Chemistry 271, Section 22xx
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General Chemistry and Energetics
Exam II (100 points total)

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:
\[ K_a = [H^+][A^-]/[HA] \quad \text{pH} = -\log([H^+]) \quad K_b = [HA][HO^-]/[A^-] \]
\[ K_w = [H^+][OH^-] \quad \text{pH} = pK_a + \log [A^-]/[HA] \quad \Delta H = q_p \]
\[ R = 0.08206 \text{ L·atm/mole K} \quad 0 \ ^\circ \text{C} = 273.15 \text{ K} \quad w = -\int PdV \]
\[ \Delta E = q + w \quad R = 8.314 \text{ J/mole K} = 1.987 \text{ cal/mole K} \]
\[ S = k_B \ln W \quad \Delta G = \Delta H - T\Delta S \quad E = \Sigma n_i \varepsilon_i \]
\[ W = N!/(\prod n_i!) \quad n/n_0 = \omega_i \exp[-(\varepsilon_i-\varepsilon_0)/kT] \quad N = \Sigma n_i \]
\[ R = N_A k_B \quad k_B = 1.38 \times 10^{-23} \text{ J/K} \quad H = E + PV \]

Chemical standard state: 1 M solutes, pure liquids, 1 atm gases

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) _____________________________ (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) _____________________________(2). The set of all possible (1)’s at a given total energy is called the _____________________________(3). For a macroscopic system, almost all of the (1)’s in a(n) (3) will belong to the ___________________________ 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:

(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

Score for the page___________
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.]

<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>
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) = Mg²⁺(aq) + 2 OH⁻(aq)</td>
<td>$5.6 \times 10^{-12}$</td>
</tr>
<tr>
<td>Ag(OH) (s) = Ag⁺(aq) + OH⁻(aq)</td>
<td>$1.52 \times 10^{-8}$</td>
</tr>
<tr>
<td>Al(OH)₃ (s) = Al³⁺(aq) + 3 OH⁻(aq)</td>
<td>$1.9 \times 10^{-33}$</td>
</tr>
</tbody>
</table>
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 and the pressure increases.

Path #2: the gas is heated 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 \(q_1-q_2\)?
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 \( A = B \), 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”:

(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 \( \text{HPO}_4^{2-} \), a form of inorganic phosphate “\( P_i \)” that is present at pH 7, whereas \( \text{H}_2\text{PO}_4^- \) is not).
(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.”

6. **(15 pts) Importance of pH for Enzymes**

The importance of active site residue $pK_a$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.
(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?