第一部分單選題(1-6)，每題 5 分，請務必於試卷第一頁「選擇題作答區」依序作答。

1. The van der Waals equation is written as $\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT$. What is the change in the internal energy $\Delta\underline{U}$ in the isothermal expansion from $\underline{V}_1$ to $\underline{V}_2$?
(A) $a\left(\frac{1}{\underline{V}_2}-\frac{1}{\underline{V}_1}\right)$, (B) $a\left(\frac{1}{\underline{V}_1}-\frac{1}{\underline{V}_2}\right)$, (C) $\frac{a}{\underline{V}^2}$, (D) 0, (E) none of the above.

2. Continue from problem 1, what is the change in the entropy $\Delta\underline{S}$ in the isothermal expansion from $\underline{V}_1$ to $\underline{V}_2$?
(A) $\frac{R}{\underline{V}-b}$, (B) 0, (C) $R\ln\frac{(\underline{V}_2-b)}{(\underline{V}_1-b)}$, (D) $R\ln\frac{(\underline{V}_1-b)}{(\underline{V}_2-b)}$, (E) none of the above.

3. The molar excess Gibbs free energy for a binary system of 1 and 2 is described by $\frac{\underline{G}^{ex}}{RT}=0.415x_1x_2$ at 50°C from the vapor-liquid equilibrium. The vapor pressures of pure 1 and pure 2 are given by $\ln P_1^*=11.92-\frac{4050}{T}$ and $\ln P_2^*=12.12-\frac{4050}{T}$, where P_i^* is in bar and T in K. Assume ideal gas behavior for the vapor phase, what is the azeotropic composition (x_1,x_2) of the system at 50°C? At the azeotrope, $\left(\frac{\partial P}{\partial x_i}\right)_T=0$ and $x_i=y_i$ for i=1 or 2.
(A) (0.42,0.58), (B) (0.58,0.42), (C) (0.26,0.74), (D) (0.74,0.26), (E) (0.5,0.5).

4. Continue from problem 3, if we express the molar excess Gibbs free energy as $\frac{\underline{G}^{ex}}{RT}=gx_1x_2$, which of the following values of g for the system fails to form an azeotrope?
(A) 0.15, (B) 0.25, (C) 0.35, (D) 0.45, (E) 0.55.

5. Find ΔG when 0.2 mole of He(g) is mixed at constant T and P with 0.3 mol of O$_2$(g) at 27°C. Assume ideal gases. Choose the closest value.
(A) 1700 J, (B) 840 J, (C) 0 J, (D) −840 J, (E) −1700 J.

6. For H$_2$O(s) at 0°C and 1 atm and H$_2$O(l) at 0°C and 1 atm, which pair of quantities must be equal for the two phases?
(A) μ and $\underline{V}$, (B) $\underline{U}$ and $\underline{V}$, (C) $\underline{U}$ and $\underline{A}$, (D) $\underline{S}$ and μ, (E) μ and $\underline{G}$.

第二部分問答或演算題(7-10 大題)，每小題 5 分。 ※ 注意：請於試卷內之「非選擇題作答區」依序作答，並應註明作答之大題及小題題號。

7. One mole of an ideal gas with $C_V=\frac{3}{2}R$ (R: gas constant) is initially at 10 bar and 298 K. It is allowed to expand reversibly against a constant external pressure of 2 bar to a final pressure of 2 bar. During this process, the temperature of the gas falls to 253.2 K. Assume that the thermal surroundings remain at 298 K throughout. Find the following properties for the process. Assume that the process is accomplished by isothermal expansion (path 1) followed by isobaric cooling (path 2).
(a) $\Delta\underline{U}$ (molar internal energy change of the system)
(b) $\Delta\underline{H}$ (molar enthalpy change of the system)
(c) $\Delta\underline{S}$ (molar entropy change of the system)
(d) $\Delta\underline{S}_{therm}$ (molar entropy change of the surroundings)

見背面

8. Consider a liquid-phase, isothermal, irreversible first-order reaction

$$A \rightarrow B$$

with rate law $-r_A = kC_A$. Pure A is fed at steady state with $k = 0.1\ \mathrm{min}^{-1}$, $C_{A0} = 1\ \mathrm{mol/L}$, $v_0 = 1\ \mathrm{L/min}$. Assume constant-density conditions.

Two reactors, one CSTR and one PFR, are connected in series to achieve an overall conversion $X_{total} = 0.9$. The conversion at the exit of the first reactor is 0.45.

(a) Compute the total reactor volume required for the sequence where the CSTR is followed by the PFR.

(b) Compute the total reactor volume required for the sequence where a PFR is followed by a CSTR.

(c) Which sequence minimizes the total volume? Use a Levenspiel plot $(1/(-r_A)$ vs. $X)$ to justify your answer.

9. Consider the gas-phase, isothermal reaction $A \rightarrow B$ using a metal catalyst. The proposed reaction mechanism is as follows

Adsorption of A: $A + S \rightleftharpoons AS$

Surface Reaction: $AS \rightarrow B + S$ (Rate-determining step)

Here S denotes an empty active site on the catalyst surface and AS denotes species A adsorbed on an active site. Let P_i be the partial pressure of species i, K_A be the adsorption equilibrium constant for species A, k_s be the surface reaction rate constant, and C_T be the total concentration of active sites (total sites).

(a) Derive the rate law expression for $-r_A'$ based on the proposed mechanism.

(b) The catalyst undergoes deactivation according to the rate law $da/dt = -k_d a$, where a is the catalyst activity ($a = 1$ at $t = 0$) and k_d is the deactivation constant. Derive the time-dependent reaction rate expression.

10. Consider the following reaction network taking place in an isothermal batch reactor:

$$1.\ A \overset{k_1}{\rightarrow} B\ ;\quad r_1 = k_1 C_A$$

$$2.\ A \overset{k_2}{\rightarrow} C\ ;\quad r_2 = k_2 C_A$$

$$3.\ B \overset{k_3}{\rightarrow} D\ ;\quad r_3 = k_3 C_B$$

$$4.\ B \overset{k_4}{\rightarrow} E\ ;\quad r_4 = k_4 C_B$$

All reactions follow first-order kinetics where the rate constants follow Arrhenius behavior. At $t = 0$, $C_{A0} = 1.0$ mol/L, and the concentrations of $B, C, D,$ and E are zero.

(a) Derive the expression for the ratio C_A/C_B at the time when the concentration of B reaches its maximum $C_{B,max}$.

(b) Derive the expression of time (t_{max}) required to reach the maximum concentration of B.

(c) Given $k_1 = 0.4$, $k_2 = 0.1$, $k_3 = 0.2$, and $k_4 = 0.1$ (all in min^{-1}), calculate the concentration C_B when the conversion of A reaches 90%.

(d) Assume that the activation energies follow the order $E_2 > E_1 > E_3 > E_4$. How would decreasing the temperature affect the selectivity of D relative to E $(S_{D/E})$?

(e) Now consider a specific case where, for simplicity, the pre-exponential factors for all four reactions are identical. Given that the activation energies are $E_1 = 30, E_2 = 90, E_3 = 4,$ and $E_4 = 3$ kJ/mol, how would decreasing the temperature affect $C_{B,max}$?

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