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研究所招生考試

1. Show that the competitive adsorption of two types of molecules, A and B, on the same surface:

$$\theta_A = \frac{K_A[A]}{1+K_A[A]+K_B[B]} \quad \& \quad \theta_B = \frac{K_B[B]}{1+K_A[A]+K_B[B]}$$

where K_A and K_B are the equilibrium constants corresponding to A and B. (12%)

2. Show that the Boyle temperature of a van der Waals gas can be expressed as $T_B = \frac{a}{bR}$. (7%)

3. An aqueous solution contains 1.0 g of sodium chloride in 100 g water and the freezing point is –0.636℃. For an aqueous solution containing 3.6 g unknown solute in 100 g water without the presence of dissociation or association, its freezing point is –0.2℃ Calculate the freezing point depression constant of water and the molar mass of the unknown solute. (12%)

4. The standard electromotive force (E°) of the cell

$$Zn(s) \mid ZnCl_2(0.05 \text{ mol kg}^{-1}) \mid AgCl(s) \mid Ag$$

is 0.9854 volts at 25℃. (a) Write the half-cell reactions and the cell reaction. (b) Estimate the mean ionic activity coefficient of 0.05 mol kg^{-1} $ZnCl_2$ using Debye-Hückel theory. (c) Calculate the electromotive force (E) and the reaction Gibbs energy of the cell (ΔG). (12%)

5. One mole of ideal monatomic gas at 0℃ and 1 bar is put through each of the reversible steps below. Calculate q_m, w_m, ΔU_m, ΔH_m, and ΔS_m. ($R = 8.314\ J\ mol^{-1}K^{-1}$)

(a) cooling at constant volume to -100℃

(b) constant pressure heating to 100℃

(c) adiabatic expansion to 0.1 bar (15%)

6. For a reversible first-order reaction $A \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} B$

$k_1 = 0.1\ s^{-1}$ and $[B]_{eq}/[A]_{eq} = 3$. If the rate constants k_1 and k_{-1} were measured by the T-jump technique, derive the relaxation time and calculate its value. (12%)

7. (a) For an ideal solution, $\Delta_{mix}V = 0$ and $\Delta_{mix}H = 0$, but $\Delta_{mix}G \neq 0$ and $\Delta_{mix}S \neq 0$. Why? Give the reason(s) for each. (8%)

(b) Induction period (3%)

(c) Joule-Thomson inversion temperature (3%)

(d) What is Trouton's rule and why it holds fairly closely for only normal liquids? (4%)

(e) Osmosis and osmotic pressure (4%)

(f) Plot the dependence of Z (compression factor) on P (pressure) for a real gas at a constant temperature below its Boyle temperature, and give the reason(s) causing the different tendencies at low P and high P. (4%)

(g) Illustrate the potential-energy surface for a reaction $A + B - C \rightarrow A - B + C$, showing contour lines connecting positions of equal energy. (4%)