1. Use the information provided to answer the following five problems:
(1) Who derived the expression that could account for the observed energy distribution of black-body radiation? (1%)
(2) Which relation indicates the particle character of electromagnetic radiation? (1%)
(3) Which product term of wave functions denotes the probability? (1%)
(4) Which term denotes the expectation value of a linear momentum? (1%)
(5) Write out the Heisenberg uncertainty principle in terms of the operators for position and linear momentum along the y-axis. (4%)

Information:
(a) Atomic and molecular spectra; (b) Born, Max; (c) Boltzmann, Ludwig;
(d) Dirac, Paul Adrien Maurice; (e) Dulong, Pierre-Louis; (f) Einstein, Albert;
(g) Feynman, R. P.; (h) Heat capacities of atomic solids at low temperatures;
(i) Heisenberg, Werner; (j) Jean, James; (k) Petit, Alexis-Therese;
(l) Planck, Max; (m) Rayleigh, Lord; (n) Schrödinger, Erwin;
(o) Stefan, Josef; (p) Wien, Wilhelm; (q) (1/2)mν² = hv - Φ;
(r) (h/2m)(d²ψ/dx²) + V(x)ψ = Eψ; (s) (h/8i)(d/dx), (h/8i)(d/dy), (h/8i)(d/dz);
(t) ∫ ψ*ψ dx = 1; (u) ∫ ψ*ρ ψ dx; (v) λ = h/p; (w) ψ*ψ; (x) ψ*ψ dx; (y) x ×, y ×, z ×.

2. The operators for the three components of angular momentum are
jₓ = (h/8i)[y(∂/∂z) - z(∂/∂y)], jᵧ = (h/8i)[z(∂/∂x) - x(∂/∂z)], and jₜ = (h/8i)[x(∂/∂y) - y(∂/∂x)].
Derive out jₓjᵧ. (8%)

3. The bonding LCAO-MO in a hydrogen molecule-ion is ψ⁺ = N⁺(A + B). Determine the normalization factor if the overlap integral is about 0.59. (8%)

4. Find the symmetry species of the normal modes of heavy formaldehyde (D₃CO), which belongs to the group C₃v.
How many normal modes are infrared active? (9%)

<table>
<thead>
<tr>
<th>C₂v (2mm)</th>
<th>E</th>
<th>C₁</th>
<th>σᵥ(xz)</th>
<th>σᵥ'(yz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A₂</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>B₁</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>B₂</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>
5. (12%) A sample consisting of 1 mole of monatomic perfect gas (for which $C_v = 1.5R$) is taken through the cycle shown in the figure below.

\[ P \text{ (atm)} \]

\[ \begin{array}{c|c}
1 & 2 \\
1.00 & \\
0.50 & \\
\end{array} \]

\[ \begin{array}{c|c}
22.44 & 44.88 \\
\end{array} \]

Please fill the blanks from (a) to (l) in the following table by calculating $q$, $w$, $\Delta U$, and $\Delta H$ for each step.

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>$q$/kJ</th>
<th>$w$/kJ</th>
<th>$\Delta U$/kJ</th>
<th>$\Delta H$/kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2</td>
<td>$p$ constant at $p_x$</td>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
<td>(d)</td>
</tr>
<tr>
<td>2→3</td>
<td>$V$ constant</td>
<td>(e)</td>
<td>(f)</td>
<td>(g)</td>
<td>(h)</td>
</tr>
<tr>
<td>3→1</td>
<td>Isothermal, reversible</td>
<td>(i)</td>
<td>(j)</td>
<td>(k)</td>
<td>(l)</td>
</tr>
</tbody>
</table>

6. (9%) Use the van der Waals equation of state \( (p + \frac{n^2a}{V^2})(V - nb) = nRT \) to evaluate the volume, pressure, and temperature of a real gas at its critical point in terms of the parameters $a$ and $b$.

7. (6%) The standard reaction enthalpy of $\text{Zn(s)} + \text{H}_2\text{O(g)} \rightarrow \text{ZnO(s)} + \text{H}_2\text{(g)}$ is approximately constant at $+224$ kJ mol$^{-1}$ from 920 K up to 1280 K. The standard reaction Gibbs energy is $+33$ kJ mol$^{-1}$ at 1280 K. Assuming that both quantities remain constant, estimate the temperature at which the equilibrium constant becomes greater than one.

8. (6%) Borneol is a pungent compound obtained from the camphorwood tree of Borneo and Sumatra. The standard reaction Gibbs energy of the isomerization of borneol to isoborneol in the gas phase at 500 K is $+9.4$ kJ mol$^{-1}$. Calculate the reaction Gibbs energy in a mixture consisting of 0.15 mol of borneol and 0.30 mol of isoborneol when the total pressure is 600 Torr.
9. (4 points) As show in the reaction energy profile below, the reactant A has two competitor reaction pathways leading to product B and C separately. For these two products, which one is the kinetic product? If C is the unwanted side product, what to do to enhance your yield, by increasing or decreasing the reaction time? How about temperature, increasing or decreasing? If you have catalysts for both these two reactions, how to use them to increase your yield?

![Reaction Energy Profile]

10. (12 points) The kinetics of the reaction \( A + B \leftrightarrow C + D + E \) was studied to find out its reaction rate law, where C acts as a catalyst. We study the following experiments at 25°C.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>([A] (M))</th>
<th>([B] (M))</th>
<th>([C] (M))</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3</td>
<td>0.05</td>
<td>0.05</td>
<td>5.7 \times 10^{-5}</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.05</td>
<td>5.7 \times 10^{-5}</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>0.05</td>
<td>0.10</td>
<td>1.2 \times 10^{-4}</td>
</tr>
<tr>
<td>4</td>
<td>0.9</td>
<td>0.1</td>
<td>0.10</td>
<td>3.6 \times 10^{-4}</td>
</tr>
</tbody>
</table>

The rate law can be expressed in the form \( -\frac{d[A]}{dt} = k[A]^a[B]^b[C]^c \) (a) find the value of \( a, b, \) and \( c \). (b) Calculate the rate constant \( k \), including its units. (c) In the first experiment, how long does it take 50% of A to be E?

11. (9 points) A photo-induced radical reaction \( A_2 + B_2 \rightarrow 2AB \)

A reasonable mechanism for this reaction with the rate equation of each step is given as the following:

\[
\begin{align*}
B_2 + h\nu & \rightarrow 2B \\
B_2 + A_2 & \rightarrow AB + A \\
A + B_2 & \rightarrow AB + A \\
B & \rightarrow \text{wall removal}
\end{align*}
\]

\( v_1 = k_1[A_2][B] \)

\( v_2 = k_2[B][A] \)

\( v_3 = k_3[B][A] \)

\( v_4 = k_4[B] \)

Derive the overall rate \( v = 0.5 \frac{d[AB]}{dt} \) with those rate constants, \( v_1 \) and concentration of the reactants and product.

12. (9 points) Radioactive \(^{64}\text{Cu}\) is unstable against decay, emitting either an electron or a positron by two separate first-order paths simultaneously. The decay of occurs exponentially with a single half-life of 10 h. (a) Calculate the rate constants for the two paths, \( K^+ \) and \( K^- \). (b) Calculate the mole of \(^{64}\text{Cu}\) nuclei left after 100 h, starting with one mole of \(^{64}\text{Cu}\). (c) Calculate the mole of \(^{64}\text{Zn}\) nuclei produced at this moment.

\[ \begin{align*}
^{64}\text{Cu} \rightarrow &^{64}\text{Zn} + e^- \quad (60\%) \\
^{64}\text{Cu} \rightarrow &^{64}\text{Ni} + \beta^- \quad (40\%)
\end{align*} \]

(For your reference: \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \), \( 0.082 \text{ atm L K}^{-1} \text{ mol}^{-1} \), \( \ln 2 = 0.6931 \))