You have 50 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:

\[ K_a = [H^+][A^-]/[HA] \]
\[ pH = -\log([H^+]) \]
\[ K_b = [BH^+][OH^-]/[B] \]
\[ F = ma \]
\[ e^{i\pi} + 1 = 0 \]
\[ PV = nRT \]
\[ K_w = [H^+][OH^-] = 10^{-14} \]
\[ pH = pK_a + \log([A^-]/[HA]) \]
\[ pH (e.p.) = (pK_{a1} + pK_{a2})/2 \]
\[ R = 0.08206 \text{ L·atm/mole K} \]
\[ 0 ^\circ C = 273.15 \text{ K} \]
\[ pK_a = -\log(K_a) \]

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; 2 points each) True or false: Place an X in the appropriate column

<table>
<thead>
<tr>
<th>Statement</th>
<th>True</th>
<th>False</th>
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<tbody>
<tr>
<td>The pH at the half-equivalence point is always the average of the pK\textsubscript{a} at the beginning of a titration and at the equivalence point.</td>
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<td>The histidine side chain is neutral at pH 4.</td>
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<td>At equilibrium the rates of the forward and reverse reactions are both zero.</td>
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<tr>
<td>The Henderson-Hasselbach equation is not correct when [A\textsuperscript{-}] is too large.</td>
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<td>When we add equations we add equilibrium constants.</td>
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<tr>
<td>The buffering range for a weak acid is between the pK\textsubscript{a} and pK\textsubscript{a} + 2, but not below the pK\textsubscript{a}.</td>
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<tr>
<td>(K_p) and (K_c) are equal to each other if there are no gases involved in the equilibrium.</td>
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<td>The percent dissociation of a weak acid decreases as its concentration decreases.</td>
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<td>In multiple equilibrium problems, all equilibria must be satisfied.</td>
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<tr>
<td>The equilibrium constant of a reverse reaction is the reciprocal of the equilibrium constant of the corresponding forward reaction.</td>
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Score for the page___________
2. **(24 pts) Chemical Equilibria**

(a; 9 pts) State LeChatelier’s principle. Define the reaction quotient Q, and give the equivalent of LeChatelier’s principle in the language of thermodynamics.

(b; 3 pts) Write the $K_c$ expression for the following reaction: $\text{BaSO}_4 (s) \rightleftharpoons \text{Ba}^{2+} (aq) + \text{SO}_4^{2-} (aq)$

(c; 2 pts) Does the amount of dissolved barium ion depend on the amount of solid barium sulfate sitting at the bottom of the beaker? Circle one: YES NO

(d; 6 pts) It turns out that the numerical value of $K_c$ is $1.1 \times 10^{-10}$. The small value for $K_c$ for some sulfate salts is the basis of selective precipitations in quantitative analysis, in which, for example, one can use a standardized sodium sulfate solution to measure the barium ion concentration in a test sample. Calculate the concentration of barium ion in solution if the $[\text{SO}_4^{2-}]$ is 75 mM. If the initial barium ion concentration before precipitation with NaSO$_4$ was 125 mM, what percentage of the barium ion remains in solution?
(e; 4 pts) Why do we use NaSO₄ instead of sulfuric acid for the barium precipitation (other than safety)?

3. (18 pts) Biological Applications

(a; 6 pts) Draw the structure of the Lysine side chain at pH 7 and give its approximate pKₐ.

(b; 12 pts) Explain why measuring the pH dependence of an enzymatic reaction is a useful probe into mechanism. Explain why, however, the experiment offers only a guide to identifying the active site residue type(s). As a concrete example, explain how a rate vs. pH curve might suggest but not prove that an aspartic acid or glutamic acid residue is involved in catalysis (vs. histidine for example).
4. **(38 pts) Acid-base chemistry and multiple equilibria**

Consider the diprotic acid malonic acid, with $pK_a$'s 2.83 and 5.89. (Malonic acid is an inhibitor of the important metabolic enzyme succinate dehydrogenase.)

(a; 8 pts) The first $pK_a$ is very low relative to a typical carboxylic acid like acetic acid, $pK_a = 4.75$. This means that malonic acid is a (circle one): stronger acid or a weaker acid than acetic acid. Sketch a structure that rationalizes this (three acceptable possible answers). On the other hand, the second $pK_a$ of malonic acid is higher than the $pK_a$ of acetic acid. Explain why.

(b; 4 pts) Why can we ignore the second $pK_a$ when calculating the pH of a malonic acid solution?

(c; 6 pts) Calculate the pH of 0.150 M malonic acid, assuming (dubiously) that “$x$” << 0.150 M.
(d; 9 pts) Sketch a curve of the pH as we titrate 0.150 M malonic acid with NaOH, ignoring dilution.

Specify the pH for the beginning (the number you just calculated in c), the two half-equivalence points, and the two equivalence points (the second one is at pH = 9.53).
(e; 4 pts) We did not learn to calculate the exact pH for diprotic acid titrations, but we do know how to set up the problem. For any point on a titration of malonic acid $H_2M$ being converted to $HM^-$ and $M^{2-}$ with added NaOH, we know the [Na$^+$] and we would like to calculate the concentrations of five other chemical species. One is hydroxide. Write down the other four. (Not a trick question)

(f; 7 pts) We need five equations to solve the problem. Two of them are the two $K_a$ relationships for the first and second acid dissociation equilibria. Write down the last equilibrium relationship needed and the two conservation equations that we need to have five equations. Hint: the total charge of the solution is zero.