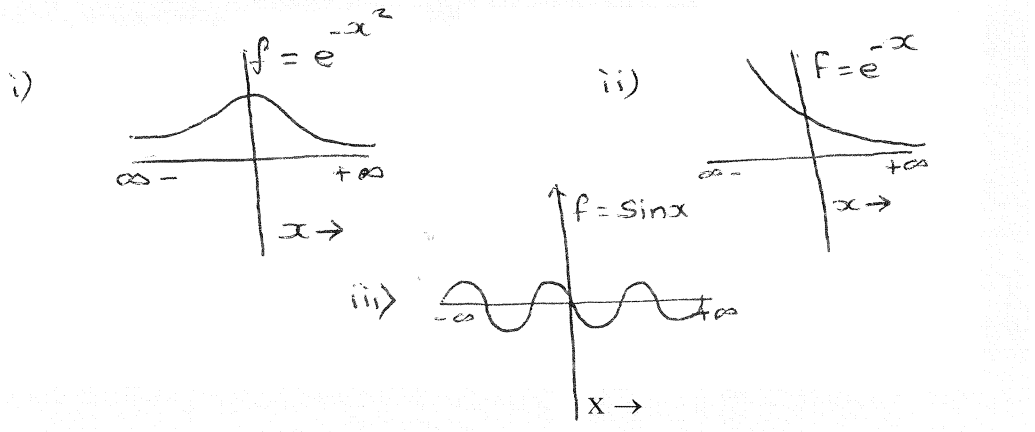
[Time : 3 Hours Total marks: 75

N.B : 1. **All** questions are **compulsory**.
2. **Figures** to the **right** indicate **full** marks.
3. Use of non-programmable scientific calculator is **allowed**.

Useful constants –

c = $2{\cdot}998 \times 10^{8}$ ms^{-1}
R = $8{\cdot}314$ $JK^{-1}mol^{-1}$
h = $6{\cdot}625 \times 10^{-34}$ Js
m_e = $9{\cdot}11 \times 10^{-31}$ kg
N_A = $6{\cdot}023 \times 10^{23}$ mol^{-1}
e^- = $1{\cdot}602 \times 10^{-19}$ C
k = $1{\cdot}3811 \times 10^{-23}$ JK^{-1}
1 J = $6{\cdot}24 \times 10^{18}$ eV
1 eV = $8{\cdot}06 \times 10^{3}$ cm^{-1},
1 a.m.u.= $1{\cdot}66 \times 10^{-27}$ kg
H = 1, I = 127

1. Attempt any **five** of the following :— **15**
   (a) Define Joule Thomson coefficient. Give its significance 'Ideal gases do not show Joule-Thomson effect.' Explain.
   (b) Explain the concept of residual entropy with suitable examples.
   (c) Explain Lambda transition with suitable examples.
   (d) State the Lippman's equation and explain the terms involved in it.
   (e) Which of the following functions representated graphically are acceptable ?



(f) Determine the degree of degeneracy of the energy level $\frac{11h^2}{8ma^2}$ and indicate its energy states.

(g) Explain the term potential energy surface. Give its significance.

(h) Predict the effect of ionic strength on the rates of following reactions.

(i) $H_2O_2 + 2H^+ + 2\ Br^- \rightarrow$ Products

(ii) $S_2O_8^{2-} + 2I^- \rightarrow$ Products

(iii) $Fe^{2+} + Co(C_2O_4)^{3-} \rightarrow$ Products.

2. (a) Obtain an expression for translational partition function for a particle. **6**

OR

(a) What is Clausius inequality ? Obtain an expression for it and explain it's significance. **6**

(b) 4 litres of an ideal gas (Mol.wt = 16) and 1 litre of another ideal gas (Mol.wt = 40) each at 1 atm and 300K are mixed isothermally in a vessel of 3 litres capacity. Calculate ΔG_{mix}, ΔH_{mix} and ΔS_{mix}. **5**

(c) Define fugacity and activity. Obtain a relation between activity and activity coefficient in terms of chemical potential. **4**

OR

(c) Prove the relation **4**

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

3. (a) State the posulates of B.E.T. theory. Write the B.E.T. equation. How is it verified experimentally ? **6**

OR

(a) Explain (i) Debye Falkenhagen effect **6**

(ii) Wein effect.

(b) Calculate the mean activity coefficient of an aqueous solution of 0·02M K_2SO_4 at 298K. **5**

Given : A = 0·509 for water at 298 K.

(c) Give the expression of **4**

(i) thickness of ionic atmosphere.

(ii) Debye-Huckel-Onsager equation for conductivity. Explain the terms involved in each equation.

OR

(c) Draw a neat labelled phase diagram of a three component system containing one pair of partially miscible liquids and explain it. **4**

4. (a) Obtain an expression for the energy of a particle in a two dimensional box. **6**

OR

(a) Obtain the Hermites differential equation for linear harmonic oscillator from the following equation. **6**

$$\frac{d^2\Psi}{dy^2} + \left(\frac{\alpha}{\beta} - y^2\right)\Psi = 0$$

(b) Explain the term 'Hermitian operator'. If $\hat{A} = 3x^2$ *and* $\hat{B} = \frac{d}{dx}$ then show that $\hat{A}$ *and* $\hat{B}$ do not commute. **5**

(c) Give the salient features of the molecular orbital theory. **4**

OR

(c) The internuclear distance in HI molecule is 163pm. Calculate the energy of the second energy level. **4**

5. (a) Write the reaction for the thermal decomposition of acetaldehyde. Identify the various steps and using the steady state approximation, show that the rate of formation of methane is given by $\frac{d(CH_4)}{dt} = k[CH_3CHO]^{3/2}$ **6**

OR

(a) Explain the shock tube and flash photolysis techniques used to study fast reactions. **6**

(b) A first order reaction has an activation energy of 104·5kJ $mole^{-1}$ and a pre-exponential factor A in the Arrhenius Equation as 5×10^{13} sec^{-1}. At what temperature will the reaction have a half-life of (i) 1 minute and (ii) 30 days? **5**

(c) Derive an expression for the rate constant of a bimolecular reaction on the basis of the Activated Complex theory. **4**

OR

(c) Derive an expression to show the influence of ionic strength on the rate of the reaction between ions. **4**
