國立成功大學75學年度化學工程研究所考試(物理化學 試題) 共 1 頁 第 1 頁

1) One mole of ideal gas expands isothermally at 273.15 K from $V_1 = 22.414$ L to a final volume $V_2 = 44.828$ L, against a constant external pressure of 0.5 atm. Calculate $\Delta U$, $q$, $w$, $\int T dS$ and $\int P dV$. Verify that $\Delta U = \int T dS - \int P dV$, but that $q \neq \int T dS$ and $w \neq \int P dV$ (14%)

2) Two flasks are connected with a stopcock. The first flask contains 1 mol He at 4 atm. The second flask contains 1 mol Ar at 0.25 atm. The temperature is held constant at 300K, and the stopcock is opened. Calculate $\Delta S$ (15%)

3) If 68.4 g of sucrose ($M = 342\ g\ mol^{-1}$) is dissolved in 1000 g of water: (a) What is the vapor pressure at 20°C? (b) What is the freezing point? The vapor pressure of water at 20°C is 2.3149 kPa. The enthalpy of fusion of water at 273.15K is 6.00 kJ $mol^{-1}$. (14%)

4) Consider the gaseous decomposition reaction of cyclopentene to $H_2$ and cyclopentadiene:

$$c\text{-}C_5H_8 = H_2 + c\text{-}C_5H_6$$

(a) How is $dP/dt$ related to $-dP_{C_5H_8}/dt$? (b) If the reaction is first-order, what are the units on $k$? (c) Derive the first-order integrated rate equation in terms of $P_{C_5H_8,0}$ and $P$ (15%)

5) The gas-phase reaction $Cl_2 + CH_4 \rightarrow CH_3Cl + HCl$ proceeds by a free-radical chain reaction in which the chain propagators are Cl and $CH_3$ (but not H), and the chain-ending step is $2Cl \rightarrow Cl_2$. Write the mechanism, identify the initiation reaction and the chain-propagation steps, and obtain an expression for the rate of the overall reaction. (14%)

6) The influence of ionic strength on the rate constant as predicted by the transition-state theory is known as the primary salt effect. Discuss the influence on $k$ if ions A and B have like charges. (14%)

7) A moving boundary experiment is carried out with a 0.1 mol $L^{-1}$ solution of hydrochloric acid at 25°C ($\kappa = 4.24\ \Omega^{-1} m^{-1}$). Sodium ions are caused to follow the hydrogen ions. Three milliamperes is passed through the tube of 0.3 $cm^2$ cross-sectional area, and it is observed that the boundary moves 3.08 cm in 1 hr. Calculate (a) the hydrogen ion mobility, and (b) the chloride ion mobility. (14%)