1. Although the bond energy for a hydrogen bond in a vacuum is estimated to be \( \sim 20 \text{ kJ/mol} \), we find that a hydrogen bond in an average folded protein contributes \( < 5 \text{ kJ/mol} \). Explain this discrepancy. (10 points)
   
a. In an unfolded protein, most of its H bond donors and acceptors will form H bonds with water. Because it is only the difference in H bonding energy between the folded and unfolded states of a protein that contributes to protein stability, the energy required to break all H bonds with water in the unfolded state must be subtracted from the energy released when new H bonds form in the folded state.

2. If you wished to synthesize a peptide that would insert into a phospholipid bilayer and then assemble into hexamer that would form an aqueous pore across the membrane, how would you optimally design this peptide? Included in your description should be the peptide's length, amino acid sequence, and orientation/assembly to form the aqueous channel in the lipid bilayer. A diagram might be useful in your response to the last request. Please also include a mechanistic explanation for each of your choices. (36 points)
   
a. Each peptide in the hexamer must be long enough to span a phospholipid bilayer in an \( \alpha \)-helical conformation because all H bond donors and acceptors along the peptide backbone are internally H bonded in an \( \alpha \)-helix. This \( \alpha \)-helix should be \( \sim 24 \) amino acids long, since the hydrophobic width of a phospholipid bilayer is \( \sim 36 \text{ Å} \) and the length of an \( \alpha \)-helix is \( \sim 1.5 \text{ Å/} \text{amino acid} \) (10 points). The six peptides will have to assemble into a hexameric arrangement that will form a central aqueous channel that is protected from exposure to the phospholipid acyl chains. The diagram below is the only arrangement that will meet this requirement (6 points). The amino acids that face the interior of the channel will have to be hydrophilic (e.g. D, E, Y, S, T, R, K, etc.), while the amino acids that face the exterior of the channel will have to be hydrophobic (e.g. L, I, W, F, V, A, etc.) (10 points). Because there is one amino acid for every 100° rotation around a helical wheel, it would be important to have the \( \sim 1/3 \) of the amino acids that face the center of the assembly be hydrophilic. Based on the diagram below, one method of assuring this orientation would be to have amino acids 1, 4, 7, 11, 15, 18, and 21 be hydrophilic (10 points).
3. The Hill coefficient for the interaction of oxygen with human hemoglobin in the red cell is ~2.8. Explain in detail i) what this number means, ii) what molecular mechanism leads to this behavior, and iii) why it is important for oxygen delivery to the tissues. (30 points) why it is important to hemoglobin function.
   a. The Hill coefficient constitutes a way to quantify the degree of interaction between ligand binding sites in a multi-subunit protein. In the case of positive cooperativity, the binding of one ligand to one site increases the affinity of a second ligand for the second site. The larger the Hill coefficient, the greater the positive cooperativity. A binding interaction that displays no cooperativity will have a Hill coefficient of one. An interaction that displays negative cooperativity (binding of one ligand reduces the affinity of subsequent ligands) will have a Hill coefficient of <1.
   b. The molecular mechanism responsible for the Hill coefficient of 2.8 in the hemoglobin (Hb) O2 interaction arises from the fact that intersubunit interactions between Hb subunits cement the Hb tetramer into a low affinity state. Then with each consecutive binding of O2, an oxygen molecule, increasing numbers of these cementing interactions are broken, allowing the Hb tetramer to relax increasingly into a high affinity state.
   c. This "S" shaped oxygen binding curve is critical for oxygen delivery since it situates the largest change in oxygen binding exactly over the range of oxygen pressures that change between the lungs (where O2 is bound) and the tissues (where O2 is released).

4. Draw the structure of the following peptide: DRLKGW. (24 points)

![Peptide Structure](image)

DRLKGW
Asp-Arg-Leu-Lys-Gly-Trp
Inorganic Chemistry Cumulative Exam Crib  
March 24, 2018

1. (10 pt) Given the standard potentials of half reactions (i) and (ii), calculate that of (iii).

(i) Fe^{2+} + 2e^- \rightarrow Fe(s) \quad \text{E}^\circ = -0.440 \text{ V}
(ii) Fe^{3+} + 1e^- \rightarrow Fe^{2+} \quad \text{E}^\circ = 0.771 \text{ V}
(iii) Fe^{3+} + 3e^- \rightarrow Fe(s) \quad \text{E}^\circ = -0.036 \text{ V}

2. (15 pt) The electron self exchange reaction between [Co(NH$_3$)$_6$]$^{3+}$ and [Co(NH$_3$)$_6$]$^{2+}$ is much slower than that between the Ru analogues. Provide a concise rationale.
   a) Co$^{2+}$ high spin & long Co-N bonds; Co$^{3+}$ low spin and much shorter Co-N bonds; large reorganization energy λ, and very slow rate.
   b) Both Ru$^{2+}$ and Ru$^{3+}$ low spin and little difference in Ru-N distances and hence small λ and much faster rate.

3. (15 pt) Calculate the equilibrium constant of the reaction ($F = 96485$ C/mol; $R = 8.31$ J/(K mol))

\[ \text{Au}^+(aq) + 2 \text{CN}^- (aq) \leftrightarrow [\text{Au(CN)}_2]^-(aq) \quad \Delta G = -220 \text{ kJ} \]

From the standard potentials:

\[ \text{Au}^+(aq) + 1e^- \rightarrow \text{Au(s)} \quad \text{E}^\circ = 1.680 \text{ V} \]
\[ [\text{Au(CN)}_2]^-(aq) + 1e^- \rightarrow \text{Au(s)} + 2 \text{CN}^- (aq) \quad \text{E}^\circ = -0.600 \text{ V} \]

\[ K \approx 3.8 \times 10^{38} \]

4. (20 pt) Consider a six coordinated V$^{3+}$ complex of an effective $D_3$ symmetry. Determine the ligand field terms originated from the free ion ground state term. ($^3F$ – derived using Hund’s rule)

Hint: $\chi(\alpha) = [\sin(L + \frac{1}{2})\alpha]/[\sin(\alpha/2)]$

<table>
<thead>
<tr>
<th>$D_3$</th>
<th>E</th>
<th>2C$_3$</th>
<th>3C$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
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<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
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<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$T_2$</td>
<td>7</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Hence, $^3F \rightarrow ^3A_1 + 2^3A_2 + 2^3E$
5. (30 pt) Use projection operator method to generate the SALCs of ligand $\sigma$ donor orbitals for an ML$_5$ ($C_{4v}$) type complex.

<table>
<thead>
<tr>
<th></th>
<th>C$_{4v}$</th>
<th>E</th>
<th>2C$_4$</th>
<th>C$_2$</th>
<th>2$\sigma_v$</th>
<th>2$\sigma_d$</th>
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<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
</tr>
<tr>
<td>A$_2$</td>
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<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>B$_1$</td>
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<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>B$_2$</td>
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<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma_{\text{apical} (\sigma_1)}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$A_1$</td>
</tr>
<tr>
<td>$\Gamma_{\text{basal} (\sigma_2-3)}$</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>$A_1 + B_1$ + E</td>
</tr>
</tbody>
</table>

$A_1$ \quad \sigma_1$

Using symmetry descent to $C_4$ for basal ligands set

$A_1 \quad (\sigma_2 + \sigma_3 + \sigma_4 + \sigma_5)/2$

$B_1 \quad (\sigma_2 - \sigma_3 + \sigma_4 - \sigma_5)/2$

$E \quad (\sigma_2 - \sigma_3)/2^{1/2}$

$(\sigma_3 - \sigma_5)/2^{1/2}$
P-CHEM CUME: SOME POSSIBLY USEFUL INFORMATION

First law of thermodynamics:
\[ dU = dq + dw = C_v \cdot dT - P \cdot dV \quad (U \equiv \text{internal energy}, P-V \text{ work only}) \]

Definitions of important state functions:
\[ H = U + P \cdot V \quad (H \equiv \text{enthalpy}) \]
\[ dS = dq_{\text{rev}}/T \quad (S \equiv \text{entropy}) \]
\[ G = H - T \cdot S \quad (G \equiv \text{Gibbs energy}) \]

Gibbs equations:
\[ dU = T \cdot dS - P \cdot dV \]
\[ dH = T \cdot dS + V \cdot dP \]
\[ dA = -S \cdot dT - P \cdot dV \]
\[ dG = -S \cdot dT + V \cdot dP \]

Definition of constant pressure and constant volume heat capacities:
\[ C_v = (\partial U/\partial T)_v, \quad C_p = (\partial H/\partial T)_p \]

Definition of the chemical potential:
\[ \mu_i = (\partial G_i/\partial n_i)_{T,P,n_{j\neq i}} \]

Chemical potential of A in an ideal solution:
\[ \mu_A = \mu_A^\circ + R \cdot T \cdot \ln \chi_A \quad \text{(note: } \mu_A^\circ \text{ depends on } T \text{ and } P) \]

Equation of state of a perfect gas:
\[ P \cdot V = R \cdot T \]

Chemical potential of a perfect gas:
\[ \mu_A = \mu_A^\circ + R \cdot T \cdot \ln(P_A/P^\circ) \quad \text{(note: } \mu_A^\circ \text{ depends on } T; ^\circ \text{ symbol indicates standard state pressure}) \]

Taylor expansion of \( \ln(x) \):
\[ \ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \ldots \]
1. (a) Show that the molar heat capacity difference for a real gas is given by:

\[
\overline{C_p} - \overline{C_v} = (\partial \overline{U}/\partial \overline{T})_p \cdot \{p + (\partial \overline{U}/\partial \overline{V})_T \}
\]

The bars over \(C_p, C_v, U,\) and \(U\) indicate molar quantities. (20 points)

\[
\overline{C_p} - \overline{C_v} = \left( (\partial \overline{H}/\partial \overline{T})_p - (\partial \overline{U}/\partial \overline{T})_v \right)
\]

but \( \overline{H} = \overline{U} + \overline{P} \overline{V} \Rightarrow (\partial \overline{H}/\partial \overline{T})_p = (\partial \overline{U}/\partial \overline{T})_p + \overline{P} (\partial \overline{V}/\partial \overline{T})_p \)

\[
\overline{C_p} - \overline{C_v} = \left\{ (\partial \overline{U}/\partial \overline{T})_p - (\partial \overline{U}/\partial \overline{T})_v \right\} + \overline{P} (\partial \overline{V}/\partial \overline{T})_p
\]

write \( \overline{U} \) as function of \( T \) and \( V \)

\[
(\partial \overline{U}/\partial \overline{T})_V \Delta \overline{T} + (\partial \overline{U}/\partial \overline{V})_T \Delta \overline{V} \quad \text{applies at constant} \quad \overline{P}
\]

\[
(\partial \overline{U}/\partial \overline{T})_p = (\partial \overline{U}/\partial \overline{T})_v + (\partial \overline{U}/\partial \overline{V})_T (\partial \overline{V}/\partial \overline{T})_p
\]

\[
\overline{C_p} - \overline{C_v} = (\partial \overline{U}/\partial \overline{V})_T \cdot (\partial \overline{V}/\partial \overline{T})_p + \overline{P} (\partial \overline{V}/\partial \overline{T})_p
\]

\[
= (\partial \overline{V}/\partial \overline{T})_p \{ p + (\partial \overline{U}/\partial \overline{V})_T \}
\]

(b) Show that \( \overline{C_p} - \overline{C_v} = R \) for a perfect (i.e., ideal) gas. (5 points)

\[
P \overline{V} = \overline{R} \overline{T} \quad ; \quad \overline{U} = \overline{U}(\overline{T}) \quad \text{only (perfect gas)}
\]

\[
(\partial \overline{V}/\partial \overline{T})_p = \overline{R}/\overline{P} \quad ; \quad (\partial \overline{U}/\overline{V})_T = 0
\]

\[
\overline{C_p} - \overline{C_v} = (\overline{R}/\overline{P}) (\overline{P}) = \overline{R}
\]

(c) Explain why \( \overline{C_p} > \overline{C_v} \) for a real gas. (10 points)

1. Constant pressure process involves work on surroundings due to expansion.
2. Intermolecular attractions in real gas make \( (\partial \overline{U}/\partial \overline{V})_T > 0 \)
3. Copper and nickel are completely miscible in both the solid and liquid states at 1 bar pressure. The melting point of pure copper at 1 bar pressure is 1085 °C, and that of nickel is 1455°C.

(a) Sketch the phase diagram of the Cu + Ni system in the solid and liquid regions, with copper mole fraction in the x-axis and temperature in the y-axis. Identify the single and two-phase regions of the diagram. (10 points)

(b) Consider a region of the phase diagram in which the solid and liquid solution phases are in equilibrium. Which phase is enriched in Cu relative to the other (i.e. which phase has the higher mole fraction of Cu)? (5 points)

The composition of each phase in the two phase region is given by composition where a tie-line intersects the phase boundary. The liquid phase is enriched in the low melting component, which is Cu.
2. Consider the chemical potential of A in an ideal liquid solution:

\[ \mu_A = \mu_A^* + R \cdot T \cdot \ln \chi_A \]

where \( \mu_A^* \) is the chemical potential of pure A, and \( \chi_A \) is the mole fraction of A.

(a) Show that the entropy change of mixing \( n_A \) moles of A with \( n_B \) moles B at constant \( T \) and \( P \) is:

\[ \Delta S_{mix} = -n_{TOT} \cdot R \cdot [\chi_A \cdot \ln(\chi_A) + \chi_B \cdot \ln(\chi_B)] \]

where \( n_{TOT} \) is \( n_A + n_B \). (15 points)

\[ G = \Sigma n_i \mu_i \Rightarrow \Delta G_{mix} = G_{(solution)} - G_{(pure)} \]

\[ \Delta G_{mix} = \{ n_A \mu_A_{(solution)} + n_B \mu_B_{(solution)} \} - \{ n_A \mu_A_{(pure)} + n_B \mu_B_{(pure)} \} \]

\[ = \left\{ \frac{n_A}{n_{TOT}} \left[ (\mu_A^* + RT \ln \chi_A) - \mu_A^* \right] + \frac{n_B}{n_{TOT}} \left[ (\mu_B^* + RT \ln \chi_B) - \mu_B^* \right] \right\} \]

\[ = n_A \cdot RT \ln \chi_A + n_B \cdot RT \ln \chi_B \]

\[ \Delta S = -\frac{\Delta H}{J} = -\frac{\Delta G}{T} \Rightarrow \Delta S = -n_{TOT} \cdot R \left( \chi_A \ln \chi_A + \chi_B \ln \chi_B \right) \]

(b) Use chemical potentials to show that the vapor pressure of A over an ideal liquid solution of A and B is equal to \( \chi_A \cdot P_A^* \), where \( P_A^* \) is the vapor pressure of pure A. Treat A in the vapor phase as a perfect gas. (10 points)

\[ \mu_{A_{(vapor)}} = \mu_A^{\theta} + RT \ln \left( \frac{P}{P_A^*} \right) \]

solution: \[ \mu_A^{\theta}_{(vapor)} + RT \ln \left( \frac{P_A}{P_A^*} \right) = \mu_A^{\theta}_{(liquid)} + RT \ln \chi_A \]

pure: \[ \mu_A^{\theta}_{(vapor)} + RT \ln \left( \frac{P_A^*}{P_A^*} \right) = \mu_A^{\theta}_{(liquid)} \]

\[ \ln \left( \frac{P_A}{P_A^*} \right) = \ln \chi_A \]

\[ P_A = \chi_A \cdot P_A^* \]
4. A is a non-ionic solute that dissolves in water to form an ideal solution. A solution of A in water is decanted into one side of a U-tube, the two sides of which are separated by a membrane that is permeable only to water. An equivalent volume of pure water is decanted into the other side of the U-tube. At equilibrium, liquid on one side of the U-tube is at a different height than liquid on the other side, as shown in the diagram to the right.

(a) Which side of the tube contains pure water? Explain your answer. (10 points)

The left side. Material flows spontaneously from regions of higher to lower chemical potential.

\[ \mu_{H_2O(\text{solution})} = \mu_{H_2O}^* + RT \ln \gamma_{H_2O} \Rightarrow \mu_{H_2O(\text{solution})} < \mu_{H_2O}^* \]

Equilibrium is reached when pressure exerted by the right column brings chemical potentials equal.

(b) Show that \( h \), the height difference between the two sides of the U-tube at equilibrium, is approximately proportional to the molarity of A for small concentrations of A. (15 points)

\[ \mu_{H_2O(eq)} = \mu_{H_2O(r)} \]

\[ \mu_{H_2O}^*(T, P_{H_2O}) = \mu_{H_2O}^*(T, P_{H_2O(r)}) + RT \ln \gamma_{H_2O} \]

\[ (\mu_{H_2O}(T, P_{H_2O}) - \mu_{H_2O}(T, P_{H_2O(r)})) = RT \ln \gamma_{H_2O} \approx -RT(1 - \gamma_{H_2O}) \]

\[ \approx \frac{\bar{V}_{H_2O}^*}{\gamma_{H_2O}}(P_{eq} - P_{r}) \]

\[ -\bar{V}_{H_2O}^* \cdot \rho_{H_2O} \cdot g \cdot h \approx -RT \gamma_A \approx -RT \frac{n_A}{n_A + n_{H_2O}} \approx -RT \frac{n_A}{n_{H_2O}} \]

\[ n_A / \bar{V}_{A} \approx n_A / \bar{V}_{H_2O} \approx \frac{(\rho_{H_2O} \cdot g)}{RT} \cdot h \]