Part I. 化工熱力學 (50 %)

1. (18 points total; 6 points each) Answer concisely the following questions:
   (a) List all the possible work interaction terms in the energy balance equation for an open system and give briefly explanation.
   (b) Explain why the partial molar properties of water in aqueous solutions are not usually the same as the molar properties of pure water at the same condition.
   (c) What is the theoretical basis of group-contribution models for thermodynamic properties estimation? What are their advantages and limitations?

2. (11 points) Pure carbon dioxide was charged into a cell with a syringe pump. The volume of the fluid in the syringe pump can be read from an indicator accurate to ±0.01 cm³. Please calculate the total mass of carbon dioxide to be loaded after the following four charging steps:

<table>
<thead>
<tr>
<th>step</th>
<th>T (K)</th>
<th>P_i (bar)</th>
<th>P_f (bar)</th>
<th>V_i (cm³)</th>
<th>V_f (cm³)</th>
<th>charging time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>298.2</td>
<td>100</td>
<td>150</td>
<td>100.00</td>
<td>92.25</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>298.2</td>
<td>150</td>
<td>100</td>
<td>92.25</td>
<td>83.79</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>298.2</td>
<td>100</td>
<td>250</td>
<td>83.79</td>
<td>72.40</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>298.2</td>
<td>250</td>
<td>100</td>
<td>72.40</td>
<td>65.50</td>
<td>15</td>
</tr>
</tbody>
</table>

where the subscripts i and f are the conditions at initial and final states, respectively. During each charging step, the feeding rate was kept a constant. The densities of carbon dioxide at 298.2 K under different pressures are given below.

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>Density (g/cm³)</th>
<th>P (bar)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.81721</td>
<td>200</td>
<td>0.91400</td>
</tr>
<tr>
<td>150</td>
<td>0.87619</td>
<td>250</td>
<td>0.94278</td>
</tr>
</tbody>
</table>

3. (21 points total; 7 points each) A turbine is employed to convert high pressure superheated steam (2.0 MPa) into both electricity and low pressure steam (0.5 MPa). The flow rate of this high pressure steam is 5000 kg/h and this co-generation system (氣電共生系統) is operated at steady state.
   (a) If the steam expansion in the turbine is assumed to be isentropic, please find the minimum superheated temperature (°C) of the inlet steam to avoid liquid droplet forming in the turbine.
   (b) If the inlet of turbine is the steam at 2.0 MPa with the minimum superheated temperature, calculate the actual rate of power generation (kW) by assuming that the efficiency of the turbine is 60 % and the turbine is well insulated, and
   (c) Estimate the rate of entropy generation (kJ/K·h) of this cogeneration system.

Note that 1 W = 1 J/s
**Saturated Steam Table**

<table>
<thead>
<tr>
<th>$P$ (MPa)</th>
<th>$T$ (°C)</th>
<th>$H^c$ (kJ/kg)</th>
<th>$H^v$ (kJ/kg)</th>
<th>$S^c$ (kJ/kg K)</th>
<th>$S^v$ (kJ/kg K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>151.86</td>
<td>640.23</td>
<td>2748.7</td>
<td>1.8607</td>
<td>6.8213</td>
</tr>
<tr>
<td>2.0</td>
<td>212.42</td>
<td>908.79</td>
<td>2799.5</td>
<td>2.4474</td>
<td>6.3409</td>
</tr>
</tbody>
</table>

**Superheated Vapor Steam Table**

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$P = 0.5$ MPa</th>
<th>$P = 2.0$ MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H$ (kJ/kg)</td>
<td>$S$ (kJ/kg K)</td>
</tr>
<tr>
<td>200</td>
<td>2855.4</td>
<td>7.0592</td>
</tr>
<tr>
<td>250</td>
<td>2960.7</td>
<td>7.2709</td>
</tr>
<tr>
<td>300</td>
<td>3064.2</td>
<td>7.4599</td>
</tr>
<tr>
<td>350</td>
<td>3167.7</td>
<td>7.6329</td>
</tr>
<tr>
<td>400</td>
<td>3271.9</td>
<td>7.7938</td>
</tr>
</tbody>
</table>
PART II. 化工動力學 (50%)

1. (20%)
An elementary gas-phase reaction

\[ A \rightarrow B + C \]

is carried out isothermally at 127°C in a flow reactor with no pressure drop. The specific reaction rate at 127°C is 0.044 min⁻¹. Pure A enters the reactor at 10 atm and 127°C and a molar flow rate of 2.5 mol/min. Calculate the reactor volume to achieve 90% conversion in:
(a) a continuous-stirred tank reactor (CSTR) (8%)
(b) a plug-flow tubular reactor (PFR) (8%).
(c) Assume that the reaction is reversible with \( K_c = 0.11 \) mol/dm³, calculate the equilibrium conversion, \( X_e \) (4%)

Hint: Useful formula, hint, and constant for this problem

\[ \int_0^1 \frac{1 + \varepsilon x}{1 - x} dx = (1 + \varepsilon x) \ln \frac{1}{1-x} - \varepsilon x \]

(2) For the reactor design in gas phase flow system \( A \rightarrow b/a B + c/a C \) for this problem, the volumetric flow rate \( v \) can be calculated as

\[ v = v_0 (1 + \varepsilon X) (P_0 / P) (T / T_0) \]

where \( X \) is the conversion, \( P \) is the pressure, \( T \) is the temperature, the subscript “0” denotes the inlet condition, \( \varepsilon = y_{a0} \delta \), \( y_{a0} \) is the mole fraction of \( A \) in the inlet, and \( \delta \) is the change in the total number of moles per mole of \( A \) reacted, i.e. \( \delta = c/a + b/a - 1 \).

(3) The gas constant \( R = 0.082 \) atm-dm³/mol-K

Show All Your Work.

2. (15%)
Titanium dioxide is a wide-bandgap semiconductor that is showing promise as an insulating dielectric in VLSI capacitors and for use in solar cells. Thin films of TiO₂ are to be prepared by chemical vapor deposition from gaseous titanium tetraisopropoxide (TTIP). The overall reaction is

\[ \text{Ti(OC₃H₇)₄} \rightarrow \text{TiO}_2 + 4\text{C}_3\text{H}_₆ + 2\text{H}_2\text{O} \]

The reaction mechanism in a CVD reactor is believed to be

\[ \text{TTIP(g)} \rightarrow I + \text{P}_1 \]
\[ I + S \rightarrow I + S \]
\[ I + S \rightarrow \text{TiO}_2 + \text{P}_2 \]

where I is an active intermediate and \( P_1 \) is one set of reaction products (e.g., \( H_2O, C_3H_₆ \) and
P₂ is another set.

(a) Assuming the homogeneous gas-phase reaction for TTIP is in equilibrium, derive a rate law for the deposition of TiO₂. (9%)

(b) The experimental results show that at 200°C the reaction is second order at low partial pressures of TTIP and zero order at high partial pressures, while at 300°C the reaction is second order in TTIP over the entire pressure range.

Discuss these results in light of the rate law you derived. (6%)

Show All Your Work.

3. (15%)
You are an engineer who is to design a CSTR for the elementary consecutive gas-phase reactions

\[ \text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C} \]

The feed conditions and desired product specifications are known, together with the temperature of the heating medium. It is your job to design the reactor, that is, to specify the reactor volume and the area of the heating coil inside the reactor. The concentration ratio \( \text{C}_\text{A}/\text{C}_\text{C} \) in the product is equal to 10 and 50% of \( \text{A} \) in the feed is converted. The feed is gas-phase and pure \( \text{A} \) with a molar flow rate of 0.05 lb mol/s and a volumetric flow rate of 7.85 ft³/s. The entering temperature is 400°F and the entering pressure in the reactor is 4 atm. The heating medium is saturated high-pressure steam at 350°F and the overall heat-transfer coefficient between the heating medium and the reaction mixture is 400 Btu/(h ft² °F).

(a) Calculate the desired operating temperature (°F) inside the reactor. (5%)

(b) Calculate the volume (ft³) of the reactor. (5%)

(c) Calculate the area (ft²) of the heating coil. (5%)

Additional information
Heat Capacities:

\[ C_{\text{PA}} = C_{\text{PB}} = C_{\text{PC}} = 25 \text{ BTU/lb-mol. °F} \]

Reaction rate constants:

\[ k_1 = A_1 \exp(-E_1/RT) \]

\[ R \text{ (gas constant)} = 1.986 \text{ BTU/lb-mol.°R.} \]

\[ T(°R) = T(°F) + 460 \]

Reaction 1:

\[ A_1 = 2 \times 10^9 \text{ s}^{-1} \]

\[ E_1 = 31,000 \text{ Btu/lb-mol} \]

\[ \Delta H_{\text{RX1}} = 15,000 \text{ BTU/lb-mol A} \]

Show All Your Work.

Reaction 2:

\[ A_2 = 1 \times 10^{11} \text{ s}^{-1} \]

\[ E_2 = 40,000 \text{ Btu/lb-mol} \]

\[ \Delta H_{\text{RX2}} = 20,000 \text{ BTU/lb-mol C} \]