

2. (a) Write the Schrodinger equation in Cartesian and polar co-ordinates, giving the significance of the terms involved in it. (4)
- (b) Calculate the percentage ionic character of HF if electro negativities of H and F are 2.1 and 4.0 respectively. (4)
- (c) Define resonance. Draw resonating structure for SO_4^{-2} , N_3^- and NO. (4)
3. (a) Write the electronic configuration for Cr (Atomic No. 24) and Cu (Atomic No. 29). Explain why half-filled and fulfilled orbitals have extra stability. (4)
- (b) Calculate the heat of formation (ΔH_f) of MgF_2 from its elements using Born-Haber cycle.
- Given Sublimation energy of Mg = 146.4 KJ/mole
 Dissociation energy of F_2 = 158.9 KJ/mole
 Ionization energy of Mg (g) = 2184.0 KJ/mole
 Electron affinity for F to F^- = -334.7 KJ/mole
 Lattice energy of MgF_2 = -2922.5 KJ/mole (4)
- (c) Define the lattice energy. What is its importance ? State Born-Lande equation for calculation of lattice energy. Give the significance of each term. What is the value of Z^2 for a crystal of TiCl_4 . (4)
4. (a) Define VESPER theory. Predict the shape of the following molecules on the basis of VESPER theory
- (i) OF_2 (ii) ClF_3 (iii) ICl_2^- (5)
- (b) What are the ordinates for radial distribution function ? (2)
- (c) What are Eigen Values ? (1)
- (d) LiI is soluble in ethanol while LiF is insoluble. (2)
- (e) Predict the shape of XeO_2F_2 on the basis of hybridization. (2)

SECTION – B

Scientific calculator is allowed.

Attempt three questions in all.

Question No. 1 is compulsory.

1. Explain (Answer any five) : (2½×5)
- (a) What are intensive properties ? State which of the following properties are intensive :
Density, volume, molar heat capacity and temperature.
- (b) Why the efficiency of a Carnot engine can never be unity ?
- (c) The solution of sodium acetate is basic in nature. Why ?
- (d) What is meant by Ionic product of water ? What is its value at 298K ?
- (e) What is the indicator used for the titration of strong acid and strong base ? Also give reason.
- (f) Explain Kirchhoff's law and its importance in thermo-chemistry.
2. (a) Show that pH of solution of a salt of strong acid and weak base is given by

$$\text{pH} = \frac{1}{2}(\text{pk}_w - \text{pk}_b - \log_{10} C)$$
 (3½)
- (b) Derive Henderson equation for pH of an acidic buffer solution. (3)
- (c) Define solubility product of sparingly soluble salt. Calculate molar solubility of PbI_2
- (i) In water
- (ii) In 0.20 sodium iodide
- Given $\{K_{sp}(\text{PbI}_2) = 7.9 \times 10^{-9}\}$ (3×2)
3. (a) Derive (any three) :
- (i) $C_p - C_v = nR$
- (ii) $(\partial P / \partial S)_T = - (\partial T / \partial V)_P$

P.T.O.

(iii) $\Delta G = \Delta A$ for an isothermal expansion of an ideal gas

(iv) $PV^\gamma = \text{constant}$

All the symbols have their usual meanings (3×2)

(b) What is meant by enthalpy of formation ? Calculate enthalpy of formation of acetylene from the fact that its enthalpy change for combustion is $-1299.6 \text{ kJ mol}^{-1}$.

$$\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) = -285.8 \text{ kJmol}^{-1}$$

$$\Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.5 \text{ kJmol}^{-1} \quad (3\frac{1}{2})$$

(c) Derive the expression of work done during reversible isothermal expansion for one mole of ideal gas. (3)

4. (a) Write short note :- **(any three)**

(i) Common-ion effect.

(ii) Integral heat of solution and differential heat of solution

(iii) Theory of acid base indicator

(iv) Third law of thermodynamics

(v) Salt hydrolysis (3×3)

(b) Calculate the entropy change when one mole of ideal gas expands reversibly from an initial volume of 1.0 dm^3 to a final volume of 10.0 dm^3 at constant temperature of 298 K . (3½)