1. N$_2$O$_4$ dissolved and reacted in water to form HNO$_3$ and NO, and the over-all reaction is in the following:

$$1.5 \text{N}_2\text{O}_4 + \text{H}_2\text{O} \leftrightarrow 2 \text{HNO}_3 + \text{NO}$$

and the equilibrium constant can be expressed:

$$K_e = \frac{(\text{HNO}_3)^2 (\text{NO})}{(\text{N}_2\text{O}_4)^{1.5} (\text{H}_2\text{O})}$$

In a constant water concentration, the relationship between the net rate equation and the concentrations is:

$$r_{\text{net}} = r_{\text{forward}} - r_{\text{reverse}} = k_1 (\text{N}_2\text{O}_4) - k_1 (\text{N}_2\text{O}_4)^{1/4} (\text{NO})^{1/2}$$

Please prove that

$$\frac{k_1}{k_1} = (K_e)^{1/2} \quad (5 \text{ 分})$$

2. Please using Pseudo-Steady-State Approximation method under the condition of $[\text{Cl}]/[\text{O}_3] < 1$, and determine the rate expression of the following Ozone decomposition reaction:

$$\text{Cl} + \text{O}_3 \rightarrow \text{O}_2 + \text{ClO}$$

and the rate constants are the function of the temperature:

$$k_1 = 5 \times 10^{-11} \exp\left(-\frac{140}{T}\right) \text{cm}^3/\text{sec} \quad \text{and} \quad k_2 = 1.1 \times 10^{-10} \exp\left(-\frac{220}{T}\right) \text{cm}^3/\text{sec}$$

If the non-catalytic reaction rate, $r_{\text{nc}} = k[\text{O}][\text{O}_3]$ with the rate constant of

$$k = 1.9 \times 10^{-11} \exp\left(-\frac{2300}{T}\right) \text{cm}^2/\text{sec}$$

assuming $[\text{O}] \ll [\text{O}_3]$ and calculate the ratio of the $r_c$ (catalytic reaction) and $r_{nc}$ (non-catalytic reaction). (10 分)
3. The catalytic reaction

\[ A \rightarrow 4R \]

is studied in a plug flow reactor using various amounts of catalyst and 20 liters/hr of pure A feed at 3.2 atm and 117\(^\circ\)C. The conversions of A in the effluent stream is recorded for the various runs as follows.

<table>
<thead>
<tr>
<th>Runs</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst weight, kg</td>
<td>0.020</td>
<td>0.040</td>
<td>0.080</td>
<td>0.160</td>
</tr>
<tr>
<td>Conversion, (X_A)</td>
<td>0.08</td>
<td>0.14</td>
<td>0.24</td>
<td>0.38</td>
</tr>
</tbody>
</table>

(a) Find the rate equation for this reaction, using the integral method of analysis. (5%)  
(b) Repeat part (a), using the differential method of analysis. (5%)  
(c) What are the differences between these two methods? (5%)

4. The following irreversible first-order reactions occur at constant density:

\[ \begin{align*} 
A & \rightarrow B \\
B & \rightarrow C 
\end{align*} \]

\( k_1 = 0.15 \text{ min}^{-1} \) \( k_2 = 0.05 \text{ min}^{-1} \)

This reaction system is to be analyzed in continuous-flow reactors with a volumetric feed rate of 5 ft\(^3\)/min and feed composition \(C_A = C_{A_0}\) and \(C_B = C_{C} = 0\). For the highest production rate of B, which of the following reactors is preferable?

(a) A single-stirred tank of volume \(V=10 \text{ ft}^3\). (5%)  
(b) Two stirred tanks in series, each with a volume of 5 ft\(^3\). (5%)  
(c) Two stirred tanks in parallel, each of 5 ft\(^3\) volume and with the feed stream split equally between them. (5%)  
(d) A plug-flow (ideal tubular-flow) reactor with a volume \(V=10 \text{ ft}^3\). (5%)
5. A particular gas is enclosed in a cylinder with a moveable piston. It is observed that if the walls are adiabatic, a quasi-static increase in volume results in a decrease in pressure according to the equation
\[ P^3 V^5 = \text{constant} \quad (\text{for} \ Q = 0) \]
(a) Find the quasi-static work done on the system and the net heat transfer to the system in each of the two processes (\( ADB \) and the direct linear process \( AB \)) as shown in the following figure. (10%)

(b) A small paddle is installed inside the system and is driven by an external motor. The motor exerts a torque, driving the paddle at an angular velocity \( \omega \), and the pressure of the gas is observed to increase at a rate given by
\[ \frac{dP}{dt} = \frac{2 \omega}{3V} \cdot \text{torque} \]
Evaluate \( \Delta U_{BD} \) and \( \Delta U_{AD} \). (Hint: \( dU = \text{torque} \cdot d\theta \)) (10%)

6. A stream of 2 mol/s of air (assume ideal gas) goes from 1000 K and 10 bar to 500K and 5 bar while doing 5.0 kW of work. Surrounding are 300 K and 1 bar. What is the lost work for this process? (with negligible changes in kinetic and potential energies, for air \( C_p = 29.1 \text{ J/mol-K} \)) (15%)

7. The molar volume (\( \text{cm}^3 \text{ mol}^{-1} \)) of a binary liquid mixture at \( T \) and \( P \) is given by:
\[ V = 120 x_1 + 70 x_2 + (15x_1 + 8x_2)x_1x_2 \]
(a) Find expressions for the partial molar volumes of species 1 and 2 at \( T \) and \( P \). (5%)
(b) Show that these expressions satisfy the summability relation for \( V \). (5%)
(c) Show that these expressions satisfy the Gibbs/Duhem equation. (5%)