B.E./B.Tech. DEGREE EXAMINATION, NOVEMBER/DECEMBER 2003.

Third Semester

Industrial Biotechnology

IB 235 — CHEMICAL THERMODYNAMICS AND BIOTHERMODYNAMICS

Time : Three hours

Maximum : 100 marks

Answer ALL questions.

PART A — (10 × 2 = 20 marks)

1. Define a closed and open system with one example for each.

2. How do you define efficiency of heat engine and C.O.P. of heat pump?

3. Work done on water stirring is 1678 watts and heat generated by stirring is transferred to surrounding at 3400 kJ/HR. What is the change in internal energy of the system?

4. An ideal gas undergoes adiabatic change from P_1, V_1, T_1 to P_2, V_2, T_2. For an ideal gas $C_p - C_v = R$ and $du = CV \cdot dT$.

$$\text{Show } \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \text{ where } \gamma = Cp/Cv.$$

5. When 2-ideal gases are mixed the change in entropy is $\Delta s = -R \Sigma x_i / n x_i$ calculate the entropy of 1 g mol of air?

6. Show $G = A + PV$ where G is free energy, A-helmholtz energy and P and V are pressures and volume.

7. Henry's law constant for O_2 in water at 25°C is 4.4×10^4 bar. Calculate the solubility of O_2 in water as kg O^2/kg Air for a partial pressure of 0.25 bar of O_2.

8. Derive activity (a_i) of a component 'i' is equal to the product of its activity coefficient γ_i and molefraction x_i.

9. Briefly state how you would use Clausius-Clapeyron equation to determine heat of vaporisation of a liquid.

10. Define respiratory quotient (RQ) and degree of reduction (γ) with reference to a Bioprocess.

PART B — (5 × 16 = 80 marks)

11. (i) Show $\left(\dfrac{\partial S}{\partial T}\right)_P = \dfrac{C_p}{T}$. (4)

    (ii) A substance is heated from 300 k to 800 k. Its heat capacity is given by

    $$C_p = 26.04 + 5.586 \times 10^{-3}T + 28.476 \times 10^4 T^{-2} \ \dfrac{J}{mol.k}.$$

    Determine increase in entropy of the substance. (8)

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

    show $ds = \dfrac{C_p}{T}dT - \left(\dfrac{\partial V}{\partial T}\right)_P dp$. (4)

12. (a) (i) Derive the energy balance equation for a flow of unit mass of fluid through a control volume, under steady state. (10)

    (ii) Using the equation obtained in (i) show shaft work $(W_s) = -\displaystyle\int_{P_1}^{P_2} V.dp$

    V-specific volume of fluid. (6)

Or

    (b) (i) Show $C_P - C_V = \dfrac{\beta^2 VT}{K}$

    Where $\beta = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$ and $K = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$. (12)

    (ii) For ideal gas show

    $$C_P - C_V = R.$$ (4)

13. (a) (i) A solution property say M for a binary system is obtained using

    $$M = x_1 \overline{M}_1 + x_2 \overline{M}_2$$

    Where x denotes mole fraction.

    $\overline{M}$ denotes partial molar property.

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Show $\overline{M}_1 = M - x_2 \dfrac{dM}{dx_2}$

$\overline{M}_2 = M - x_1 \dfrac{dM}{dx_1}$.

(6)

(ii) Explain graphically using M Vs x_2 data how you would determine $\overline{M}_1, \overline{M}_2$.

(2)

(iii) 30 lit of Ethanol and 70 lit of water are mixed. One engineer says the total volume is 100 lit. Another engineer says it is not so. Prove who is right using the following data :

(1) Density of EtOH and water are 0.789 and 0.997 gm/cc.

(2) Partial molar volumes of EEOH and water are 53.6×10^{-3} lit/mol, and 18×10^{-3} lit/mol.

(8)

Or

(b) (i) Assume a single phase homogeneous solution having 2 components A and B. The system is open so that n_1 moles of A and n_2 moles of B may change. [Remember $n = n_1 + n_2$ always]. Show starting from fundamentals.
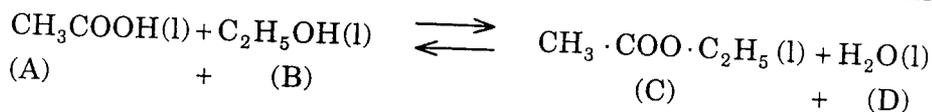
$d(nG) = (nV)dp - (n.s)dT + \{\mu_1 \, dn_1 + \mu_2 \, dn_2\}$

where μ_1, μ_2 are chemical potentials of A, B.

(6)

(ii) If a liquid solution having A and B, is in equilibrium with its vapour (having A, B) and this V–L system is a closed system.

(10)

Show Chemical potential of each component in liquid phase = Chemical potential of the same component in vapour phase.

14. (a) Acetic acid is esterified in liquid phase with ethanol at 100°C and atmospheric pressure to produce ethyl acetate and water. The reaction is

$\underset{(A)}{CH_3COOH(l)} + \underset{(B)}{C_2H_5OH(l)} \rightleftharpoons \underset{(C)}{CH_3 \cdot COO \cdot C_2H_5 \, (l)} + \underset{(D)}{H_2O(l)}$
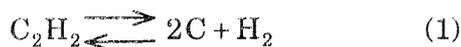
1 mole of acetic acid and 1 mole of ethanol are fed. Using the data given below determine the mole fraction of ethyl acetate in the mixture at equilibrium.

(16)

| Data :	A	B	C	D
Heat of formation at 298 K (J/Mole)	−484500	−277690	−285830	−463250
Free energy of formation at 298 k (J/mole)	−389900	−174780	−237130	−318280

Or

(b) Acetylene is catalytically hydrogenated to ethylene at 1120°C and 1 bar pressure. The feed consists of equimolar mixture of acetylene and H_2. Calculate the composition of equilibrium mixture :

Reactions :

$$C_2H_2 \rightleftarrows 2C + H_2 \qquad (1)$$

$$2C + H_2 \rightleftarrows C_2H_4 \qquad (2)$$

$$\overline{C_2H_2 + H_2 \rightleftarrows C_2H_4} \qquad (3)$$

Equilibrium constants K_1 and K_2 for reactions (1) and (2) are 4×10^5 and 2.5×10^{-6}. (16)

15. (a) Production of single cell protein (Bio-Mass) is given by

$$C_{16}H_{34} + aO_2 + 6NH_3 \rightarrow C.CH_{1.66}O_{0.27}N_{0.20} + dCO_2 + eH_2O.$$
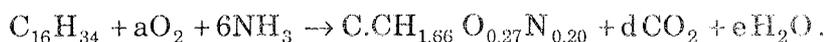
(i) Can you determine the stoichiometric coefficients a, b, c, d, e. If you cannot, explain the reason. (4)

(ii) If respiratory quotient = 0.43 determine the stoichiometric coefficients use elemental balance. (12)

Or

(b) (i) A system is at non equilibrium state and heat is transferred to surrounding then you have $ds_{s>st} - \dfrac{dQ}{T} > 0$ you know by First Law of thermodynamics

$$dQ - pdV = du$$

Show then $(dG)_{T,P} < 0$. (6)

(ii) In metabolic reaction as

$ATP + H_2O \rightarrow ADP + Pi$ (Inorganic phosphate) $\Delta G = -Ve$.

Explain with suitable example how ATP essentially required is regenerated in eek cycle. (10)