

科目 物理化學(熱力學) 類組別 DA 共 1 頁第 1 頁 *請在試卷答案卷(卡)內作答

1. A liquid has vapor pressures P_1 and P_2 respectively at the temperatures T_1 and T_2 . Calculate the standard enthalpy and entropy of vaporization of this liquid. Also estimate its normal boiling point. (15%)

2. It is known that the autoprotolysis constant of water is equal to 10^{-14} at 298 K.

(a) Calculate the standard reduction potential of the half-reaction at this temperature,



(b) What is the reduction potential when $pH = 7$. (5%)

3. The first law of thermodynamics for a reversible process in a closed system can be represented by $dU = dq_{rev} - PdV$, where U, P , and V are the internal energy, pressure, and volume of the system, respectively, and q_{rev} is the heat absorbed by the system.

(a) Show that $dq_{rev} = C_V dT + \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] dV$ where C_V is the heat capacity at constant volume. (10%)

(b) Show that dq_{rev} is not an exact differential, while dq_{rev}/T is an exact differential. (10%)

4. For a homogeneous mixture system containing n_A moles of A and n_B moles of B, the Gibbs free energy of the system can be represented by $G = n_A \mu_A + n_B \mu_B$, where μ_A and μ_B are the chemical potentials of A and B, respectively.

(a) Show that the volume of the system, V , can be expressed by

$$V = n_A V_{A,m} + n_B V_{B,m},$$

where $V_{A,m}$ and $V_{B,m}$ are the partial molar volume of A and B, respectively. (10%)

(b) Prove that $n_A dV_{A,m} + n_B dV_{B,m} = 0$ (10%)

5. It is known that one mole of a certain gas obeys a simplified van der Waal equation of state,

$$P(V-b) = RT.$$

(a) If the gas undergoes a reversible adiabatic expansion from (P_1, V_1, T_1) to (P_2, V_2, T_2) , write an equation which relates these two set of state variables. (10%)

(b) What is the work done by the system in (a). (10%)

(c) Prove for this gas heat capacity at constant volume, C_V , is independent of volume. (10%)