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.

Generous partial credit will be given, *i.e.*, if you don’t know, guess.

Useful Equations:

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

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.”

(3 pts extra credit for filling out this page accurately and completely)
1. (20 pts) Multiple choice: Circle the single best answer for each question

(a; 4 pts) The Henderson-Hasselbach relationship is
   (a) Always true, not always useful
   (b) A useful shortcut for calculating pH when either [HA] or [A\(^-\)] is very small relative to [H\(^+\)] or [HO\(^-\)]
   (c) Useful especially for strong acids and bases
   (d) Equivalent to the water self-dissociation equilibrium
   (e) (a) and (c)

(b; 4 pts) At equilibrium,
   (a) The concentrations of reactants and products remain constant
   (b) The rates of the forward and reverse reactions are zero
   (c) The rates of the forward and reverse reactions are equal
   (d) All molecular motion has stopped
   (e) (a) and (c)

(c; 4 pts) The relationship \( K_a \cdot K_b = K_w \) arises because
   (a) It refers to protonation and deprotonation of the same intermediate state of a polyprotic acid
   (b) The \( K_a \) and \( K_b \) equilibria add to give the water self-dissociation equilibrium
   (c) Mixing acid and base gives water
   (d) \( K_a \) and \( K_b \) are simply the same reaction written in forward and reverse directions
   (e) None of the above

(d; 4 pts) At high pH, enzymes can cease to work because
   (a) The protein unfolds
   (b) A residue acting as a base is protonated
   (c) A residue acting as base is deprotonated
   (d) A residue acting as an acid is deprotonated
   (e) (a) and/or (d)

(e; 4 pts) The definition of an ideal gas is that
   (a) It is completely unreactive
   (b) It exerts pressure on the container only because the particles repel each other
   (c) Its temperature is inversely proportional to pressure at constant volume
   (d) It condenses to a liquid at low temperature
   (e) None of the above
2. **(45 pts) Acid-base chemistry**

Consider the tricarboxylic acid citric acid drawn at the right in its fully protonated (pH 0) form. Its pKₐs are 3.13, 4.76, and 7.40 (actually the last one is 5.40, but I changed it for this problem so that you can assume that only the pKₐ closest to the pH is relevant).

(a; 10 pts) What is the pH of a 0.150 M solution of citric acid?

(b; 3 pts) What is the average net charge on citrate at pH = 4.76?

(c; 6 pts) Does citrate have a pI between 1 and 13? If it does, what is it? If it doesn’t, why not?
(d; 7 pts) Use the H-H relationship to calculate the pH of a solution of 0.150 M total citric acid/citrate after addition of 0.275 M NaOH.

(f; 3 pts) Assuming the H-H still applies, what would the pH be if you diluted the above solution 10-fold (to 0.015M citrate)?

(g; 5 pts) If you diluted the solution further 10000-fold (to $1.5 \times 10^{-6}$ M), would the pH go up or down, and why (qualitatively)?
(h; 9 pts) On the graph below, sketch the titration curve for NaOH addition to citric acid. Label the buffering regions and the equivalence points. Indicate the pH’s of the centers of the buffering regions, but don’t worry about the exact pH’s at equivalence points. Indicate the parts of the curve that would be different depending on the actual concentration of citric acid rather than just the number of NaOH equivalents added. Assume the pKₐ’s are 3.13, 4.76, and 7.40.

(i; 3 pts) Why is the actual last pKₐ (5.40) for citrate higher than the pKₐ for acetic acid (4.74)?
3. **(18 pts) An ideal gas, maybe.**
   
The hydrogen economy has been proposed as a possible future solution to political and technological problems.
   
   (a; 6 pts) What reaction is used to get useful energy from hydrogen? Why is H₂ viewed as a desirable fuel for cars, especially in urban areas?
   
   (b; 6 pts) Why would some US policymakers love to have an efficient method of producing H₂ from coal? Explain why such a process, in and of itself, either would or would not help at all with global climate change caused by anthropogenic CO₂.
   
   (c; 7 pts) If a car has a 50 L hydrogen fuel tank that holds H₂ gas at 200 atm pressure (roughly the pressure found in a scuba tank), at 25°C, how many grams of hydrogen are in the tank? What would be the pressure be if the same amount of hydrogen were allowed to occupy a 75 L tank?
Fundamentals of equilibrium.

(a; 4 pts) State LeChatelier’s Principle.

Consider our favorite reactions $A + B \leftrightarrow C$, with $K_{eq} = K_1$, and $C + D \leftrightarrow E$, with $K_{eq} = K_2$.

(b; 3 pts) In terms of $K_1$ and $K_2$, what is the equilibrium constant for $C \leftrightarrow B + A$?

(c; 9 pts) Prove that the equilibrium constant for $A + B + D \leftrightarrow E$ is $K_1 \cdot K_2$. 

Score for the page___________