You have 52 minutes for this exam.

Exams written in pencil or erasable ink will not be re-graded under any circumstances.

Explanations should be concise and clear. I have given you more space than you should need. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Partial credit will be given, i.e., if you don’t know, guess.

Useful Equations:

\[ K_a = [\text{H}^+][\text{A}^-]/[\text{HA}] \]
\[ K_w = [\text{H}^+][\text{OH}^-] \]
\[ R = 0.08206 \text{ L·atm/mole K} \]
\[ \Delta E = q + w \]
\[ S = k_B \ln W \]
\[ W = N!/(\Pi n_i!) \]

**Honor Pledge:** At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

“I pledge on my honor that I have not given or received any unauthorized assistance on this examination.”
1. (20 pts) Short Answer/True-False

(a; 10 pts) Fill in the blanks: a(n) _____ microstate (+2)____ (1) is an instantaneous description of all the positions, velocities, and electronic/vibrational/rotational states of all the particles in a system. A collection of (1)’s that all have the same observables like P, V, and T is called a(n) _____ configuration (+3)____ (2). The set of all possible (1)’s at a given total energy is called the _____ ensemble (+3)________(3). For a macroscopic system, almost all of the (1)’s in a(n) (3) will belong to the _____ predominant (+2)______ member of the set of (2)’s.

(b; 10 pts) Identify whether each of the following statements about the Boltzmann Distribution is true or false: +2 each for correct

(i) Energy is distributed among particles such that all particles have the same energy. Circle one: True  False

(ii) The number of particles with a given energy is an exponentially decreasing function of the energy (ignoring degeneracy). Circle one: True  False

(iii) The B.D. is observed in the maximum possible number of different possible microstates that have a given total energy. Circle one: True  False

(iv) The B.D. allows us to determine whether one particular microstate with a given total energy is more likely to be observed than a second particular microstate. Circle one: True  False

(v) The B.D. predicts a Gaussian distribution of energy among particles. Circle one: True  False
2. **(15 pts) Thermochemistry (adapted from Oxtoby)**

Zinc is commonly found as the mineral sphalerite, ZnS (s). It must be roasted to give zinc oxide during smelting, according to the reaction below:

\[
2 \text{ZnS (s)} + 3 \text{O}_2 (g) \rightarrow 2 \text{ZnO (s)} + 2 \text{SO}_2 (g)
\]

Calculate the standard enthalpy of reaction \(\Delta H_{\text{rxn}}^\circ\) using data in the table at the right. Why is \(\Delta H_f^\circ\) of \(\text{O}_2 (g)\) exactly equal to zero? [Note that smelting doesn’t occur at 25 °C, but the magic of thermodynamics is that we can calculate the \(\Delta H\) that would be observed if we could actually do the reaction.]

\+ 3 \(\Delta H_f^\circ\) of \(\text{O}_2\) is 0 because \(\Delta H_f^\circ\) is defined as the heat released upon formation of a compound from the standard stable state of its elements, so since \(\text{O}_2 (g)\) is already the standard state of an element the \(\Delta H_f^\circ\) is 0.

\+ 4 \(\Delta H_{\text{rxn}}^\circ = \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants})\)

\+ 4 \[= 2\*(-348.28) + 2\*(-296.83) - 2\*(-205.98) - 3\*0\]

\+ 4 \[= -878.26 \text{ kJ/mol}\]

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<table>
<thead>
<tr>
<th>Substance</th>
<th>(\Delta H_f^\circ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{N}_2\text{H}_4 (l))</td>
<td>50.63</td>
</tr>
<tr>
<td>(\text{NO}_2 (g))</td>
<td>33.18</td>
</tr>
<tr>
<td>(\text{N}_2 (g))</td>
<td>0</td>
</tr>
<tr>
<td>(\text{H}_2\text{O (l)})</td>
<td>-285.83</td>
</tr>
<tr>
<td>(\text{NH}_3 (g))</td>
<td>-46.11</td>
</tr>
<tr>
<td>(\text{ZnS (s)})</td>
<td>-205.98</td>
</tr>
<tr>
<td>(\text{ZnO (s)})</td>
<td>-348.28</td>
</tr>
<tr>
<td>(\text{Zn (s)})</td>
<td>0</td>
</tr>
<tr>
<td>(\text{SO}_2 (g))</td>
<td>-296.83</td>
</tr>
<tr>
<td>(\text{S (g)})</td>
<td>278.80</td>
</tr>
<tr>
<td>(\text{S (s, rhombic)})</td>
<td>0</td>
</tr>
<tr>
<td>(\text{O}_2 (g))</td>
<td>0</td>
</tr>
</tbody>
</table>

Score for the page______________
3. (15 pts) Solubility Equilibria

What is the pH of a saturated solution of silver hydroxide AgOH (s)? What would the [Ag⁺] (aq) ion concentration be if the pH were adjusted to 14 with NaOH?

Aqueous Solubility Products (25 °C)

<table>
<thead>
<tr>
<th>Heterogeneous Equilibrium</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)$_2$ (s) = Mg$^{2+}$(aq) + 2 OH$^-$ (aq)</td>
<td>5.6 x 10$^{-12}$</td>
</tr>
<tr>
<td>Ag(OH) (s) = Ag$^+$(aq) + OH$^-$ (aq)</td>
<td>1.52 x 10$^{-8}$</td>
</tr>
<tr>
<td>Al(OH)$_3$ (s) = Al$^{3+}$(aq) + 3 OH$^-$ (aq)</td>
<td>1.9 x 10$^{-33}$</td>
</tr>
</tbody>
</table>

+3 $K_{sp} = [Ag^+][OH^-] = 1.52 \times 10^{-8}$

+2 The concentrations $[Ag^+] = [OH^-] = x$

+2 $x^2 = 1.52 \times 10^{-8}$ so

+2 $x = \sqrt{1.52 \times 10^{-8}} = 1.233 \times 10^{-4}$ M

+3 $pOH = -\log(1.233 \times 10^{-4}) = 3.909$ so pH = 14 − pOH = 10.091 (+1 for 3.91)

+3 If the pH is 14, that means 1 M [OH$^-$], so $[Ag^+] = K_{sp}/[OH^-] = 1.52 \times 10^{-8}$ M
4. (15 pts) Fundamental Thermodynamics

Consider compressing and ideal gas in a piston by doing work on it, so that we change from an initial \((n, P_i, V_i, T_i)\) to a final \((n, P_f, V_f, T_f)\) state, with \(V_f < V_i\) and \(P_f > P_i\).

**Path #1:** the external pressure is maintained at \(P_i\), which requires that we gradually cool the gas to decrease its volume, for example by packing ice around it. After the volume reaches \(V_f\) the gas is warmed up [should have specified explicitly at constant volume] and the pressure increases.

**Path #2:** the gas is heated [should have specified at constant \(V\)] until pressure reaches \(P_f\), and then the system is cooled at constant pressure until \(V_f\) is reached.

Write an expression for the work \(w_1\) and \(w_2\) required for compression on each path (since we are doing work on the gas, \(w_1\) and \(w_2\) are positive).

We do not know enough yet to calculate the change in heat on each path, but we can calculate the difference \((q_1-q_2)\) in the amount of heat that is transferred. What is \(q_1-q_2\)?

At constant pressure \(w = -P \Delta V\) because if the system expands it does work on the surroundings and \(w < 0\). Heating and cooling at constant volume proceeds with \(w = 0\). Each path includes a constant pressure step and a constant volume step, just like the box we looked at in class, in reverse.

\[+3\] So \(w_1 = -P \Delta V = -P_i \cdot (V_f - V_i) = P_i \cdot (V_i - V_f) > 0\)

\[+3\] And \(w_2 = -P \Delta V = -P_f \cdot (V_f - V_i) = P_f \cdot (V_i - V_f) > w_1\) because \(P_f > P_i\) -- it requires more work to compress the hot gas.

\[+3\] We know that the change in energy \(\Delta E = q + w\) on either path must be the same because energy is a state function, so

\[+3\] \(q_1 + w_1 = q_2 + w_2\)

\[+3\] so \(q_1 - q_2 = w_2 - w_1 = P_i \cdot (V_i - V_f) - P_f \cdot (V_i - V_f) = (P_i - P_f) \cdot (V_i - V_f) > 0\)

Note that we don’t know whether either \(q\) is positive or negative without knowing the actual value of \(\Delta E\), but we can predict the difference. We know that on pathway #2 we are doing more work on the system and getting the same change in energy, so the heat input must be less (or even negative, so the heat that must be removed from the system is larger).
5. (20 pts) **High Energy Bonds**

“High energy bonds” are not somehow spring-loaded to release energy upon bond breakage. Rather, they are “high energy” because there is an available reaction pathway that leads to much more stable products, meaning that at equilibrium we see a large excess of products over reactants.

(a; 6 pts) Consider the reaction \( A \rightleftharpoons B \), with \( K_1 = 10 \). We can calculate the fraction of the \( A+B \) mixture found as “A”: \([B]\) must be \(10 \times [A] \), so the fraction is \([A]/([A]+[B]) = 1/(1+10) = 0.099\). If we couple the \( A = B \) reaction to \( B = C \), with \( K_2 = 1000 \), similarly calculate the fraction of the \( A+B+C \) mixture that is found in the form of “A”:

\[
\text{The ratio of concentrations of A, B, and C must be } 1:10:10000, \text{ because } [B] = 10 \times [A] \text{ and } [C] = 1000 \times [B]. \text{ Linkage. LeChatelier. Multiple equilibria.}
\]

\[
\frac{[A]}{[A]+[B]+[C]} = \frac{1}{1+10+10000} = 9.99 \times 10^{-5}
\]

(b; 5 pts) We used ATP as an example of a high-energy molecule. One molecule involved in glycolysis that actually has a higher-energy P-O bond than ATP itself is phosphoenolpyruvate (PEP), below. Draw the products of the hydrolysis reaction that breaks the P–O bond as indicated, assuming that the RO⁻ leaving group picks up a proton from a water molecule so that there is no net consumption or production of protons as written (the other product is \( HPO_4^{2-} \), a form of inorganic phosphate “Pₗ” that is present at pH 7, whereas \( H_2PO_4^- \) is not).

![Diagram of PEP hydrolysis](image)

Ans:
The squiggle indicates that in this step there is no net uptake/release of protons from/to solution.

+3 for enol pyruvate
+2 for Pᵢ
(c; 9 pts) Now, consider the equilibrium between the keto and enol forms of carbonyl compounds. $K_{eq}$ for acetone in equilibrium with its enol form is about $10^{-7}$. Draw the dominant form of the final product, and explain why PEP is a “high energy molecule.”

+3 The enol/pyruvate (= B above) is much less stable than the corresponding ketone, pyruvate itself (= C above).

+3 So PEP (= A above) is a high energy molecule because it converts to much more stable products, pyruvate and inorganic phosphate. The additional driving force comes from the tautomerization reaction.

+3 The final structure is:

![Image of pyruvate structure]

6. (15 pts) Importance of pH for Enzymes

The importance of active site residue pKₐ's is not limited to residues whose only job is to provide or abstract protons. For example, the enzyme glucose-6-phosphatase is responsible for hydrolyzing a phosphate group from glucose-6-phosphate to give glucose and inorganic phosphate $P_i$. [Irrelevant fun fact: The glucose is then shipped out to the bloodstream to maintain blood glucose homeostasis. Deficiency of this enzyme is the cause of glycogen storage disease I or von Gierke’s disease.]

(a; 5 pts) Draw the product of the step shown in the mechanism below.

![Mechanism of glucose-6-phosphatase]

+2 for the N-P bond
+2 for the glucose product
+1 for deprotonated histidine

Score for the page____________
(b; 10 pts) G6Pase exhibits a bell-shaped curve for enzymatic activity vs. pH that is very similar to the one we saw for ribonuclease. Explain why the mechanism does not work if the pH is too high, and separately explain why it does not work if the pH is too low. Which histidine residue will have a lower pKa?

+3 If the pH is too high, His119 will deprotonate and it will not be able to stabilize the developing negative charge on the –O\(^-\) leaving group.

+3 If the pH is too low, the His176 will protonate and the lone pair will no longer be available as a good nucleophile. The \(p\) orbital electrons are tied up in the ring, so they don’t count.

+2 Given that His119 is initially protonated and His176 is deprotonated at the same pH, +2 His176 must be the stronger acid, so it will have the lower pKa.