1. Consider first order parallel reactions

$$A \xrightarrow{k_1} B \quad and \quad A \xrightarrow{k_2} C$$

The initial concentration of A is $[A]_0$. Neither B or C are present initially.

(a) Derive the expressions for the variations of [A], [B], and [C] with time.

(b) Show that the activation energy E for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by

$$E = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

(15%)

2. According to Langmuir adsorption isotherm, 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 θ_A and θ_B are the fractions of a surface covered by adsorbed molecules A and B, respectively, and K_A and K_B are the equilibrium constants corresponding to A and B.

(13%)

3. One mole of ideal gas expands isothermally at 27℃ into an evacuated vessel so that the pressure drops from 10 to 1 bar. Calculate q, w, ΔU, ΔH, ΔS, ΔA, and ΔG.

(14%)

4. One mole of liquid water at 0℃ is placed in a freezer that is maintained at -10℃. Calculate the change in entropy in the system and in surroundings (the freezer), and the net entropy change. $C_{p,w}(water) = 75.3JK^{-1}mol^{-1}$, $C_{p,w}(ice) = 37.7JK^{-1}mol^{-1}$, $\Delta_{fus}H = 6.02kJmol^{-1}$ at $0°C$.

(13%)

5. Design a cell without liquid junction that could be used to determine the activity coefficient of aqueous solution of NaOH. Give the equations relating electromotive force to the mean ionic activity coefficient at 25℃.

(15%)

6. (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? (6%)

(b) The residual entropy of $N_2O(cr)$ at 0 K is about 5.8 $J\ mol^{-1}K^{-1}$. Please show that the value is consistent with that the calculated value based on the statistic probability. (cr : crystalline) (6%)

(c) Explain the meanings of the three terms: $\left(\frac{\partial U}{\partial V}\right)_T$, $P\left(\frac{\partial V}{\partial T}\right)_P$, and $\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$. (6%)

(d) What is Trouton's rule and why it holds fairly closely for only normal liquids? (6%)

(e) Describe the phenomenon of Retrograde condensation. (6%)

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