Chemistry 271 – 23XX
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General Chemistry and Energetics
Exam II (100 points)

Your Name: Key

Your SID #:

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 $= N_A k_B$ $K_a \times K_b = K_w$

$°C = °K - 273.15$ $P(v)dv = Cv^2 exp(-mv^2/2kT)$ $\ln k = (-E_a/RT) + \ln A$

$pH = pK_a + \log([A^-]/[HA])$ $K_p = K_c(RT)^{\Delta n}$ $K_w = [H^+][OH^-] = 10^{-14}$

$e^{i\pi} + 1 = 0$ $PV = nRT$ $\left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$

$pK_a = -\log(K_a)$ $pH(e.p.) = \frac{1}{2}(pK_{a1} + pK_{a2})$

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 (42 pts)

(a; 15 pts) Calculate the pH and the pOH of a 0.125 M solution of propanoic acid (CH_3CH_2COOH), pK_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.

(+2)

$$CH_3CH_2COOH \rightleftharpoons H^+ + CH_3CH_2COO^- \quad K_a = 10^{-4.87} = 1.3490 \times 10^{-5}$$

$$K_a = 1.35 \times 10^{-5} = \underbrace{\frac{[H^+][A^-]}{[HA]} = \frac{x^2}{0.125 - x}}_{(+5)} \approx \frac{x^2}{0.125} \quad x = \sqrt{0.125 \times 1.35 \times 10^{-5}} = 1.299 \times 10^{-3}$$

$(\ll 0.125 \checkmark)$

$[H^+] = 1.299 \times 10^{-3}$

(+2)

$\underline{pH = 2.87}$ (+3) $\underline{pOH = 14 - pH = 11.13}$

(+3)

- Chloroacetic acid will be dissociated to a greater extent since it is a stronger acid, so the $x = [ClCH_2COO^-]$ will be larger (in fact ≈ 0.013 ~ 10% of C_0).

(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?

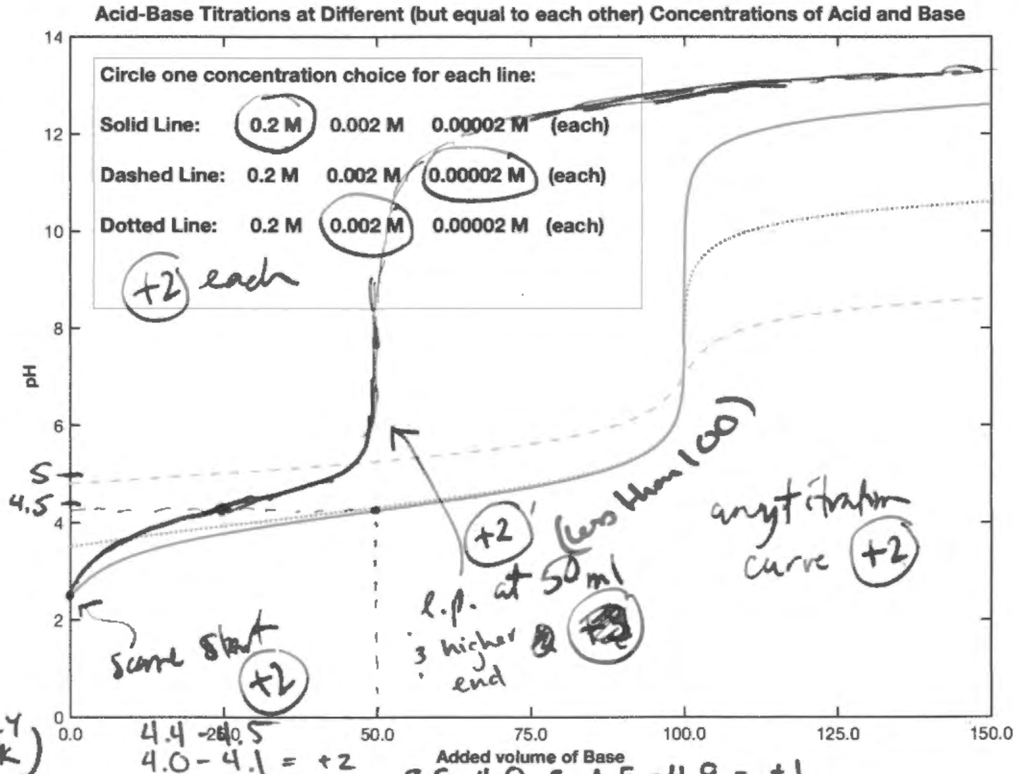
(+3)

The pH must be < the pKa because at the pKa $[A^-] = [HA]$ whereas we know that for a weak acid $[A^-] \ll [HA]$.

} (+2) for any explanation or writing out H-H.

Score for the page /20

(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. <u>Circle the concentration choices in the box in the graph.</u>



Circle one concentration choice for each line:

Solid Line: [✓ 0.2 M] 0.002 M 0.00002 M (each)

Dashed Line: 0.2 M 0.002 M [✓ 0.00002 M] (each)

Dotted Line: 0.2 M [✓ 0.002 M] 0.00002 M (each)

+2 each

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

<u>4.3</u> +3 (4.1-4.4 ok)

4.4 -4.5
4.0 - 4.1 = +2
3.8 - 4.0 3 4.5 - 4.9 = +1

(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.

+2

The <u>dashed line</u> gives the "wrong" pKa – it is <u>too dilute</u>, so the [HA] and [A-] are <u>small enough</u> to change materially when they equilibrate in water.

+2

$pH = pKa + \log \frac{[A^-]}{[HA]}$ } need to know that these are ~~constant to use H~~ set by the stoichiometry to use HH as a shortcut

+2

(f; ~~3~~ 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.

- will start the same as the 0.2 M/0.2 M curve

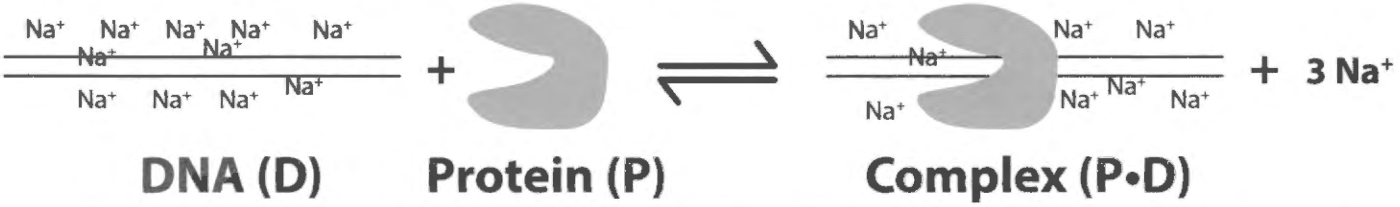
* - e.p. will be at <u>50 ml</u>, so ½ e.p. at 25 ml.

- limit pH 3 higher – 13.61

Score for the page 21/~~22~~

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."

(+3) $K_{bind,apparent} = \frac{[P\cdot D]}{[P][D]}$ (1) (analogous to Ka eq'n)

(2) $P_T \overset{(+3)}{=} [P] + [P\cdot D]$ conservation of total protein

(3) $D_T = \underbrace{[D]}_{\text{free}} + \underbrace{[P\cdot D]}_{\text{bound}}$ (+3) " " " DNA

need three independent equations, not rearrangements

(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:

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

(+2) (~~+3~~)

$[P\cdot D] = K_{bind} \cdot [P][D]$ plug in given Sub (+2)

$$\theta = \frac{K_{bind}[P][D]}{K_{bind}[P][D] + [D]} \approx \frac{K_{bind}[P]_T\cancel{[D]}}{K_{bind}[P]_T\cancel{[D]} + \cancel{[D]}} = \frac{K_{bind} P_T}{K_{bind} P_T + 1}$$

(+2) for cleanup.

Divide through by K_{bind} top + bottom → $\theta = \frac{P_T}{P_T + (1/K_{bind})}$

Score for the page /15

(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.)

$$0.1 = \frac{P_T}{P_T + 6\times10^{-9}\,M} \Big\} \text{(+3) for idea} \qquad 0.5 = \frac{P_T}{P_T + 6\times10^{-9}\,M}$$

$$P_T(0.1) + 6\times10^{-10}\,M = P_T$$

Similarly

$$0.9\,P_T = 6\times10^{-10}\,M \qquad 0.5\,P_T = 3\times10^{-9}\,M$$

$$\underline{P_T \simeq 6.67\times10^{-10}\,M} \text{ (+2)} \qquad \text{(+1) } \underline{P_T = 6\times10^{-9}\,M}$$

(To measure this would need DNA at lower [ ], can be difficult)

(makes sense – $0.5 = \frac{P_T}{P_T + 1/K}$ so $P_T = 1/K$)

(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] (+3) as the concentration of Na^+ ions in solution increases?

$$K_{bind,\,true} = \frac{[P\cdot D]\,[Na^+]^3}{[D]\,[P]} \text{ (+3) } = K_{app}\cdot[Na^+]^3$$

As $Na^+\uparrow$, $K_{bind,\,true}$ is constant so $K_{app}\downarrow$. Or – LeChatelier –) no explanation needed

3. Short answers (33 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?

TH^+ hemoglobin → Lungs

(+3) O_2 binding switches Hb to the R state

$$TH^+ + 4\,O_2 \rightarrow RH^+(O_2)_4$$

(+3) The R state is a stronger acid than the T state ⇒

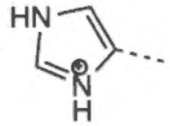
$$RH^+(O_2)_4 \rightleftharpoons R(O_2)_4 + H^+$$

(+3) The protons react with bicarbonate ~~released~~ in the RBC to give CO_2 that we breathe out.

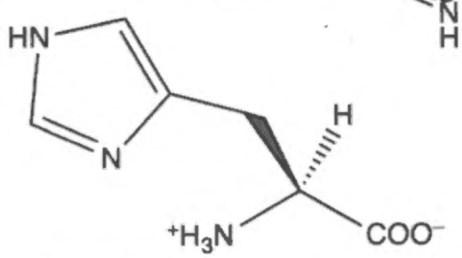
Score for the page 21

(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?

pKa of protonated side chain

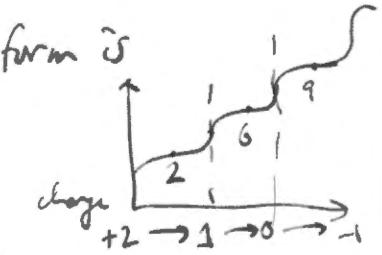


= 6.04 } closest pKa ⇒ minor form is protonated

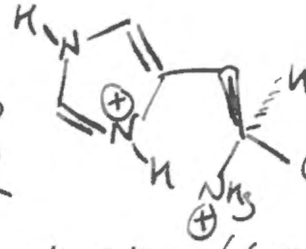


pKa = 9.17 pKa of COOH = 1.92

this form has charge = 0



+3



2nd e.p. at pH = (6.04+9.17)/2 = 7.60 +3

At pH 12, all three ionizable groups are deprotonated, so charge = -1 +2

(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.

~~+2~~ +3 $H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+$ transfer of proton to water

"HA" "A⁻"

K = 1 so pKa = 0 +3

+3

Any stronger acid (pKa < 0) will simply dissociate = transfer a proton to H_2O, so we see H_3O^+ – "leveling", so we cannot measure how strong the acid is

(c; ~~4~~ 6 pts) Explain why the pH of 100 mM HOAc plus 50 mM NH_3 is the same as the pH of 100 mM HOAc plus 50 mM NaOH.

~~+4~~ +3

Acid-base neutralization is highly favorable – in both cases, we will have simply

50 mM OAc^- + 50 mM HOAc

independent of the base we see

$pH = pK + \log \frac{[A]}{[HA]}$ +3

Page	Score
2	/~~23~~ 20
3	/~~21~~ ~~22~~ 21
4	/~~19~~ 15
5	/~~13~~ 21
6	~~/23~~ 23
Total	/100

Score for the page /~~23~~ 23