

- 1) The electromotive force of the cell:  $\text{Cd}|\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}; \text{sat. solution}|\text{AgCl}|\text{Ag}$  at  $25^\circ\text{C}$  is  $0.67533\text{ V}$ , and the temperature coefficient is  $-6.5 \times 10^{-4}\text{ VK}^{-1}$ . Calculate the value of  $\Delta G$ ,  $\Delta S$ , and  $\Delta H$  at  $25^\circ\text{C}$  for the reaction  

$$\text{Cd}(\text{cr}) + 2\text{AgCl}(\text{cr}) = 2\text{Ag}(\text{cr}) + \text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}(\text{cr}) \quad (16\%)$$
- 2) Assuming that toluene vapor is a perfect gas and that the volume of the liquid is negligible. (a) Calculate the work done against the atmosphere when 1 mol of toluene is vaporized at its boiling point,  $111^\circ\text{C}$ . The heat of vaporization at this temperature is  $361.9\text{ Jg}^{-1}$ . For the vaporization of 1 mol, calculate (b)  $q$ , (c)  $\Delta H$ , (d)  $\Delta U$ , (e)  $\Delta G$ , and (f)  $\Delta S$ . (16%)
- 3) The measured density of an equilibrium mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  at  $15^\circ\text{C}$  and  $1.013\text{ bar}$  is  $3.62\text{ gL}^{-1}$ , and the density at  $75^\circ\text{C}$  and  $1.013\text{ bar}$  is  $1.84\text{ gL}^{-1}$ . What is the enthalpy change of the reaction  $\text{N}_2\text{O}_4(\text{g}) = 2\text{NO}_2(\text{g})$ ? (17%)
4. Suppose the density of a binary solution is known as a function of mole fraction composition. (a) Show that the partial molar volume of component 1 will be given by the expression  

$$\bar{V}_1 = [ \rho M_1 - X_2(X_1 M_1 + X_2 M_2) (\partial \rho / \partial X_1)_{T,P} ] / \rho^2$$
 where  $M_1$  and  $M_2$  denote molecular weights. (b) The density of methanol (1) and water (2) mixtures at  $25^\circ\text{C}$  is  

$$\rho(\text{g/mL}) = 0.9971 - 0.18527X_1 + 0.22013X_1^2 - 0.60418X_1^3 + 0.53912X_1^4 - 0.18012X_1^5$$
 Calculate the partial molar volume of methanol at  $X_1 = 0.5$  (18%)
- 5). A fresh metal surface with  $10^{15}$  atoms per square centimeter is prepared. This surface is exposed to oxygen at  $10^{-2}\text{ Pa}$ . If every oxygen molecule that strikes the surface reacts so that there is one oxygen atom per metal atom in the surface, how long will it take for half of the surface to become oxidized at  $25^\circ\text{C}$ ? (16%)
- 6). An imidazole buffer of pH 7 containing  $0.05\text{ mole L}^{-1}$  imidazole has a relaxation time of  $2.9 \times 10^{-9}\text{ s}$  at  $25^\circ\text{C}$ , what are the values of the rate constants for the reaction  

$$\text{C}_3\text{N}_2\text{H}_4 + \text{H}^+ \xrightleftharpoons[k_{-1}]{k_1} \text{C}_3\text{N}_2\text{H}_5^+$$
 The  $\text{pK}$  for the imidazole at this temperature is 7.21. (17%)