I. Spectroscopy

1. A carotenoid is a pigment that can absorb radiation for transfer to the photosynthetic Reaction Center. A carotenoid was discovered with 16 conjugated carbons as shown in the Figure. Use the free electron model to determine whether the carotenoid is higher in energy than the P680 chlorophyll of Photosystem II. [NOTE: In the free electron model you may assume that the electrons from the p-orbitals of the carbon atoms populate energy levels derived from the particle-in-a-box solution to the Schrödinger equation.]

A. Assuming that the box length 17.5 Å, please calculate the wave number (cm⁻¹) and the maximum of the absorption spectrum (in nm). (10 points)

Solution: all-trans

\[ \Delta E = \frac{h}{8mcL^2}(n_e^2 - n_g^2) \]

\[ = \frac{6.626 \times 10^{-34} \text{Js}}{8(9.1 \times 10^{-31} \text{kg})(2.99 \times 10^{10} \text{cm/s})(1.55 \times 10^{-9} \text{m})^2(72 - 62)} \]

\[ = 3.92 \times 10^{-19} \text{J} = 19,810 \text{cm}^{-1} \text{ (which corresponds to 670 nm)} \]

Transition energy of the carotenoid in cm⁻¹ = ____________________________.

Transition wavelength of the carotenoid in nm = ____________________________.

B. Is the carotenoid higher in energy than P680 (i.e. the chlorophyll pigment that absorbs at 680 nm)? YES NO (2 points)

C. The absorbance of the carotenoid is 0.9. What percentage of the light passing through the leaf is absorbed by the carotenoid? (4 points)

Solution: \%T = 10⁻^A (100%) = 10⁻^0.9 (100%) = 12.5%

Transmittance of the carotenoid in the antennae complex = ____________________________.
D. Assuming that the leaf has a thickness of 3 millimetres and the effective concentration of carotenoids is $2 \times 10^{-3}$ moles/liter, with an absorbance of 0.9 as given in part C. calculate the extinction coefficient for the absorption band. (4 points)

**Solution:**

$$
\varepsilon = \frac{A}{cd} \Rightarrow \varepsilon = 0.9 / (2 \times 10^{-3} \text{ M})(4\times10^{-3} \text{ cm}) = 150,000 \text{ M}^{-1}\text{cm}^{-1}
$$

$\varepsilon$ of carotenoid = ____________________________.

E. Assuming that the energy transfer rate constant for the carotenoid is $k_{ET} = 10^{12} \text{ s}^{-1}$, and the internal conversion rate is $k_{IC} = 2 \times 10^{11} \text{ s}^{-1}$, calculate the energy transfer quantum yield. (4 points)

**Solution:**

$$
\Phi_{ET} = \frac{k_{ET}}{(k_{ET} + k_{IC})} = \frac{(10^{12})}{(10^{12} + 2 \times 10^{11})} = 0.833
$$

Energy transfer quantum yield, $\Phi_{ET} =$ ____________________________.

2. The photosynthetic reaction center pumps protons by delivering hydroquinone, $Q_B H_2$, to the bc1 complex. The electron transfer reaction is:

$$
2e^- + Q_B \rightarrow Q_B^{2-} \quad \text{(Eqn. 1)}
$$

which has a driving force of $\varepsilon = 2000 \text{ cm}^{-1}$. The net proton uptake reaction is:

$$
2e^- + 2H^+ + Q_B \rightarrow Q_B H_2 \quad \text{(Eqn. 2)}
$$

where $Q_B$ is the acceptor. This process has a driving force of $\varepsilon = 4000 \text{ cm}^{-1}$ for each electron if proton uptake is included. During this process 2 $H^+$ are pumped across the membrane. This process is called proton coupled electron transfer. It results in an increase of the electron transfer rate constant by effectively increasing the driving force $\varepsilon$.

Throughout this problem, you may assume that $\lambda = 4000 \text{ cm}^{-1}$, for all electron transfer reactions.

A. Calculate the rate enhancement of the electron transfer to $Q_B$ of Eqn. 1 relative to Eqn. 2. Expressed as single electron transfers these are:

$$
e^- + Q_B \rightarrow Q_B^- \quad (\varepsilon_B = 2000 \text{ cm}^{-1} \text{ for Eqn. 3})
$$

$$
e^- + H^+ + Q_B \rightarrow Q_B H \quad (\varepsilon_{BH} = 4000 \text{ cm}^{-1} \text{ for Eqn. 4})
$$

You may assume that the electronic coupling for both of these processes is equivalent. (4 points)
Based on the contribution of the activation energy calculated from $\epsilon_B$, $\epsilon_{BH}$ and $\lambda$ determine the ratio of the rate constants, which is the rate enhancement.

Solution:

$E_B = (\epsilon_B - \lambda)^2/4\lambda = (2000 \text{ cm}^{-1} - 4000 \text{ cm}^{-1})^2/4(4000 \text{ cm}^{-1})$

$= 250 \text{ cm}^{-1}$

and

$E_{BH} = (\epsilon_{BH} - \lambda)^2/4\lambda = (4000 \text{ cm}^{-1} - 4000 \text{ cm}^{-1})^2/4(4000 \text{ cm}^{-1})$

$= 0$

Rate enhancement = ________________.

B. Calculate $kT$ in eV (or cm$^{-1}$) at 300 K. (4 points)

Solution: $kT = (0.697 \text{ cm}^{-1}/K)(300 \text{ K}) = 207 \text{ cm}^{-1}$

C. The electron transferred to $Q_B$ comes from the quinone, $Q_A$. The “back reaction” is,

$$P^+Q_A^-Q_B \rightarrow PQ_AQ_B$$

($\epsilon_R = 4000 \text{ cm}^{-1}$ for Eqn. 3)

and the forward reaction

$$P^+Q_A^-Q_B + H^+ \rightarrow P^+Q_AQ_B H$$

($\epsilon_{BH} = 4000 \text{ cm}^{-1}$ for Eqn. 4)

is the same as the proton coupled reaction in part A. Assuming the prefactors are the same calculate the quantum yield for the forward reaction. (4 points)

Solution: $k = \exp\{-E_A/kT\}$ and = $(10^{12} \text{ s}^{-1})\exp\{-100/200\} = 6 \times 10^{11} \text{ s}^{-1}$

D. What factor might increase the quantum yield for the productive electron transfer (Eqn. 4)? (2 points)

Answer: the electronic factors must be different. The factor $|V|^2$ in the kET rate constant would need to be larger for the reaction

$$P^+Q_A^-Q_B + H^+ \rightarrow P^+Q_AQ_B H$$

Than for the reaction

$$P^+Q_A^-Q_B \rightarrow PQ_AQ_B$$
3. A. Calculate the vibrational wavenumber of H₂ in cm⁻¹ given that its force constant of vibration is 571 N/m. (8 points)

Solution:

\[ \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \frac{1}{2(3.14159)(2.99 \times 10^{10} \text{ cm/s})} \sqrt{\frac{571 \text{ N/m}}{(0.5)(1.672 \times 10^{-27} \text{ kg})}} \]

\[ \tilde{\nu} = 4,400 \text{ cm}^{-1} \]

Vibrational wavenumber = ____________________________ cm⁻¹.

B. Sketch the vibrational potential energy surface for the H₂ stretching vibration. Sketch the v = 0 and v = 1 wavefunctions. What is the mathematical form of the potential energy surface? (4 points)

Sketch:

\[ V = \frac{1}{2} kx^2 \text{ or } \frac{1}{2} kQ^2 \]

Mathematical equation for the potential energy surface is \( V = \) ________________.

C. Calculate the pure rotational line spacing for H₂ given that its bond length is 0.95 Å (6 points).

\[ \bar{B} = \frac{h}{8\pi c \mu R^2} \]

\[ \bar{B} = \frac{6.626 \times 10^{-34}}{8(31415) \left(\frac{2.99 \times 10^{10} \text{ cm/s}}{s}\right)(0.5)(1.672 \times 10^{-27} \text{ kg})(0.95 \times 10^{-10})^2} = 117 \text{ cm}^{-1} \]

Rotational line spacing = ____________________________ (cm⁻¹).
D. Sketch the pure rotational spectrum of H₂ assuming that k_BT >> 2B (4 points).

Answer: There is no pure vibrational spectrum.

E. Sketch the rovibrational spectrum of H₂ assuming that k_BT >> 2B. Label the three branches. (6 points)

Answer: There is no rovibrational spectrum.

4. N₂O (laughing gas) is no laughing matter. It is a serious greenhouse gas. It has both pure rotations and vibrations that can give rise to absorption in the microwave and infrared, respectively. The structure of N₂O is given below:

![Structure of N₂O](image)

A. Considering water a rigid rotator, sketch the three moments of inertia of N₂O. Which of these gives rise to microwave absorption? What is the reason for the microwave absorption activity? (6 points)

Sketch:

![Moments of inertia](image)

1. (active/not active)  
2. (active/not active)  
3. (active/not active)

Reason for microwave activity: The permanent dipole moment rotates physically in space

B. Sketch the vibrational normal modes of N₂O. Which have the greatest infrared activity? (6 points)

![Vibrational modes](image)

1. (active/not active)  
2. (active/not active)  
3. (active/not active)

The symmetric stretch and bend have the greatest IR activity.
C. Given that the stretching vibrations of N\(_2\)O are near 10 microns in wavelength suggest a reason why these vibrations are particularly prone to increasing the temperature of the atmosphere of the Earth. (3 points)

Answer: the peak of the thermal emission of the earth is near 10 microns.

5. Which of the following obey the selection rule for absorption (6 points).  c and e
II. Thermodynamics

5. There is a great deal of excitement about biofuels. This means adding ethanol derived from sugar or corn to octane. However, there are some who question whether ethanol has as much heat energy as octane. You are asked to test this using the data in the table below.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$C_p$ (J/mol-K)</th>
<th>$S^o$ (J/mol-K)</th>
<th>$\Delta H^o$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH$_2$OH(ℓ)</td>
<td>111.5</td>
<td>160.7</td>
<td>-277.7</td>
</tr>
<tr>
<td>CH$_3$CH$_2$OH(g)</td>
<td>65.4</td>
<td>282.7</td>
<td>-235.1</td>
</tr>
<tr>
<td>O$_2$ (g)</td>
<td>29.4</td>
<td>205.1</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$O(ℓ)</td>
<td>75.3</td>
<td>69.9</td>
<td>-285.8</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>33.6</td>
<td>188.8</td>
<td>-241.8</td>
</tr>
<tr>
<td>CO$_2$ (g)</td>
<td>41.3</td>
<td>213.7</td>
<td>-393.5</td>
</tr>
</tbody>
</table>

Please note the following,

$\Delta_{vap} H^o = 40.65$ kJ/mol for H$_2$O at 373 K
$\Delta_{vap} H^o = 38.7$ kJ/mol for CH$_3$CH$_2$OH at 358 K

The combustion reaction for ethanol at 298 K is,

$$CH_3CH_2OH(ℓ) + XO_2(g) \rightarrow YH_2O(ℓ) + ZCO_2(g)$$

A. Please write a balanced chemical equation (4 points)

$$H_3CH_2OH(ℓ) + 3O_2(g) \rightarrow 3H_2O(ℓ) + 2CO_2(g)$$

B. Calculate the enthalpy of combustion at 560 K, $\Delta_{comb} H^o$, without taking the enthalpy of vaporization into account. Show that the heat capacity difference makes a negligible contribution. (8 points)

$$\Delta_{comb} H^o = 2\Delta H^o(CO_2) + 3\Delta H^o(H_2O) - 3\Delta H^o(O_2) - \Delta H^o(CH_3CH_2OH(ℓ))$$

$$\Delta_{comb} H^o = 2(-393.5) + 3(-285.8) - (-277.7)$$

$$\Delta_{comb} H^o = -1760.2 \text{ kJ/mol}$$

$$\Delta_{comb} H^o(560K) = \Delta_{comb} H^o(298K) + \Delta C_p (T_2 - T_1)$$

$$\Delta_{comb} H^o(560K) = -1760,200 \frac{J}{mol} + 90.5(560 - 298)$$

$$\Delta_{comb} H^o(460K) = -1,760,100 \frac{J}{mol}$$

$$\Delta_{comb} C_p = 2C_p(CO_2) + 3H_2O - 3C_p(O_2) - C_p(CH_3CH_2OH(ℓ))$$

$$\Delta_{comb} C_p = 2(41.3) + 3C_p(69.2) - 3(29.4) - (111.5)$$

$$\Delta_{comb} C_p = 90.5 \frac{J}{molK}$$

$\Delta_{comb} H^o(560K) =$

______________________________.
C. Calculate $\Delta_{\text{comb}} H^\circ$ taking the enthalpy of vaporization into account and ignoring the heat capacity difference. (4 points)

\[
\Delta_{\text{comb}} H^\circ = 2\Delta H^\circ (CO_2) + 3\Delta H^\circ (H_2O) - 3\Delta H^\circ (O_2) - \Delta H^\circ (CH_3CH_2OH) + 3\Delta_{\text{vap}} H^\circ (H_2O) - \Delta_{\text{vap}} H^\circ (CH_3CH_2OH) = 2(-393.5) + 3(-285.8) - (-277.7) + 3(40.65) - 38.5 = -1,680 \text{ kJ/mol}
\]

D. Calculate the number of moles of C\textsubscript{2}H\textsubscript{5}OH in a gallon gas (1 gallon = 3.8 liters, $\rho = 0.78 \text{ g/cm}^3$). (3 points)

Solution: $\frac{(3800 \text{ cm}^3)(0.78 \text{ g/cm}^3)}{(46 \text{ g/mol})} = 64.4 \text{ moles}$.

E. Calculate the heat contained in one gallon of ethanol. (3 points)

Solution:

\[
q = n\Delta_{\text{comb}} H^\circ (560K) = (64.4 \text{ moles}) \left(-1680 \frac{\text{kJ}}{\text{mol}}\right) = -108,200 \text{ kJ/mol}
\]

F. Given that octane has an enthalpy of combustion of $\Delta_{\text{comb}} H^\circ (560K) = -5200 \text{ kJ/mol}$, a molar mass of 114 g/mol and a density of $\rho = 0.7 \text{ g/cm}^3$, compare the heats of both on a per mol basis and then on a per gallon basis. (2 points)

Solution: the number of moles of octane per gallon is $\frac{(3800 \text{ cm}^3)(0.7 \text{ g/cm}^3)}{(114 \text{ g/mol})} = 47.6 \text{ moles}$.

The total heat for octanol is

\[
q = n\Delta_{\text{comb}} H^\circ (560K) = (47.6 \text{ moles}) \left(-5200 \frac{\text{kJ}}{\text{mol}}\right) = -247,500 \text{ kJ/mol}
\]

Octane still wins by more than a factor of two.

6. If octane and ethanol powered engines run at 560 K, what is the thermodynamic efficiency of each? (6 points)

Answer: the maximum efficiency is $\eta = 1 - \frac{298}{560} = 0.476$.

It does not matter what the fuel is.

7. NO\textsubscript{2} enters the ocean and forms nitric acid. The Henry’s law constant for NO\textsubscript{2} is 0.012 mol/kg/atm. One in water NO\textsubscript{2} reacts to form both nitrous and nitric acids according to,

\[
2NO_2 + H_2O \rightarrow HNO_2 + HNO_3
\]

Subsequently, there are two equilibria, which exist in parallel,

\[
HNO_2 \rightarrow NO_2^- + H^+, \quad pK_a, 1 = 3.3
\]
\[ HNO_3 \rightarrow NO_3^- + H^+, \quad pK_a, 2 = -1.3 \]

A. Assuming that the average level of NO\(_2\) in the atmosphere is 0.012 ppm. Calculate the concentration of NO\(_2\) in the ocean (without taking the acid equilibria into account). (6 points)

Solution:

\[ K_{H,NO_2} = \frac{P_{NO_2}}{m_{NO_2}} \]

\[ m_{NO_2} = \frac{P_{NO_2}}{K_{H,NO_2}} = \frac{0.012 \times 10^{-6}}{0.012} = 10^{-6} \text{ mol/kg} \]

B. Assuming that the NO\(_2\) in the ocean is equally partitioned between HNO\(_2\) and HNO\(_3\), calculate the concentration of NO\(_2^-\) and NO\(_3^-\) in the ocean from the gaseous NO\(_2\) taken up from the atmosphere. Assume that the pH of the ocean is 8.1 and is not affected by the uptake of NO\(_2\). (10 points)

Solution:

\[ K_{a,1} = \frac{[NO_2^-][H^+]}{[HNO_2]} = 10^{-pK_a,1} \]

\[ K_{a,2} = \frac{[NO_3^-][H^+]}{[HNO_3]} = 10^{-pK_a,2} \]

\[ \frac{x}{[HNO_2]} - x = \frac{10^{-pK_a,1}}{[H^+]} = 10^{-pK_a,1+pH} = 10^{-3.3+8.1} = 10^{4.8} \]

\[ x = (6.3 \times 10^4)(5 \times 10^{-7} - x) \]

\[ x = 10^{4.8}(5 \times 10^{-7} - x) \]

\[ x \approx 5 \times 10^{-7} \]

\[ \frac{y}{[HNO_3]} - y = \frac{10^{-pK_a,2}}{[H^+]} = 10^{-pK_a,2+pH} = 10^{-(1.3)+8.1} = 10^{9.4} \]

\[ y = (2.5 \times 10^9)(5 \times 10^{-7} - y) \]

\[ y \approx 5 \times 10^{-7} \]

They are both completely dissociated in the ocean.

8. Calculate the molar mass of a protein determined from a measurement of the osmotic pressure. If 4 milligrams of the protein is dissolved in 1 mL and osmotic pressure of 4x10\(^{-5}\) atm
develops at a temperature of 310 K, what is the molar mass of the protein? (8 points)

Solution: \( \Pi = cRT = (m/VM)RT \rightarrow M = mRT/IV \)

\[
M = (0.004 \text{ kg/L})(0.08206 \text{ L-atm/mol-K})(310 \text{ K})/(4\times10^{-5} \text{ atm}) = 25400 \text{ daltons}
\]

Molar mass = _______________________________.

9. What temperature is required to achieve a pressure of 8 atm in a pressure cooker (10 points) ?

Solution: Use the Clausius-Clapeyron equation starting at \( T_1 = 373 \text{ K} \) and \( P_1 = 1 \text{ atm} \)

\[
\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta_{vap} H^o}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

\[
\frac{R \ln \left( \frac{K_2}{K_1} \right)}{\Delta_{vap} H^o} = \frac{1}{T_1} - \frac{1}{T_2}
\]

\[
\frac{1}{T_2} = \frac{1}{T_1} - \frac{R \ln \left( \frac{K_2}{K_1} \right)}{\Delta_{vap} H^o}
\]

\[
T_2 = \frac{1}{\frac{1}{T_1} - \frac{R \ln \left( \frac{K_2}{K_1} \right)}{\Delta_{vap} H^o}} = \frac{T_1}{1 - \frac{RT_1 \ln \left( \frac{K_2}{K_1} \right)}{\Delta_{vap} H^o}}
\]

\[
T_2 = \frac{373 \text{ K}}{(8.31(373)\ln \left( \frac{5}{1} \right)}} = 443 \text{ K}
\]

Temperature of Boiling Water at 8 atm = _______________________________.

10
10. A mercury barometer is shown in the figure. One atmosphere of pressure corresponds to a supported column of Hg that is 760 mm high.

A. Calculate the density of mercury. Show your work.

B. Suppose the barometer is taken to the top of Mt. Mitchell, the highest point in North Carolina. Assume that Mt. Mitchell is 2000 m in elevation at the top. How high will the column of Hg be at that elevation. (12 points)

Solution:

A. \( P = \rho g h \rightarrow \rho = \frac{P}{gh} = (1.01325 \times 10^5 \text{ Pa})/(9.8 \text{ m/s}^2)/0.76 \text{ m}) \)

\[ = 13604 \text{ kg/m}^3 = 13.6 \text{ g/cm}^3. \]

B. Calculate the pressure at the top of Mt. Mitchell using the barometric pressure formula.

\[ P = \exp \left\{ - \frac{Mgh}{RT} \right\} = \exp \left\{ - \frac{(0.029 \text{ kg/mol})(9.8 \text{ m/s}^2)(2000 \text{ m})}{(8.31 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \right\} = 0.795 \text{ atm} \]

For this part we can accept \( M = 0.028 \text{ kg/mol} \) if you just used the value for \( \text{N}_2 \). We can also accept \( g = 10 \text{ m/s}^2 \) as an approximate value.

If the atmospheric pressure is reduced to 0.795 atm the column of Hg will be reduced by the same factor so it will be:

\[ h_2 = h_1 \left( \frac{P_2}{P_1} \right) = 760 \text{ mm} \left( \frac{0.795 \text{ atm}}{1 \text{ atm}} \right) = 604 \text{ mm} \]

11. Tall trees must transport water from their roots to the leaves. Two obvious mechanisms for transporting water are suction and capillary action. Consider each of these:

A. Suction requires that the tree create a vacuum inside a xylem tube. Then the water will rise due to the external pressure of the atmosphere. What is the tallest column of water that can be supported by this mechanism? [HINT: this is equivalent to asking the depth in water that has the equivalent pressure of the atmosphere] (6 points)

\[ P = \rho gh \]

\[ h = \rho g/P = (1000 \text{ kg/m}^3)(9.8 \text{ m/s}^2)/10^5 \text{ Pa} = 10.2 \text{ m} \]

Height of a column of water created by suction = __________________________ meters.
B. Capillary action requires a thin column. Calculate the height of a column of water in the xylem of a tree that has a radius of 300 nanometers ($\gamma = 72 \times 10^{-3}$ N/m). (4 points)

Solution: $h = \frac{2\gamma}{\rho g r}$, $\gamma = 72 \times 10^{-3}$ N/m

$\rho = 1000$ kg/m$^3$

$h = \frac{2(72 \times 10^{-3}$ N/m)/(1000 kg/m$^3$)/(9.8 m/s$^2$)(300 x $10^{-9}$ m)}{}

= 48.9 m

Height of a column created by capillary action = __________________________ meters

12. Ammonium nitrite (NH$_4$NO$_3$) is used in cold packs. These can cool a wound very quickly due to the spontaneous solution of the salt in water. However, the cold packs do not work at all temperatures possible outdoors.

A. Calculate the free energy of reaction at 298 K and at 273 K for the solvation of NH$_4$NO$_3$.

$\text{NH}_4\text{NO}_3(s) \rightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq)$

($\Delta_{\text{rxn}H}^0 = +25.7$ kJ/mol, $\Delta_{\text{rxn}S}^0 = +108.7$ J/mol-K are independent of temperature). (4 points)

Solution: A. The free energy is

$\Delta_{\text{rxn}}G^0 = \Delta_{\text{rxn}}H^0 - T \Delta_{\text{rxn}}S^0 = 25,700$ J/mol $-$ (298 K)(108.7 J/mol-K) = -6,690 J/mol

$\Delta_{\text{rxn}}G^0 = \Delta_{\text{rxn}}H^0 - T \Delta_{\text{rxn}}S^0 = 25,700$ J/mol $-$ (273 K)(108.7 J/mol-K) = -3,800 J/mol

A. The Standard Free Energy Change $\Delta_{\text{rxn}}G^0 = \text{_______________}$ at 298 K.

The Standard Free Energy Change $\Delta_{\text{rxn}}G^0 = \text{_______________}$ at 273 K.

B. Calculate $\Delta_{\text{rxn}}G$ if there are three moles of NH$_4^+$ and NO$_3^-$ in a beaker containing 1 L of water at 298 K. (3 points)

B. $\Delta_{\text{rxn}}G = \Delta_{\text{rxn}}G^0 + RT\ln Q = -6690$ J/mol + (8.31 J/mol-K)(298 K)ln([3][3]) = -1250 J/mol

The Free Energy Change $\Delta_{\text{rxn}}G = \text{_______________}$ at 3 molar concentration.

C. Now, Calculate $\Delta_{\text{rxn}}G$ if there are three moles of NH$_4^+$ and NO$_3^-$ in a beaker containing 1 L of water at 273 K. (3 points)

C. $\Delta_{\text{rxn}}G = \Delta_{\text{rxn}}G^0 + RT\ln Q = -3800$ J/mol + (8.31 J/mol-K)(273 K)ln([3][3]) = +1000 J/mol

The Free Energy Change $\Delta_{\text{rxn}}G = \text{_______________}$ at [NH$_4$NO$_3$] = 3M and 273 K.

D. Assuming that 3 moles of NH$_4$NO$_3$ were to dissolve in the water, calculate the final temperature of the solution. (6 points)

D. The heat absorbed by the reaction is equal to that removed from the water.
q(water) = - nNH₄NO₃\Delta_{\text{rxn}}H^\circ
n_{\text{water}}C_p(\text{water})\Delta T = - nNH₄NO₃\Delta_{\text{rxn}}H^\circ
\Delta T = -n_{\text{NH₄NO₃}}\Delta_{\text{rxn}}H^\circ / n_{\text{water}}C_p(\text{water})
= - (3 \text{ mol})(25,700 \text{ J/mol})(55.5 \text{ mol})(75.3 \text{ J/mol-K}) = -18.4 \text{ K}

The final temperature is T_{\text{final}} = 298 \text{ K} - 18.4 \text{ K} = 279.6 \text{ K}

The Temperature is ________________________________.

13. 1.00 moles of a diatomic ideal gas initially at 10 atm and 300 K undergoes the following processes:

A. a constant volume cooling step until the pressure is 1 atm.
B. a constant pressure expansion until the final volume at 1 atm is reached.
C. a isothermal compression until the original pressure is restored.

I. Sketch a P vs. V diagram for the cycle. (4 points)

II. Calculate q, w, \Delta U and \Delta H (in Joules) for each step and for the total cycle. (32 points)

A. For the constant volume step w = 0, and
\Delta U = q = nC_v\Delta T = n5/2R(T_f-T_i) = (1 \text{ mol})(2.5)(8.31 \text{ J/mol-K})(300 \text{ K} – 300 \text{ K}) = -5610 \text{ J}
\Delta H = \Delta U for this step since P\Delta V = 0 by definition.

B. For this part we will need to know the volume, which was not given in the set up.
V_1 = nRT/P = (1 \text{ moles})(0.08206 \text{ L-atm/mol-K})(300\text{K})(10 \text{ atm}) = 2.46
V_2 = nRT/P = (1 \text{ moles})(0.08206 \text{ L-atm/mol-K})(300\text{K})(1 \text{ atm}) = 24.6
constant pressure expansion w = -P\Delta V = -(1 \text{ atm})(24.6 \text{ L} – 2.46 \text{ L}) = -22.1 \text{ L-atm} = -2240 \text{ J}
for this step q = nC_p\Delta T = n7/2R(T_f-T_i) = (1 \text{ mol})(3.5)(8.31 \text{ J/mol-K})(300 \text{ K} – 30 \text{ K}) = 7850 \text{ J}
\Delta U = w + q = -2243 \text{ J} + 7850 \text{ J} = 5607 \text{ J}, \Delta H = \Delta U + P\Delta V = 7850 \text{ J}

C. For the reversible compression \Delta U = 0, therefore q = -w.
w = -nR\ln(V_1/V_2) = -(1 \text{ mol})(8.31 \text{ J/mol-K})(300 \text{ K})\ln(1/10) = 5740 \text{ J}, q = -5740 \text{ J}

<table>
<thead>
<tr>
<th></th>
<th>q</th>
<th>w</th>
<th>\Delta U</th>
<th>\Delta H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.</td>
<td>-5610</td>
<td>0</td>
<td>-5610</td>
<td>-7850</td>
</tr>
<tr>
<td>B.</td>
<td>7850</td>
<td>-2240</td>
<td>5610</td>
<td>7850</td>
</tr>
<tr>
<td>C.</td>
<td>-5740</td>
<td>5740</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>-3500</td>
<td>3500</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
14. Assuming that the pH in the periplasmic space is 5.2 and that of the cytoplasm is 7.5, calculate the molar free energy at 280 K stored by pumping protons. (10 points)

Solution: The transmembrane potential is \( \Delta E = RT/F \ln(c_o/c_i) \). and the molar free energy is \( \Delta G = -RT \ln(c_o/c_i) \). We know the following:

- \( c_o = 10^{pH_o} = 10^{-5.2} \)
- \( c_i = 10^{pH_i} = 10^{-7.5} \)
- \( \frac{c_o}{c_i} = 10^{pH_o+pH_i} = 10^{-5.2+7.5} = 10^{-2.3} = 0.005 \text{ M} \)
- \( \Delta G = -RT \ln \left( \frac{c_o}{c_i} \right) = (8.31 \text{ J/mol-K}) (280 \text{ K}) \ln(0.005) = -12,300 \text{ J/mol or } -12.3 \text{ kJ/mol} \)

Free energy change \( \Delta G = \boxed{-12,300 \text{ J/mol or } -12.3 \text{ kJ/mol}} \).

15. A balloon filled with \( \text{H}_2 \) is released into the air. Assuming that the balloon is inelastic (has a constant shape) determine the elevation to which it will rise. (10 points)

Solution: The balloon will rise until the density of the air is equal to the density of the gas inside the balloon (\( \text{H}_2 \) gas at 1 atm). First we calculate the density of the gas inside the balloon.

\[ \rho = \frac{MP}{RT} = \frac{(0.002 \text{ kg/mol})(10^5 \text{ Pa})}{(8.31 \text{ J/mol-K})(298 \text{ K})} = 0.161 \text{ kg/m}^3 = 8.05 \times 10^{-5} \text{ g/cm}^3 \]

We will also need to know the density of the atmosphere at sea level as a reference.

\[ \rho_0 = \frac{M_0P}{RT} = \frac{(0.029 \text{ kg/mol})(10^5 \text{ Pa})}{(8.31 \text{ J/mol-K})(298 \text{ K})} = 1.17 \text{ kg/m}^3 = 1.17 \times 10^{-3} \text{ g/cm}^3 \]

Since the density is proportional to the pressure we can rewrite the barometric pressure formula.

\[ \rho = \rho_0 e^{\frac{Mgh}{RT}} \]

and then solve for \( h \)

\[ h = -\frac{RT}{Mg} \ln \left( \frac{\rho}{\rho_0} \right) = \frac{(8.31 \text{ J/mol-K})(298 \text{ K})}{(0.029 \text{ kg/mol})(9.8 \text{ m/s}^2)} \ln \left( \frac{1.17}{0.0805} \right) = 23,230 \text{ m} \]

III. Kinetics

16. An enzyme that follows Michaelis-Menten kinetics has a \( K_m \) of 170 \( \mu \text{M} \). The initial velocity is 2.6 \( \mu \text{M/min} \) at a substrate concentration of 260 \( \mu \text{M} \) and an enzyme concentration of 2 \( \mu \text{M} \). Determine \( V_{max} \) and \( k_{cat} \) (the latter in units of \( \text{s}^{-1} \)) (10 points)

Solution: First determine \( V_{max} \) using the Michaelis-Menten equation.

\[ V_{max} = \frac{V(K_m + [S])}{[S]} = \frac{(2.6 \mu\text{M/min})(170 \mu\text{M} + 260 \mu\text{M})}{260 \mu\text{M}} = 4.3 \mu\text{M/min} \]

\[ k_{cat} = \frac{V_{max}}{[E]_0} = \frac{4.3 \mu\text{M/min}}{2 \mu\text{M}} = 2.15 \text{ min}^{-1} = 129 \text{ s}^{-1} \]
\[ V_{\text{max}} = \underline{\underline{}}. \]

\[ k_{\text{cat}} = \underline{\underline{}} \,(s^{-1}). \]

17. Given that the half-life of \(^{14}\text{C}\) is 5770 years, calculate the age of a sample that has 6\% of the original level of \(^{14}\text{C}\) obtained from the atmospheric ratio of \(^{14}\text{C}/^{12}\text{C}\) (10 points)

Solution:

\[
\frac{[^{14}\text{C}]}{[^{14}\text{C}]_0} = 0.06
\]

\[
\ln \left( \frac{[^{14}\text{C}]}{[^{14}\text{C}]_0} \right) = -kt = -\frac{\ln(2)}{\tau_{1/2}}t
\]

\[
t = \ln \left( \frac{[^{14}\text{C}]}{[^{14}\text{C}]_0} \right) \frac{\tau_{1/2}}{\ln(2)} = \ln \left( \frac{1}{0.06} \right) \frac{5770 \text{ years}}{\ln(2)} = 23,420 \text{ years}
\]

Age of the sample = \underline{\underline{}}.

18. The rate data and thermodynamic data for the unfolding of gobulascia is given below. Determine the rate constants for folding and unfolding. The reaction is a two-state process shown below:

\[ F \leftrightarrow U \]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Equilibrium Constant</th>
<th>Observed Unfolding Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>310</td>
<td>0.15</td>
<td>(4.2 \times 10^5 \text{ s}^{-1})</td>
</tr>
<tr>
<td>340</td>
<td>10.6</td>
<td>(5.7 \times 10^4 \text{ s}^{-1})</td>
</tr>
</tbody>
</table>

A. Calculate the rate constant for folding and unfolding at each temperature (8 points).

\[ \text{At } 310 \text{ K} \]

\[ k_f = \frac{4.2 \times 10^3 \text{ s}^{-1}}{1.15} = 3650 \text{ s}^{-1} \]

\[ k_u = k_{\text{obs}} - k_f \approx 4200 \text{ s}^{-1} - 3650 \text{ s}^{-1} = 550 \text{ s}^{-1} \]

\[ \text{At } 340 \text{ K} \]

\[ k_f = \frac{5.7 \times 10^4 \text{ s}^{-1}}{10.6} = 5400 \text{ s}^{-1} \]

\[ k_u = k_{\text{obs}} - k_f \approx 51600 \text{ s}^{-1} \]
\[ K = \frac{k_u}{k_f}, \quad k_{\text{obs}} = k_f + k_u \]

- \[ k_u = k_{\text{obs}} - k_f \]
- \[ k_f K = k_{\text{obs}} - k_f \]
- \[ k_f (K + 1) = k_{\text{obs}} \]
- \[ k_f = \frac{k_{\text{obs}}}{(K + 1)} \]

B. Calculate the activation energy for the folding and unfolding processes (8 points).

**Solution:**

\[
E_{a_{\text{folding}}} = R \ln \left( \frac{k_2}{k_1} \right) = 8.31 \left( \frac{J}{mol \cdot K} \right) \ln \left( \frac{5400}{3650} \right) = 11.4 \text{ kJ/mol}
\]

\[
E_{a_{\text{unfolding}}} = R \ln \left( \frac{k_2}{k_1} \right) = 8.31 \left( \frac{J}{mol \cdot K} \right) \ln \left( \frac{51600}{550} \right) = 132.6 \text{ kJ/mol}
\]

19. Domain swapped proteins have a folding pathway that involves formation of a dimer as an on-pathway intermediate. There are two possible mechanisms:

**Mechanism A**

\[
2 \ U \leftrightarrow 2 \ I \leftrightarrow F_2
\]

**Mechanism B**

\[
2 \ U \leftrightarrow I_2 \leftrightarrow F_2
\]

Assuming that \( k_2 >> k_1 \) determine an expression for the rate of formation of the folded dimer \( F_2 \) as a function of the concentration of the starting unfolded polypeptide \( [U] \) according to each mechanism. Is there an experimental means of distinguishing between these mechanisms? (12 points)

**Solution:**
Mechanism A

\[ \frac{d[F_2]}{dt} = k_2[I]^2 \]

\[ \frac{d[I]}{dt} = -(k_{-1} + k_2)[I]^2 + k_1[U]^2 \approx 0 \]

Mechanism B

\[ \frac{d[I]}{dt} = -\left(k_{-1} + k_2\right)[I] + k_1[U]^2 \approx 0 \]

\[ [I]^2 = \frac{k_1[U]^2}{k_{-1} + k_2} \]

Answer: no, it is not possible to distinguish between these mechanisms.

20. The kinetics of double-stranded formation for a dodecamer containing two G.T base pairs was measured by temperature-jump kinetics. The reaction is:

\[ 2 \text{CGTGAATTCGCG} \rightleftharpoons \frac{k_1}{k_{-1}} \text{CGTGAATTCGCG} \leftrightarrow \text{CGCCTTAAGCGC} \]

The following data were obtained:

<table>
<thead>
<tr>
<th>T °C</th>
<th>( k_1 ) ((10^5 \text{ M}^{-1} \text{ s}^{-1}))</th>
<th>( k_{-1} ) ((\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.0</td>
<td>1.00</td>
<td>0.8</td>
</tr>
<tr>
<td>31.0</td>
<td>1.13</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Determine \( E_a \), for the forward and reverse processes, assuming that the value of \( E_a \) is independent of temperature. (10 points)

**Solution:** Use the Arrhenius equation

\[ k = A \exp \left\{ -\frac{E_a}{RT} \right\} \]

Solve for \( E_a \)

\[ E_a = \frac{-R \ln \left( \frac{k_2}{k_1} \right)}{\left( \frac{1}{T_2} - \frac{1}{T_1} \right)} \]

For the forward (hybridization process) we have
\[ E_a = \frac{-\left(8.31\ln \left(\frac{1.13}{1.0} \right)\right)}{\left(\frac{1}{3.04} - \frac{1}{3.00}\right)} = 23.2 \text{ kJ/mol} \]

For the reverse (denaturation) process we have

\[ E_a = \frac{-\left(8.31\ln \left(\frac{1.4}{0.8} \right)\right)}{\left(\frac{1}{3.04} - \frac{1}{3.00}\right)} = 106 \text{ kJ/mol} \]

21. Sketch the relationship between standard enthalpy, \( \Delta H^o \) and \( \Delta H^\dagger \) for the forward and reverse reactions. (10 points)

Solution: According to transition state theory the relationship between the enthalpies is as given in the Figure below.

\[ \Delta H^o = \Delta H^\dagger(\text{reverse}) - \Delta H^\dagger(\text{forward}) \]
Final Exam Equations, Constants and Data

\[ g = 9.81 \text{ m/s}^2 \]
\[ R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \]
\[ 1 \text{ a.m.u.} = 1.67 \times 10^{-27} \text{ kg} \]
\[ \text{electron mass} = 9.31 \times 10^{-31} \text{ kg} \]
\[ \sigma = 5.67 \times 10^{-8} \text{ W/m}^2/\text{K}^4 \]
\[ \text{Electron charge} = 1.62 \times 10^{-19} \text{ C} \]
\[ \text{The Rydberg constant} = 13.6 \text{ eV} = 109690 \text{ cm}^{-1} \]
\[ 1 \text{ Debye} = 3.33 \times 10^{-30} \text{ Cm} \]
\[ 1 \text{ atm} = 1.0133 \times 10^5 \text{ Nm}^{-2} = 760 \text{ Torr} \]
\[ F = 96,450 \text{ C/mol} \]
\[ h = 6.626 \times 10^{-34} \text{ Js} \]
\[ c = 2.99 \times 10^8 \text{ m/s} \]
\[ k_B = 1.38 \times 10^{-23} \text{ J/K} = 0.697 \text{ cm}^{-1}/\text{K} \]

\[ W = \sigma T^4 \quad \lambda_{\text{max}} \quad T = 2.88 \times 10^6 \text{ nm-K} \quad E = -ZR/n^2 \]

\[ h\nu = \Phi + 1/2mv^2 \quad \Delta E = h\nu \quad \lambda = h/p \]

\[ E = \left( \nu + \frac{1}{2} \right) h\nu \quad E = \frac{h^2m^2}{8m_e\pi^2R^2} \quad E = \frac{h^2n^2}{8m_eL^2} \]

\[ \omega = 2\pi
\nu \quad \omega = \frac{\sqrt{k}}{\mu} \quad \bar{\nu} = \frac{\nu}{c} \quad \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \]

\[ \mu = \frac{m_1m_2}{m_1 + m_2} \quad I = \mu R^2 \quad E_j = \frac{h^2}{8\pi^2 I}J(J + 1) \]

\[ g_j = 2J + 1 \quad \ddot{B} = \frac{h}{8\pi^2 c\mu R^2} \quad \frac{-h^2}{2m\partial^2} \Psi = E\Psi \]

\[ \Phi_f = \frac{k_f}{k_f + k_{IC}} \quad \Phi_f = \frac{k_f}{k_f + k_{IC} + k_Q[Q]} \quad I(\alpha) = \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \frac{\sqrt{\pi}}{\sqrt{\alpha}} \]
\[ k_f = \frac{1}{\tau_f} \quad k = \frac{\ln(2)}{\tau_{1/2}} \quad \tau_{1/2} = \frac{1}{k[A]} \]

\[
U = 1/2Mv^2 = \frac{3}{2}RT \quad \sqrt{\langle v^2 \rangle} = \frac{3RT}{\sqrt{M}} \quad R = k_B N_A
\]

\[ \Delta U = q + w \quad dw = -PdV \quad w = -nRT \ln(V_2/V_1) \]

\[ w = -P_{\text{ext}} \Delta V \quad q_v = C_v \Delta T \quad \Delta H = q_p = C_p \Delta T \quad \Delta H = \Delta U + P \Delta V \]

\[ \Delta H = \Delta U + \Delta nRT \quad \Delta H = \Delta U + nRT \Delta T \quad dU = C_v dT = \delta w = -PdV \]

\[ \left( \frac{T_2}{T_1} \right) = \left( \frac{V_1}{V_2} \right)^{nR/C_v} \quad \frac{P_2 V_2}{P_1 V_1} = \frac{T_2}{T_1} \quad dS \geq \frac{\delta q}{T}, \quad \Delta S \geq \frac{q}{T} \]

\[ \Delta S = \frac{\Delta H}{T} \quad \Delta S = C_p \ln \left( \frac{T_2}{T_1} \right) \quad \Delta S = C_v \ln \left( \frac{T_2}{T_1} \right) \quad \Delta S = nR \ln \left( \frac{V_2}{V_1} \right) \]

\[ \Delta S = -nR(x_1 \ln x_1 + x_2 \ln x_2) \quad S = R \ln W, \quad W = M^N \]

\[ \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \]

\[ \eta = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} = \frac{|w|}{q_{\text{hot}}} \]

\[ T_{\text{eq}} = \frac{C_pT_1 + C_pT_2}{C_p + C_p} \]

\[ P = P_0 \exp \left\{ -\frac{Mgh}{RT} \right\} \]

\[ P = \rho gh \quad \rho = \frac{m}{V} = \frac{MP}{RT} \quad \mu = ezd \]

\[ \Delta G = \Delta G^0 + RT \ln Q \quad \mu_i = \mu_i^0 + RT \ln x_i \quad \mu_i = \mu_i^* + RT \ln x_i \]

\[ P_2 = P_1 + \frac{\Delta_{\text{trans}}}{V} \ln \left( \frac{T_2}{T_1} \right) \quad \ln \left( \frac{P_2}{P_1} \right) = -\frac{\Delta_{\text{trans}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

\[ \ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \ln \left( \frac{k_2}{k_1} \right) = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

\[ a_2 = -\frac{\Delta_{\text{fus}} H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]
\[ dU = TdS - PdV \quad dG = -SdT + VdP \]
\[ dH = TdS + VdP \]
\[ D = \frac{k_B T}{f} \quad f = 6\pi\eta r \quad M = \frac{RTs}{D(1 - \nu_2 \rho)} \quad a = \omega^2 x \]
\[ \Delta E = \frac{RT}{nF} \ln \left( \frac{c_o}{c_i} \right) \quad \Delta G^o = -nF\Delta E \quad \Pi = cRT \quad P_i = K_{H,i}c_i \]
\[ a_i = \gamma_i x_i \quad P_i = x_i P_{i}^{*} \quad P_i = \gamma_i P_{\text{total}} \quad \frac{P_2}{P_1} = e^{-\Delta E/kT} \quad P_{\text{in}} = P_{\text{out}} + \frac{2\gamma}{r} \]
\[ k = Ae^{-E_a/RT} \quad k = \frac{k_B T}{h} e^{-E_a/RT} \]
\[ E_a = \frac{(\varepsilon - \lambda)^2}{4\lambda} \quad k = \frac{V^2}{\sqrt{4\pi\lambda kT}} \exp \left\{ - \frac{(\varepsilon - \lambda)^2}{4\lambda} \right\} \]
\[ V = \frac{V_{\text{max}}[S]}{K_M + [S]} \quad K_M = \frac{k_{-1} + k_{\text{cat}}}{k_1} \quad V_{\text{max}} = k_{\text{cat}}[E]_0 \]
\[ q_{\text{trans}} = \left( \frac{2\pi mk_B T}{h} \right)^{\frac{3}{2}} V \]

### Surface Tension Data

<table>
<thead>
<tr>
<th>Substance</th>
<th>Surface tension (mN/m)</th>
<th>Temperature (°C)</th>
<th>Cp (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72</td>
<td>25</td>
<td>75.3</td>
</tr>
<tr>
<td>Water</td>
<td>59</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>29</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Water Phase Data

<table>
<thead>
<tr>
<th>Point</th>
<th>Pressure (atm)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triple Point</td>
<td>0.006</td>
<td>273.16</td>
</tr>
</tbody>
</table>
For H₂O: $V_m = 0.018 \text{ L/mol (liquid)}$
\[ \rho = 1.00 \text{ g/cm}^3 \text{ (liquid)} \]
$\Delta H_{\text{fus}} = 6.0 \text{ kJ/mol}$
$\Delta H_{\text{vap}} = 40.65 \text{ kJ/mol}$

**Thermodynamic data**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^\circ$</th>
<th>$S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>-1207.9</td>
<td>93</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>-986.09</td>
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</tr>
<tr>
<td>Ca(OH)₁₂</td>
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<td></td>
</tr>
<tr>
<td>CaO</td>
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<tr>
<td>C</td>
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<td>CO₂</td>
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<tr>
<td>CO</td>
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</tr>
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<td>H₂O (l)</td>
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</tr>
<tr>
<td>H₂O (g)</td>
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</tr>
<tr>
<td>H₂O₂</td>
<td>-187.78</td>
<td></td>
</tr>
</tbody>
</table>