Q1 What is thermodynamic excess function? Define regular solutions in terms of excess function (2)

Q2. Derive and explain electrochemical potential. (3)

Q3. How can degree of dissociation for electrolytes be obtained from colligative properties. (3)

Q4. Provide physical justifications for first-order, second-order and lamda phase transitions. (3)

Q5. Calculate the ionic strength of a solution by mixing 25 ml of 0.01 M $K_4Fe(CN)_6$ AND 25 ml of 0.01 M $K_3Fe(CN)_6$. (2)

Q6. Explain high and low-boiling azeotropes with examples (3)

Q7. For a reaction: $NH_3 (g) \rightleftharpoons (1/2)N_2(g) + (3/2)H_2(g)$

K_p^0 = 79.1 at 400 C. Show that the fraction of NH_3 dissociated at a total pressure p is given by

$$\alpha = \left(1 + \frac{3\sqrt{3}}{4} \left(\frac{p/p^0}{K_p^0} \right) \right)^{-1/2}$$. Calculate the value of K_c^0 for the given reaction. [R = 8.314 kPa dm³K⁻¹mol⁻¹] (4)

Q8. In an investigation of thermophysical properties of toluene, expressions for two coexistence curves (phase boundaries) were presented. The solid-liquid coexistence curve was given by:

$p / bar = p_3 / bar + 1000 \times (5.60 + 11.727x)x$, where $x = \frac{T}{T_3} - 1$ and the triple point pressure and

temperature are p_3 = 0.4362 μbar and T_3 = 178.15 K. The liquid-vapor curve is given by:

$\ln(p / bar) = -10.418 / y + 21.157 - 15.996y + 14.015y^2 - 5.0120y^3 + 4.7224(1 - y)^{1.70}$, where $y = T/T_c$ = T/(593.95 K).

(a) Estimate the standard melting point of toluene
(b) Compute the standard enthalpy of vaporization of toluene, given that the molar volumes of the liquid and vapor at the normal boiling point are 0.12 dm³/mol and 30.3 dm³/mol, respectively. Standard b.pt (T) = 383.6 K. (2.5 + 2.5)

Q9. Hexane and perfluorohexane show partial miscibility below 22.70 C. The critical concentration at the upper critical temperature is x = 0.355, where x is the mole fraction of C_6F_{14}. At 22.0 C the two solutions in equilibrium have x = 0.24 and x = 0.48, respectively, and at 21.5 C the mole fractions are 0.22 and 0.51. Sketch the phase diagram. Describe the phase changes that occur when perfluorohexane is added to a fixed amount of hexane at (a) 23 C, (b) 22 C. (1+2)

Q10. The steam distillation of chlorobenzene is observed to occur at a temperature of 90.6 C when the total pressure is 1.0 atm. Assuming complete immiscibility of these liquids, calculate the mass of chlorobenzene in 0.1 kg of distillate. The vapor pressure of water at 90.6 C is 538.9 torr. (2)

Q11. A certain substance exists in two solid modifications **A** and **B**, as well as liquid and vapor. Under a pressure of 1 atm, **A** is more stable at lower temperatures than **B**, which melts at a still higher temperature to form the liquid, **A** is denser than the liquid, but **B** is less dense than the liquid. No metastable equilibria are observed. Sketch the pressure temperature phase diagram indicating the significance of each point, line and region. Include in your diagram every triple point that can be observed. (5)

Q12. Assuming ideal behaviour, determine ΔG_{mix} and ΔS_{mix} when a solution of 1 mol of liquid M in 9 mol of liquid N is mixed with 10 mol of liquid N at 300 K. (2)

Q13. The empirical expression for the vapor pressure is given by:

$P_1 = x_1 P_1^* e^{\alpha x_2^2 + \beta x_2^3 + \cdots}$ is sometimes called the Margules equation. Using Gibbs-Duhem equation to prove that there can be no linear term in the exponential factor in P_1, for otherwise P_2 will not satisfy Henry's law as $x_2 \to 0$. (3)

Q14. Find relationship between activity, its molality, and its mean ionic activity coefficient for the following strong electrolytes (in aqueous soln): KCl, CaCl$_2$, LaCl$_3$, Na$_2$SO$_4$, ZnSO$_4$, Na$_3$Fe(CN)$_6$ (2)

Q15. Consider the reaction described by
Cl$_2$(g) + Br$_2$ (g) $\rightleftharpoons$ 2 BrCl (g) at 500 K and a total pressure of 1 bar. Suppose that we start with one mole each of Cl$_2$ (g) and Br$_2$ (g) and no BrCl (g). Show that

$$G(\xi) = (1-\xi)G_{Cl_2}^0 + (1-\xi)G_{Br_2}^0 + 2\xi G_{BrCl}^0 + 2(1-\xi)RT\ln\frac{1-\xi}{2} + 2\xi RT\ln\xi \;,$$ where ξ is the extent of

reaction. Given that G_{BrCl}^0 = -3.694 kJ/mol at 500 K, plot $G(\xi)$ versus ξ. Differentiate $G(\xi)$ with respect to ξ and show that the minimum value of $G(\xi)$ occurs at ξ_{eq} = 0.549. Also show that

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_r G^0 + RT\ln\frac{P_{BrCl}^2}{P_{Cl_2}P_{Br_2}} \text{ and that } K_p = \frac{4\xi_{eq}^2}{(1-\xi_{eq})^2} = 5.9 \qquad (5)$$

Q16. At 353 K, the v.p. of pure **X** and **Y** are 22.93 and 16.93 kN/m^2, respectively and these compounds form a nearly ideal solution. 3 mol of **X** and 2 mol of **Y** are equilibrated at 353 K and a total pressure of 20.4 kN/m^2. (a) What is the composition of the liquid phase? (b) What amount of each component is present in the vapor phase? (3)

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(Please attach the question paper with the answer script. Use the remaining space for rough)