells:- orbital belongs to each shell is further classified in to subshell distinguished by quantum no l. called angular momentum no. described the motion of electrons. $\sqrt{l(l+1)} \cdot \frac{h}{2\pi}$. — 1½

$l = 0, 1, 2, 3 \ldots (n-1)$ have positive values. it is governed by n. — ½

n=1 only one subshell. l=0 when n=2 two subshells l=0 and 1, n=3 - Three. 0, 1, 2

orbitals:- The region around the nucleus in which probability of finding electron is maximum are called orbitals. — 01

09

Q. No.		Marks
c)	Limitations of Bohr's atomic model	(05)
1)	It could explain the speetral line in hydrogen atom He^{+2}, Li^{+} etc. with one electron, can not explain more than one electron.	01.
2)	It could not explain splitting of speetral line	
	Magnetic field (zeeman effect)	01
	Electric field (stark effect	01
3)	It regard the electron in an atom discrete particles with precisely defined position & velocity	01
4)	- It could not explain Fine speetrum	01

(10)

Page No.....

Q. No. | Marks

Q3 D) Alfred & Rochow Electronegativities :-

Applications of pauling & mulliken methods are limited. Alfred & Rochow defined electronegativity as the electrostatic force of attraction, exerted by the nucleus on an atom on the valence e^-. — 1 M

A & R suggested that $F = \frac{Z \cdot e^2}{r^2}$ — 1 M

Z - effective nuclear charge (determined by slater's rule)

r - internuclear dist. (half for homonuclear diatomic molecule), F - may be absolute electronegativity

A & R added certain parameter — 1 M

$EN_{AR} = \chi$

$= 0.359 \frac{Z}{r^2} + 0.744$

$EN_{AR} = \chi$ — Alfred-Rochow electronegative value — 1 M

r - covalent radius in A^0

AR electronegativity values & pauling eleltronegativities are in agreement, of main gr. elements. — 1 M

E) Periodic table (s, p, d, f) (any three — 1 M

s - IA & IIA, p - IIIA to VIII - noble gases — 1 M
metal ns^2 Non metals $ns^2 np^{1-6}$

d - Transition elements - Sc - Zn - metals — 1 M
(3d, 4d, 5d, 6d) (n-1)d Y - Cd

f - Inner transition elements (IIIB gr.) - 4f — 1 M

Lanthanides & 5f - Actinides. (n-2)f

12/19

(ii)

Page No.....

Q. No.		Marks
Q3	F) Ionisation enthalpy :- $\Delta_{ion}H$ - defined as the enthalpy change for the removal of one electron from each atom in one mole of gaseous atoms or ions	1 M
	$Na_{(g)} \rightarrow Na^{+}_{(g)} + e^{-}$ $\Delta_{ion}H = 494 KJmol^{-1}$	1 M
	Heat absorbed ΔH - positive & Heat evolved ΔH - negative	1 M
	Removal of 1st e^- is 1st ionisation enthalpy	1 M
	$M \rightarrow M^{+} + e^{-}$ $\Delta_{ion}H$.	
	If second e^- is removed - then it is 2nd ionisation enthalpy & so on.	1 M
	Enthalpy of ionisation expressin $KJmol^{-1}$.	

F.Y.B.Sc. chemistry - Paper-I Sem-I Examination Nov-2018 | 3 | 19

Synoptic Answer key - organic section.

12 Q.1 A] XIII) sp^3 XIV) electron rich XV) two

XVI) Debyes XVII) ~~Four~~ ~~Each~~ ~~pyramidal~~. pyramidal. XVIII) substitution

- 1 - mark each.

B] V) False VI) True.

C] Acid halide - R-CO-X ; Electrophile - H^+

Q.4 A] 1) Cyclohexane carbonyl bromide 2) Cyclopentane carboxamide.

3) Propanamine. 4) Ethyl propanoate 5) 3-Methyl-2-pentene.

- 1-mark each

B] sp^2 - hybridisation of oxygen:

Example - 1 mark

Structure - 1 - mark

Explanation - 1 - mark.

Orbital picture of dimethyl ether - 2 - mark.

C] Carbocation - definition - 1 - mark.

sp^2 - hybridisation - 1 - mark

Trigonal planar - 1 - mark

Structure - 1 - mark

Explanation - 1 mark.

D] Free radicals - defination - 1 - mark

Resonating structures - 2 - mark

Explanation - 2 - mark.

E] i] sp^2 - hybridisation of carbon - Example - 1 - mark

structure - 1 - mark

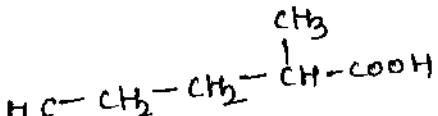
Explanation - 1 - mark

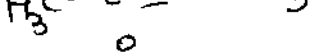
ii] Alcohols are ~~weakly~~ acidic than carboxylic acids.

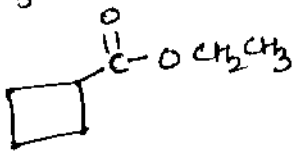
(stability) Resonating structure of carboxylate ion - 1 - mark

Explanation - 1 - mark.

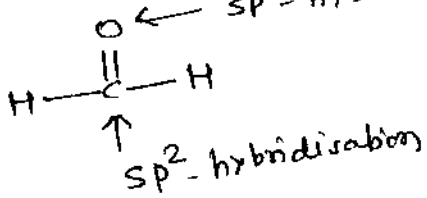
Q 4. (13)

F) i] 1) 

2) 

3) 

1 - mark each

ii] 

1 - mark each.

04

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III

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

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Q5 b Definition 1 Mark

It is defined as the number of moles of a solute dissolved in (1 litre) 1 dm^3 of the solution.

Molarity = $\frac{moles\ of\ solute\ dissolved}{volume\ of\ solution\ in\ dm3}$

$= \frac{weight\ of\ solute}{Mol.wt\ \ X\ \ volume\ in\ dm3}$

Molarity = $\frac{weight\ of\ solute\ \ X\ \ 1000}{Mol.wt\ \ X\ \ volume}$ 2 Marks

$= \frac{9.8\ \ X\ \ 1000}{98\ \ X\ \ 100}$ 1 Mark

= 1M 1 Mark

16

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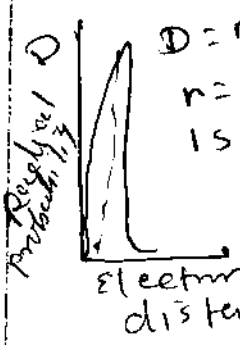
Page No.....

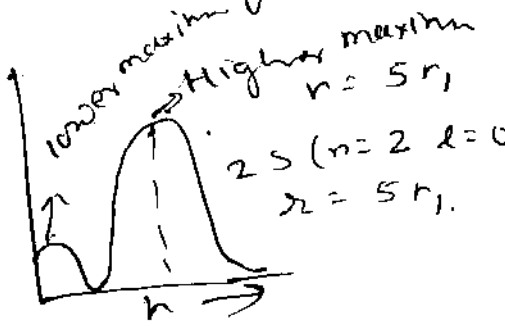
Q. No.

Marks

Q.5 c) Explain the distribution curve for radial wave function of 1s and 2s orbital.

Probability of the electron being at a distance r from the Nucleus is called radial probability distribution function. 0.1





0.2

D = zero at r = 0 D ↑ as r ↑ forms zero passes through maximum at r = 0.529 A° (or 52.9 pm) equal to the radius of Bohr's first orbit, r and finally falls to zero r tend to ∞ curve 2s electron. D is zero at r = 0 value of D ↑ as the value of r ↑ es passes through a lower maximum at r = 0.529 A° = r_1 and falls to zero at r = 2 x 0.529 A° = $2r_1$. 0.2

greater probability of finding electron further away from the nucleus.
some chances of finding electron very close to the nucleus.
At intermediate distance (= $2r_1$) there is surface probability of finding the electron zero. charge cloud representation of 2s electron consist of sphere surrounded by second spherical shell.

12

Page No.....

Q. No.		Marks
Q 5 D)	The actual charge or nuclear attraction which is felt by the outermost electron in an atom is called effective nuclear charge Z^*. $Z^* < Z$ (nuclear charge) by an amount S – called shielding constant.	1 M
	$Z^* = Z - S$	1 M
	~~S calculated from Slater rule 1930~~ for calculating S. Elements are divided into groups as 1s, 2s, 2p, 3s, 3p, 3d 4s 4p 4f 4d etc.	1 M
	$S = 0$ for each electron in a group	
	$S = 0.35$ for each electron in the same group	1 M
	$S = 0.85$ for electron in n-1 group	
	$S = 1.00$ for electron closer in n-1 group.	

15

Q.5 E) stability of carbanion:-

Inductive effect - example - 1 mark

explanation - 1½ mark

S-character example : 1½ mark

explanation : 1 mark

f] i) orbital structure of Ethyne :

Hybridisation - 1-mark

structure - 1-mark

Explanation - 1-mark

ii] Addition reaction : any one example with reaction - 1-mark

Elimination reaction : any one example with reaction - 1-mark