

1. A gas obeys the van der Waals equation. Derive the relation for work done if the gas expands isothermally and reversibly from volume  $V_1$  to  $V_2$ . (10%)

2. Prove that, for any substance,

$$C_p - C_v = \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_p \quad (10\%)$$

3. Please derive an expression of  $\alpha = 1/T$  where  $\alpha$  is the thermal expansion coefficient of perfect gas and  $T$  is the temperature. (10%)
4. Suppose you have a weight on a rubber band so as to keep it under constant tension. If you then heat the rubber band, will the weight rise or fall? Give a thermodynamic answer. (10%)
5. The chemical reaction in a "lead storage" cell of a car battery during charging involves the reduction of  $\text{PbSO}_4(\text{s})$  to  $\text{Pb}(\text{s})$  and the oxidation of  $\text{PbSO}_4(\text{s})$  to  $\text{PbO}_2(\text{s})$ , both reactions occurring in the presence of  $\text{H}_2\text{SO}_4(\text{aq})$ . Please write the balanced reaction. (10%)

6. For an experiment to determine the Osmotic pressure of a solution, at equilibrium the solvent molecules pass through the membrane raising the level of the solution to height,  $h$ . At this height, the Osmotic pressure of the solution is equal to the hydrostatic pressure. If the solution is ideal, show that

$$RT \ln(P/P^\circ) = -Mgh$$

where  $P$  and  $P^\circ$  are the vapor pressure of the solution and the pure solvent respectively.  $M$  is the molecular weight of the solvent. (15%)

7. A certain liquid solution contains two components 1 and 2. Component 1 follows Henry's law for the mole fraction range  $0 \leq x_1 \leq a$  at constant temperature and at low pressure. Show that component 2 must follow Raoult's law for the mole fraction range  $(1-a) \leq x_2 \leq 1$ . (10%)
8. (a) A solution contains  $n_1$  moles of component 1 and  $n_2$  moles of component 2. Their molecular weights are  $M_1$  and  $M_2$ , respectively. Please provide the expression for the partial molar volume  $\bar{V}_2$  of component 2 in terms of  $n_1$ ,  $n_2$ , the density  $\rho$  with respect to  $n_2$  at constant  $n_1$ , and the molecular weights.  
(b) Let  $x_1$  and  $x_2$  be the mole fractions of 1 and 2 in the solution. Show that

$$\bar{V}_2 = \frac{M_2}{\rho} - (M_1 x_1 + M_2 x_2) \frac{x_1}{\rho^2} \frac{d\rho}{dx_2} \quad (15\%)$$

9. Please define the following terms: (10%)
- (a) Fugacity (b) Gibbs-Duhem equation  
(c) Maxwell relations (d) Nernst equation  
(e) Thermodynamic Second Law