Part I

1. Please verify that for 1 mole of ideal gas, \( C_p - C_v = R \). (10%) 

2. Calculate \( \Delta S \) and \( \Delta S_{\text{arr}} \) if 1 mole of ideal gas expands isothermally and irreversibly at 298.15 K from a volume of 10 L to a volume of 40 L at a constant external pressure of 1 atm. Assume that the surroundings remain at thermal equilibrium of 298.15 K. \( (R = 8.314 \ J \cdot K^{-1} \cdot mol^{-1}) \) (10%) 

3. Consider a reaction, \( K \) is the equilibrium constant, \( \Delta G^0 \) is the standard-state Gibbs energy change, and \( \Delta H^0 \) is the standard-state enthalpy change. Since \( K = e^{-\Delta G^0 / RT} \), show that 
\[
\frac{d \ln(K)}{dT} = \frac{\Delta H^0}{RT^2}.
\] (10%) 

4. The wave function of Hydrogen's 1S orbital is \( \psi_{1S} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-r/a_0} \), where \( a_0 \) is the Bohr radius. Show that the most probable value of \( r \) in the 1S orbital is \( a_0 \). (10%) 

5. Suppose that we want to synthesize a polyene which has its lowest excitation energy at a wavelength of 113 nm. Consider the \( \pi \) electrons as particles in a 1-dim. box, what would the structure of this molecule be? \( \) (The carbon-carbon single bond length is 0.134 pm, and carbon-carbon double bond length is 0.146 pm. \( h = 1.0546 \times 10^{-34} J \cdot \text{sec} \) ) (10%)
PART II

I.

(a) Figure 1 is the heating curve and cooling curve of Na$_2$SO$_4$·$\text{H}_2\text{O}$ at 1 atm. Find the transition point of this compound. (5%)

(b) Figure 2 is the temperature-composition diagram for water and phenol at 1 atm. Find the critical solution temperature and composition of this system. (5%)

(c) What is the degree of freedom and the compositions of the phases at point $P$? (5%)
2. The concentrations and bromine consuming rates for the bromination of acetone in an acidic solution measured by a spectrophotometer at 25°C are listed in Table 1.

![Chemical Reaction Diagram]

Table 1.

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>[C₃H₆O] (M)</th>
<th>[H⁺] (M)</th>
<th>[Br₂] (M)</th>
<th>-Δ[Br₂]/Δt (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.60</td>
<td>0.403</td>
<td>4.14</td>
<td>28.0</td>
</tr>
<tr>
<td>2</td>
<td>1.60</td>
<td>0.202</td>
<td>4.38</td>
<td>12.7</td>
</tr>
<tr>
<td>3</td>
<td>0.80</td>
<td>0.110</td>
<td>3.70</td>
<td>2.85</td>
</tr>
<tr>
<td>4</td>
<td>0.80</td>
<td>0.403</td>
<td>4.26</td>
<td>12.9</td>
</tr>
<tr>
<td>5</td>
<td>0.80</td>
<td>0.202</td>
<td>4.28</td>
<td>5.99</td>
</tr>
<tr>
<td>6</td>
<td>0.40</td>
<td>0.202</td>
<td>3.96</td>
<td>2.94</td>
</tr>
</tbody>
</table>

A plot of bromine concentration vs. time is also shown in figure 3.

![Graph with [Br₂] versus Time (s)]

(a) Estimate the order of this reaction. (10%)

(b) Determine the rate constant \( k \) of this reaction. (5%)

(c) Write the rate law of this bromination reaction. (5%)

Figure 3
3. According to the Arrhenius law, the reaction rate is dependent on temperature.

\[ k = A \ e^{-\frac{E_a}{RT}} \]

\( k \) is the rate constant of a reaction, \( A \) is a pre-exponential factor, \( E_a \) is the activation energy of the reaction, \( T \) is the temperature

(a) The activation energy of a reaction is about 50 kJ at 300 K. Estimate the change of the rate constant of this reaction when temperature raised from 25°C to 45°C. \( (5\%) \)

(b) The rate of a decomposition reaction was measured over a temperature range 300 K to 500 K. The rate constants \( (k) \) were recorded in table 2. Find the activation energy and the pre-exponential factor. \( (10\%) \)

Table 2.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k ) (L/mol s)</td>
<td>8.0×10^6</td>
<td>3.0×10^7</td>
<td>8.0×10^7</td>
<td>1.8×10^8</td>
<td>3.5×10^8</td>
</tr>
</tbody>
</table>