**Chemistry 271 – 23XX** **Your Name:** ______________________

**Prof. Jason Kahn**

**University of Maryland, College Park** **Your SID #:** ______________________

**General Chemistry and Energetics**

**Exam II (100 points)** **Your Section # or time:** ______________________

**October 31, 2018**

You have 53 minutes for this exam.

Explanations should be concise and clear. 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:**

| | | |
|---|---|---|
| $K_a = [H^+][A^-]/[HA]$ | $pH = -\log([H^+])$ | $K_b = [BH^+][HO^-]/[B]$ |
| $R = 0.08206$ L·atm/mole K | $k_B = 1.38 \times 10^{-23}$ J/K | $\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$ |
| $R = 8.314$ J/mole K $= 1.987$ cal/mole K $= N_A k_B$ | | $K_a \times K_b = K_w$ |
| $°C = °K - 273.15$ | $P(v)dv = Cv^2 exp(-mv^2/2kT)$ | $\ln k = (-E_a/RT) + \ln A$ |
| $pH = pK_a + \log([A^-]/[HA])$ | $K_p = K_c(RT)^{\Delta n}$ | $K_w = [H^+][OH^-] = 10^{-14}$ |
| $e^{i\pi} + 1 = 0$ | $PV = nRT$ | $\left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$ |
| $pK_a = -\log(K_a)$ | $pH(e.p.) = ½ (pK_{a1} + pK_{a2})$ | |

**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. Acid-base equilibria I (41 pts)**

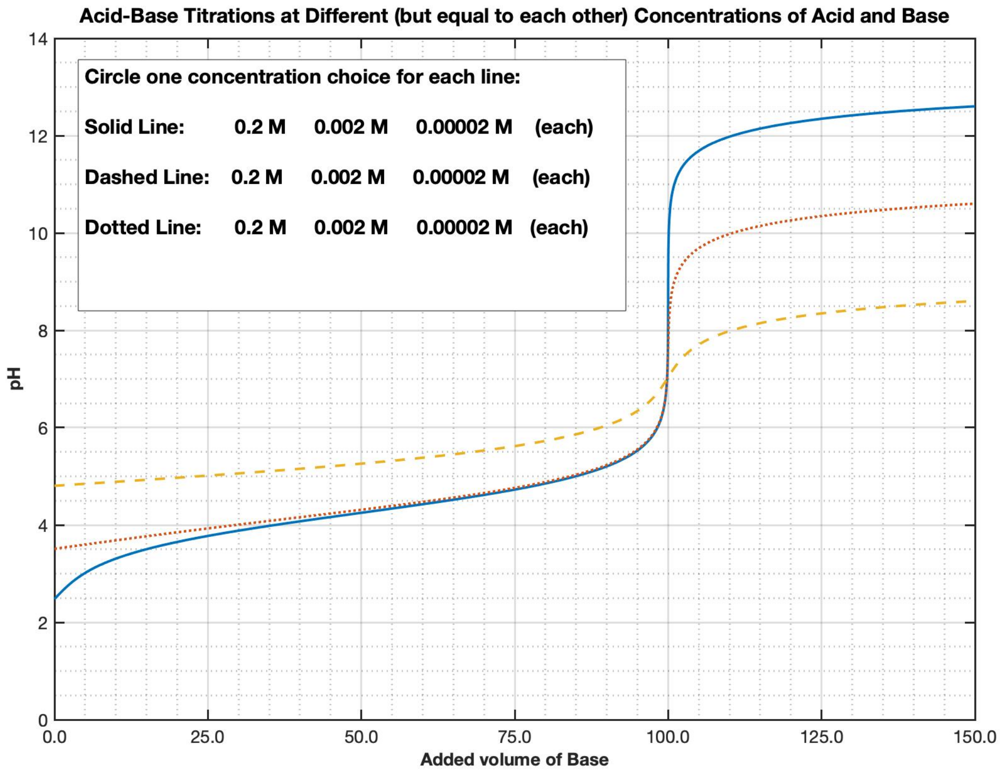
(a; 15 pts) Calculate the pH and the pOH of a 0.125 M solution of propanoic acid ($CH_3CH_2COOH$), p$K_a$ = 4.87, making the approximation that "*x* is small." Would that approximation be better or worse for chloroacetic acid ($ClCH_2COOH$), with a pKa of 2.87? Circle one: Better or Worse. Explain your reasoning.

(b; 5 pts) Without doing a calculation, how do you know that the pH of 0.1 M chloroacetic acid is less than 2.87?

Score for the page____________

(c; 6 pts) Consider the three titration curves in the graph at the right, which are three different concentrations of the same weak acid, titrated with a concentration of strong base equal to the acid concentration in each case. Circle the concentration choices in the box in the graph.

(d; 3 pts) Estimate the pKa of the weak acid above:




(e; 6 pts) At least one of the curves above was not much help for part (d). Explain why, in terms of the Henderson-Hasselbalch equation and the assumptions that go into using it as a shortcut.

(f; 6 pts) In the graph above, sketch in the titration curve you would get for titrating 0.2 M of the same weak acid with 0.4 M strong base.

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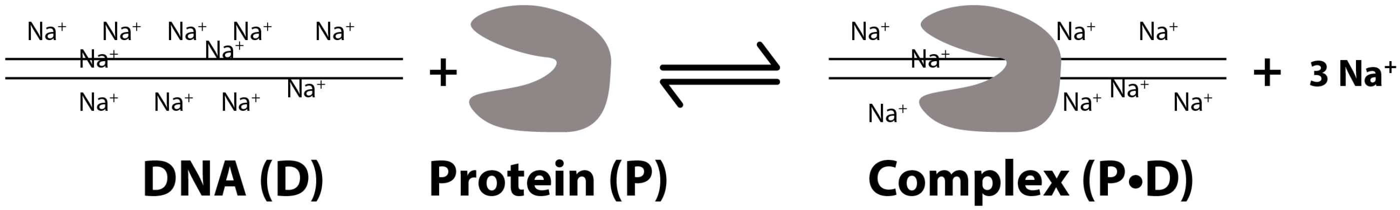
## 2. Equilibria (27 pts)

Consider the protein-DNA binding reaction shown below. We add a known total concentration $[P]_T$ of a protein to a known concentration of DNA, $[D]_T$. When the protein binds DNA, it displaces three sodium ions that were previously bound near the DNA (which, as you know, is a polyanion).




(a; 9 pts) We cannot actually detect the $Na^+$ directly, so the apparent equilibrium constant is quoted just in terms of protein and DNA: $K_{bind,apparent} = \frac{[P \bullet D]}{[P][D]}$ . We want to calculate the concentrations of [P] = the free protein; [D] = the free DNA; and [P•D] = the protein DNA complex at equilibrium. That is three species. Write down the three equations that we need. [Note: the $Na^+$ is irrelevant at this point; it is baked into $K_{bind,apparent}$]. Hint: "Conservation."

(b; 6 pts) Frequently the experiment can be set up so that the protein concentration is much larger than the DNA concentration, so the free protein concentration $[P] \approx P_T$, which is known. Given this assumption, derive that the fraction of DNA that is bound to protein, θ, is given by the following expression:

$$\theta \equiv \frac{[P \bullet D]}{[D]_T} = \frac{[P \bullet D]}{[P \bullet D] + [D]} = \frac{P_T}{P_T + (1/K_{bind})}$$

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(c; 6 pts) If $(1/K_{bind}) = 6 \times 10^{-9}$ M, what value of $P_T$ gives $\theta = 0.1$? How about $\theta = 0.5$? (We measure $K_{bind}$ by titrating DNA with increases concentrations of protein and measuring how much of the DNA is bound.)

(d; 6 pts) Write down the true equilibrium constant, including consideration of the $Na^+$ ions. Will the protein bind (circle one) more tightly or less tightly as the concentration of $Na^+$ ions in solution increases?

**3. Short answers (32 pts)**

(a; 9 pts) When blood arrives back at the heart after passing through the tissues, it is in the T state and it is carrying protons. In the lung, it is then flooded with $O_2$. Explain how this leads to the release of protons from hemoglobin. What happens to those protons?

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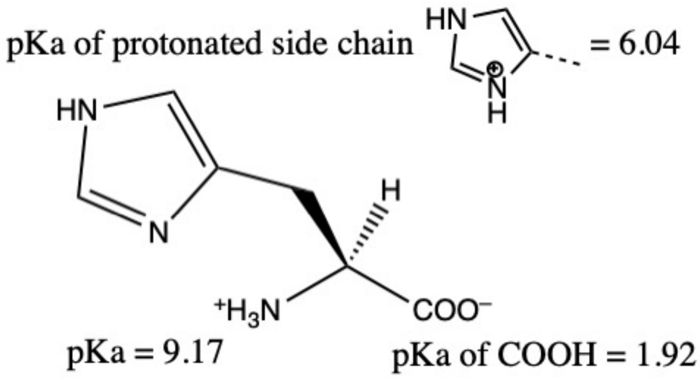
(b; 8 pts) The amino acid Histidine is shown in its predominant form at pH 7. Draw the structure of the minor form present at this pH. What is the pI of histidine? What is the charge of histidine at pH 12?




(c; 9 pts) What is the pKa of the hydronium ion $H_3O^+$? Explain why we can only set an upper limit on the pKa's of nitric acid or hydrochloric acid in aqueous solution.

(d; 6 pts) Explain why the pH of 100 mM HOAc plus 50 mM of the weak base $NH_3$ is the same as the pH of 100 mM HOAc plus 50 mM of the strong base NaOH.

| **Page** | **Score** |
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| 2 | /20 |
| 3 | /22 |
| 4 | /15 |
| 5 | /21 |
| 6 | /23 |
| **Total** | **/100** |

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