

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 $(P + \frac{n^2 a}{V^2})(V - nb) = nRT$. What is the change in the internal energy ΔU in the isothermal expansion from V_1 to V_2 ?

(A) $a(\frac{1}{V_2} - \frac{1}{V_1})$, (B) $a(\frac{1}{V_1} - \frac{1}{V_2})$, (C) $\frac{a}{V^2}$, (D) 0, (E) none of the above.

2. Continue from problem 1, what is the change in the entropy ΔS in the isothermal expansion from V_1 to V_2 ?

(A) $\frac{R}{V-b}$, (B) 0, (C) $R \ln \frac{(V_2-b)}{(V_1-b)}$, (D) $R \ln \frac{(V_1-b)}{(V_2-b)}$, (E) none of the above.

3. The molar excess Gibbs free energy for a binary system of 1 and 2 is described by $\frac{G^{ex}}{RT} = 0.415x_1x_2$ 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, $(\frac{\partial P}{\partial x_i})_T = 0$ 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 $\frac{G^{ex}}{RT} = gx_1x_2$, 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 O₂(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 H₂O(s) at 0°C and 1 atm and H₂O(l) at 0°C and 1 atm, which pair of quantities must be equal for the two phases?

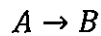
(A) μ and \underline{V} , (B) \underline{U} and \underline{V} , (C) \underline{U} and \underline{A} , (D) \underline{S} and μ , (E) μ and \underline{G} .

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) ΔU (molar internal energy change of the system)
 (b) ΔH (molar enthalpy change of the system)
 (c) ΔS (molar entropy change of the system)
 (d) ΔS_{therm} (molar entropy change of the surroundings)

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

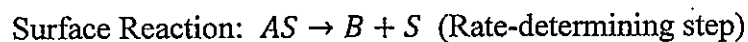
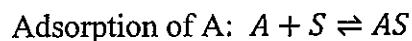


with rate law $-r_A = kC_A$. Pure A is fed at steady state with $k = 0.1 \text{ min}^{-1}$, $C_{A0} = 1 \text{ mol/L}$, $v_0 = 1 \text{ L/min}$. Assume constant-density conditions.

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.

- Compute the total reactor volume required for the sequence where the CSTR is followed by the PFR.
- Compute the total reactor volume required for the sequence where a PFR is followed by a CSTR.
- Which sequence minimizes the total volume? Use a Levenspiel plot ($1/(-r_A)$ vs. X) to justify your answer.

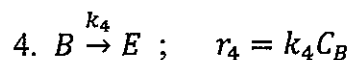
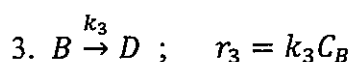
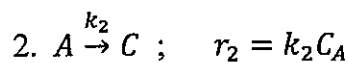
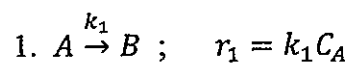
9. Consider the gas-phase, isothermal reaction $A \rightarrow B$ using a metal catalyst. The proposed reaction mechanism is as follows



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).

- Derive the rate law expression for $-r'_A$ based on the proposed mechanism.
- 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:



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

- Derive the expression for the ratio C_A/C_B at the time when the concentration of B reaches its maximum $C_{B,max}$.
- Derive the expression of time (t_{max}) required to reach the maximum concentration of B .
- 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%.
- 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 ($S_{D/E}$)?
- 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 $E_4 = 3 \text{ kJ/mol}$, how would decreasing the temperature affect $C_{B,max}$?