RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

M.A./M.Sc. SECOND SEMESTER EXAMINATION, MAY 2014

FIRST YEAR

APPLIED CHEMISTRY

Date : 23/5/2014

Time : 11 am – 1 pm

Paper : IX

Full Marks : 50

[Use a separate Answer Book for each Group]

Group – A

*(Answer **any one** question)*

1. a) How will you determine the bond length of a homonuclear diatomic molecule A_2 from the spectral studies? [4]

   b) The fundamental and first overtone transitions of $^{14}N^{16}O$ are centred at 1876·06 cm^{-1} and 3724·20 cm^{-1} respectively. Evaluate the equilibrium vibration frequency, the anharmonicity constant and the zero point energy. [3]

   c) What are stokes and anti-stokes Raman Scatterings?
   Stokes lines are generally more intense than anti-stokes lines —justify or criticise. [1+1+3]

   d) Derive an expression for the dissociation energy of a diatomic molecule considering the anharmonic oscillator model. [3]

2. a) The vibrational potential energy of a diatomic molecule can be represented approximately by the Morse function, $E = Deq\left[1-\exp\{a(r_{eq}-r)\}\right]^2$ where terms have their usual significance. Show that E has a minimum value at $r = r_{eq}$. [4]

   b) Show that the quantum number of the rotational level is given by the expression, $J = \left(\frac{kT}{2Bhc}\right)^{1/2} - \frac{1}{2}$
   where terms have their usual significance, has a maximum population. [4]

   c) Show that the symmetric stretching mode for CO_2 is Raman active whereas antisymmetric and bending modes are Raman inactive. Explain your answer with the help of α versus ξ plot, where α is the polarizability and ξ represents the displacement coordinate. [4]

   d) The first line in the pure rotational spectrum Q $^1H^{35}Cl$ occurs at 21·18 cm^{-1} (=2B). Calculate the bond length of the molecule. [3]

Group – B

*(Answer **any two** questions)*

3. a) State and explain Raoult's law. [2]

   b) What is meant by an azeotropic mixture? [3]

4. a) Calculate the freezing temperature of an aqueous solution having its boiling temperature 100·1°C. The molal ebullioscopic constant and the molar cryoscopic constants are 0·518 and 1·86 K $kgmol^{-1}$ respectively. [3]

   b) Explain whether as a general rule you would expect K_b to be greater or smaller then K_f for a given solvent. [2]

5. Draw and explain the phase diagram of phenol-water system. [5]

Group – C

All questions carry 5 marks. Answer question no 1 and any other 4.

Q1. Answer the following:
i) define the term "activity"
ii) give the definition of "acentric factor"
iii) State the mixing rule for second virial coefficient- which gives ts variation with composition
iv) How is "coefficient of performance" for a vapor compression refrigeration cycle defined ?
v) What is the ideal entropy of mixing of a mixture containing n_i moles of component i, with mole fractions x_i at temperature T.

Q2. A standard Rankine cycle operates with water as operating fluid.
The pressures in the condenser and heater/ boiler are 20 and 1000 kPa respectively.
Draw the diagram of the cycle in the T-S chert provided. List the enthalpies and entropies of the working fluid at (i) inlet of the turbine (expander), (ii)outlet of the expander, (iii) outlet of the condenser from the diagram. Attach the diagram to your answer script.
Calculate the efficiency of this cycle.

Q3. Sarting with the expression for fugacity coefficient of a real gas :

$$\ln \phi = \int_0^P \frac{Z-1}{P} dP$$

show that

$$\ln \phi = (Z-1) - \ln Z + \int_V^\infty \left(\frac{P}{RT} - \frac{1}{V}\right) dV$$

Hence obtain an expression for the fugacity coefficient of a real gas obeying Redlich-Kwong equation of state.

Q4.
a) From the definition of Cp $\left(C_p = \left(\frac{\partial H}{\partial T}\right)_P \right)$, show that $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$

b) In a heat exchanger, a process stream with specific heat of 1.55 kJ/kg and a flow rate of 2000 kg /hr, is heated from 70 C to 110 C by a hot stream flowing at the rate of 1000 kg/hr which enters the exchanger at 130 C and has a specific heat of 2.1 kJ/kg.
Find the outlet temperature of this hot stream and calculate the the rate of entropy generation in this heat exchanger.

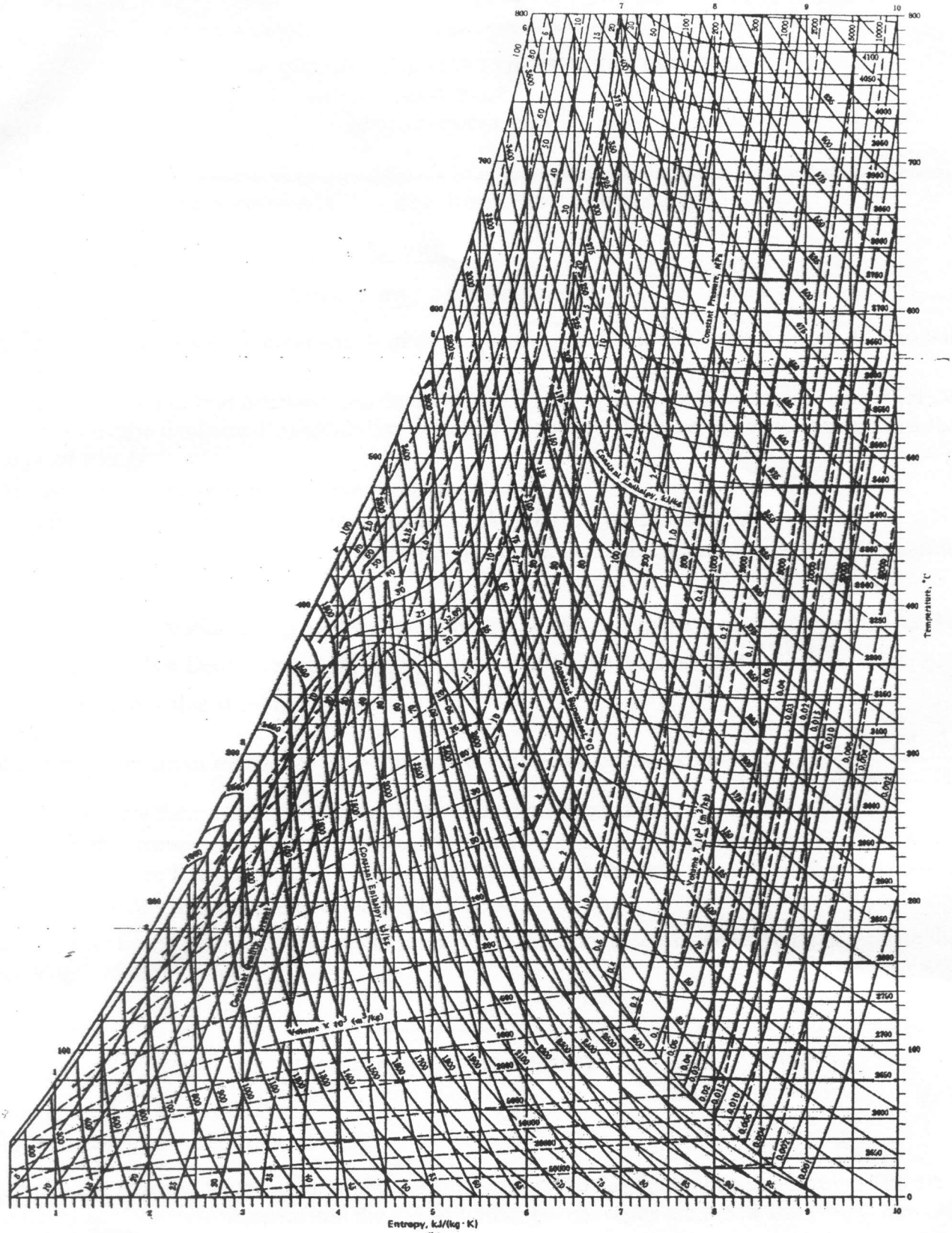
Q5. A liquid mixture of Benzene and Toluene at 95 C , containing 65 mole% benzene is at equilibrium with a vapor containing these two components only. Assume the liquid mixture as well as the vapor to behave ideally.
Find the total pressure of the system and the composition of the vapor phase.
Vapor pressures are given by Antoine equation given below.
First write down the relationship between equilibrium compositions of the two phases for both the components and obtain a relationship for the total pressure. Note ideal behaviour of the mixtures in both phases.

Antoine equation: $\ln P\ (\text{mm Hg}) = A - B/(T \text{ in } K + C)$

Component	A	B	C
Benzene	15.9008	2788.51	- 52.36
Toluene	16.0137	3096.52	- 53.67

Q6.
a) Obtain an expression for variation of fugacity with pressure for a liquid phase starting from the definition of fugacity.

b) Consider an ideal solution of a solute in water (solvent), with mole fraction of solute being x. What will be the ratio of fugacity of pure water and water in the solution.
Assume solution temperature to be 27 C and pressure to be 1 atm.
c) The solution is now pressurized at constant temperature.
At what pressure fugacity of water in solution will become same as fugacity of pure liquid water at 1 atm and 27 C [use 18 cc as molar volume of water wherever required]



(b)

Figure 2.4-1b
Temperature–entropy diagram for steam. (*Source:* J. H. Keenan, F. G. Keyes, P. G. Hill and J. G. Moore, *Steam Tables* (International Edition–Metric Units). Copyright © 1969, John Wiley & Sons, Inc., New York. Used with permission.)