1. (7%) The reaction \(2\text{NOBr}(g) \rightarrow 2\text{NO}(g) + \text{Br}_2(g)\) is a second-order reaction with a rate constant of \(0.80 \text{ M}^{-1} \text{ s}^{-1}\) at \(11^\circ\text{C}\). If the initial concentration of NOBr is \(0.0440 \text{ M}\), the concentration of NOBr after 6.0 seconds is ______.

2. (8%) When aqueous A and aqueous B (\(C_{A0} = C_{B0}\)) are brought together they react in two possible ways:
\[
\begin{align*}
\text{A} + \text{B} & \rightarrow \text{R} + \text{T}, \quad r_{R} = 50 \text{ C}_{A} \text{ mol/m}^{3} \text{hr} \\
\text{A} + \text{B} & \rightarrow \text{S} + \text{U}, \quad r_{S} = 100 \text{ C}_{A} \text{ mol/m}^{3} \text{hr}
\end{align*}
\]
to give a mixture whose concentration of active components (A, B, R, S, T, U) is \(C_{\text{total}} = C_{A0} + C_{B0} = 60 \text{ mol/ m}^{3}\). Find the size of reactor needed and the R/S ratio produced for 90% conversion of an equimolar feed of \(F_{A0} = F_{B0} = 300 \text{ mol/hr}\) in a mixed flow reactor.

3. (10%) The kinetics of the aqueous-phase decomposition of A is investigated in two mixed flow reactors in series, the volume of the second reactor is four time greater than that of the first reactor. At steady state with a feed concentration of 1 mol A/liter and mean residence time of 100 seconds in the first reactor, the concentration in the first reactor is 0.5 mol A/liter and in the second is 0.125 mol A/liter. Find the kinetic equation for the decomposition.

4. (25%) The principles of the kinetics of enzyme reactions were suggested by Levine and LaCourse. The kinetics can be used to design artificial kidney to remove nitrogenous waste products. In general, this enzymatic reaction involves the enzyme-substrate complex, that can be treated as the following sequence of elementary reactions.
\[
\begin{align*}
\text{E} (\text{enzyme}) + \text{S} (\text{substrate}) & \rightarrow \text{E.S} (\text{complex}) [\text{Note: Reversible reaction}] \\
\text{E.S} + \text{H}_{2}\text{O} & \rightarrow \text{P} (\text{product}) + \text{E}
\end{align*}
\]
Note that it is difficult to measure either the concentration of free enzyme (E) or bound enzyme (E.S). But it is relatively easy to measure the total concentration of enzyme (E).

(1) (10%) Please derive the rate law of this enzymatic reaction \(E + S \rightarrow P + E\)

(2) (10%) Comment on the reaction order at low substrate (S) concentration and at high substrate (S) concentration

(3) (5%) Derive the relation between the batch reactor time and a certain conversion \(X\) in this enzymatic reaction.

5. (7%) Nitrogen flows at steady state through a horizontal, insulated pipe with the inner diameter of 4 cm. The pressure drops when the nitrogen flows through a partially opened valve. The pressure, temperature, and average velocity of the nitrogen just upstream the valve are 700 kPa, 50°C, and 6 m/s, respectively. Given that the pressure just downstream the valve is 140 kPa, along with the assumption of \(PV/T = \text{constant}\), \(C_{r} = 2.5R\), and \(C_{r} = 3.5R\), determine the temperature of the nitrogen at the same point. Make your assumption and reason your calculation explicitly.

6. Answer the following short questions:

(1) (6%) Explain the second law of thermodynamics and use it to prove the maximal efficacy of a cyclically run heat engine being \((T_{1} - T_{2})/T_{1}\), where \(T_{1}\) and \(T_{2}\) are the temperatures for the heat inflow to and heat outflow from the engine, respectively.
(2) (6%) Use the relation \( G = VdP - SdT \), where \( G \) is the molar Gibbs energy, \( V \) is the molar volume, and \( S \) is the molar entropy, to derive the Clapeyron equation \( \frac{dP_{\text{eq}}}{dT} = \frac{\Delta H}{T\Delta V} \), where \( P_{\text{eq}} \) is the equilibrium coexistence pressure and \( \Delta H \) and \( \Delta V \) are the molar enthalpy difference and molar volume difference between the coexisting phases, respectively. Use the Clapeyron equation to explain why the melting temperature of ice decreases with increasing pressure.

(3) (6%) Prove that the equilibrium condition for a closed system at constant pressure and temperature is that the Gibbs energy reaches its minimum, and explain why molecular self-assembling occurs even though the configurational entropy apparently decreases in the process.

7. (25%) Solubility of a solid solute \( (x_i) \) at a given temperature \( T \) can be estimated from the following equation:

\[
\ln(x_i) = \frac{\Delta_{\text{h fus}} H_i}{RT} \left( 1 - \frac{T}{T_{m,i}} \right)
\]

where \( \Delta_{\text{h fus}} H_i \) and \( T_{m,i} \) are melting enthalpy and melting temperature of substance \( i \); \( \gamma_i \) is the activity coefficient of substance \( i \) in the mixture; \( R \) is the ideal gas constant.

(a) (5%) Please estimate the ideal solubility of naphthalene in neopentane at 300 K. (\( \Delta_{\text{h fus}} H_i = 18.804 \text{ kJ/mol} \) and \( T_{m,i} = 80.2 ^\circ \text{C} \) for naphthalene)

(b) (10%) The Hildebrand solubility parameter \( (\delta) \) is a good indication of solubility and can be determined from the square root of the cohesive energy density:

\[
\delta_i = \sqrt{\frac{\Delta_{\text{vap}} U_i}{\gamma_i}} = \sqrt{\frac{\Delta_{\text{vap}} H_i - RT}{\gamma_i}}
\]

where \( \Delta_{\text{vap}} H_i \) and \( \gamma_i \) is the heat of vaporization and liquid molar volume of substance \( i \). Please estimate the Hildebrand solubility parameter in unit of \( (\text{J/cm}^3)^{1/2} \) for naphthalene with the following information: (1) sublimation pressure: \( \log_{10} P_{\text{sub}} \) (\( P \) in bar) = 8.722 - \( 3783/T \) (\( T \) in K) and (2) liquid molar volume = 124 \( \text{cm}^3/\text{mol} \).

(c) (10%) Please estimate the solubility of naphthalene in neopentane by using the regular solution equations to model the non-ideality of the binary system considered. The regular solution equations:

\[
RT \ln \gamma_1 = \gamma_i \Phi_i \left( \delta_1 - \delta_2 \right)^2, \quad RT \ln \gamma_2 = \gamma_2 \Phi_i \left( \delta_1 - \delta_2 \right)^2, \quad \text{and} \quad \Phi_i = \frac{x_i \gamma_i}{\sum_j x_j \gamma_j}.
\]

The Hildebrand solubility parameter and liquid molar volume for neopentane are 12.7 \( (\text{J/cm}^3)^{1/2} \) and 124 \( \text{cm}^3/\text{mol} \). (Hint: Use an iterative procedure to determine the solubility with the ideal solubility as the initial guess.)