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

Your Name: 

Your SID #: 

Your Section # or time: 

April 6, 2016

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:

\[ K_a = [H^+][A^-]/[HA] \]
\[ pH = -\log([H^+]) \]
\[ K_b = [BH^+][HO^-]/[B] \]
\[ R = 0.08206 \text{ L·atm/mole K} \]
\[ k_B = 1.38 \times 10^{-23} \text{ J/K} \]
\[ R = 8.314 \text{ J/mole K} = 1.987 \text{ cal/mole K} = N_A k_B \]
\[ °C = °K - 273.15 \]
\[ P(v)dv = Cv^2 \exp(-mv^2/2kT) \]
\[ \ln k = (-E_a/RT) + \ln A \]
\[ pH = pKa + \log([A^-]/[HA]) \]
\[ K_p = K_c(RT)^\Delta n \]
\[ K_w = [H^+][OH^-] = 10^{-14} \]

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. **Straightforward Acid-Base (30 pts)**

The equation for the dissociation of benzoic acid in water is

\[ \text{PhCOOH} \rightleftharpoons \text{H}^+ + \text{PhCOO}^- \quad K_a = 6.25 \times 10^{-5} \]

(a; 3 pts) Calculate the pKa of benzoic acid.

\[ \rho K_a = -\log (K_a) = -\log (6.25 \times 10^{-5}) = 4.20 \quad \text{[3 pts]} \]

(b; 9 pts) Calculate the pH of a 0.150 M solution of benzoic acid in water, assuming \( x \ll C_0 \). Explain or demonstrate why the \( x \ll C_0 \) condition is not satisfied for a 0.000015 M solution of benzoic acid.

\[ \begin{align*}
\text{Ph COOH} & \quad \text{Ph COO}^- & \quad \text{H}^+ \\
I & 0.150 \text{ M} & 0 & 0 \\
C & -x & +x & +x \\
E & 0.150 - x & x & x \\
\end{align*} \]

\[ K_a = 6.25 \times 10^{-5} = \frac{x \cdot x}{0.150 - x} \approx \frac{x^2}{0.150} \]

\[ x = \sqrt{6.25 \times 10^{-5} \times 0.150} = 3.0619 \times 10^{-3} \]

\[ \rho \text{H} = -\log (x) = 2.514 \quad \text{[3 pts]} \]

(c; 4 pts) We could use benzoic acid/sodium benzoate as a buffer. Over what range of pH would such a buffer system be useful, and why?

- A Ph COOH / Ph COO\(^-\) buffer would be useful over a range of \( \pm 2 \) (or \( \pm 1.5 \) or \( \pm 1 \)) pH units away from the pKa, so between about \( \text{pH} 2.2 \) and \( \text{pH} 6.2 \) (or 2.7 to 5.7 or 3.2 to 5.2).

- Outside this range, either [Ph COOH] or [Ph COO\(^-\)] is so small that it will change markedly upon addition of acid or base - or just say that the pH-H is true but not useful.

Score for the page: 16
(d; 6 pts) Write down the base dissociation equilibrium reaction and the equilibrium constant expression for benzoate (PhCOO\(^-\), = the conjugate base of benzoic acid). Calculate the pK\(b\) for benzoate.

\[
\text{PhCOO}^- + H_2O \rightleftharpoons \text{PhCOON}^- + H_3O^+
\]

\[
K_b = \frac{[\text{PhCOON}^-][H_3O^+]}{[\text{PhCOO}^-]}
\]

\[
K_b = \frac{K_w}{K_a} \Rightarrow pK_b = 14 - pK_a = 14 - 4.204 = 9.796
\]

(e; 8 pts) Calculate the pH of 0.100 M Na\(^+\)PhCOO\(^-\) (the pH you would get by dissolving 0.1 moles of sodium benzoate in 1 L of water). How did you know before you started that the answer must be > 7?

\[
K_b = 10^{-9.796} = \frac{[\text{PhCOON}^-][Na^+]}{[\text{PhCOO}^-]} = \frac{x^2}{0.100 - x}
\]

\[
x \approx \sqrt{10^{-9.796} \times 0.100} = \sqrt{16 \times 10^{-2}} = 4 \times 10^{-6} = [H_3O^+] \ll [COO^-]
\]

So \[ pH = 14 - p[COO^-] = 14 - 5.398 = 8.602 \]

Sodium benzoate is the salt of a weak acid (PhCOOH) and a strong base (Na\(^+\)), therefore a solution of Na\(^+\)PhCOO\(^-\) should be basic.

Score for the page: 14
2. Linkage and Equilibria (30 pts)

(a: 10 pts) We described in class that protonation of hemoglobin is linked to the interconversion of R and T states. The R state binds O₂ much more tightly than the T state. What acid is generated by aerobic metabolism? Which state of hemoglobin is favored at acidic pH? Why is this important for mammalian physiology?

- Aerobic metabolism generates CO₂ which dissolves to give carbonic acid, \( H_2CO_3 \) (for any), \([\text{Lactic acid} : +1]\)
- The T state is favored in acidic conditions (the Bohr effect).
- This means that actively working muscles or tissues have lower pH, and that induces Hb to shift into the T state, which causes Hb to drop off more O₂ in more tissues.

The DNA double helix can bend to form small circles (hundreds of base pairs), and the circles are readily distinguishable from linear DNA. The diagram below illustrates equilibria between linear DNA on the left and circular DNA on the right. Transcription factors are proteins that bind to DNA, and in some cases they induce DNA bending, as shown for the double-quadrilateral protein. The equilibria for protein binding to linear or circular DNA are shown running vertically, with free DNA at the top and bound at the bottom. Finally, the bold lines indicate a stretch of DNA that is permanently, intrinsically curved.
(b; 8 pts) It has been found experimentally for some systems that $K_{\text{c, bound}}$ is 200x larger than $K_{\text{c, free}}$. Write down the mathematical relationship among the four equilibrium constants in the diagram. What is the value of $K_{\text{bind, circle}} / K_{\text{bind, linear}}$? Explain the linkage in words.

\[ \frac{K_{\text{c, free}} \cdot K_{\text{bind, circle}}}{K_{\text{bind, linear}} \cdot K_{\text{c, bound}}} = \text{by linkage} \]

\[ \frac{K_{\text{c, free}}}{K_{\text{c, bound}}} = 200 \]

The TF induces a conformational change that step for the sugar-closed form of the DNA, and linkage tells us that therefore the TF must bind more tightly to the sugar-closed form in many possible product of the cyclization reaction. Organic chemists call this preorganization.

(c; 12 pts) From Gilbert Problem 15.90. The equilibrium constant $K_p$ of the reaction

\[ 2 \text{SO}_3 (g) \rightleftharpoons 2 \text{SO}_2 (g) + \text{O}_2 (g) \]

is 7.69 at 830 °C. A vessel at this temperature initially contains pure SO$_3$ and the partial pressure of SO$_3$ at equilibrium is 0.100 atm. Set up the cubic equation that would give the partial pressure of O$_2$ at equilibrium. How would you solve the equation? Also, what is the numerical value of $K_p$?

\[ \frac{\text{PCB: SO}_3 \text{ SO}_2 \text{ O}_2}{\text{I} \quad y^{0.100} \quad 0 \quad 0} \]

\[ C \quad -2x \quad +2x \quad x \quad \text{atm} \]

\[ E \quad y-2x \quad 2x \quad x \quad \text{atm} \]

But $y-2x = 0.100 - y$ is irrelevant!

Well, I would solve this using the cubic root function on my calculator. But OK to answer using Matlab, but don't use alpha, successive approximation, et al.

\[ K_p = \frac{(2x)^2 (x)}{(0.100)^2} \]

\[ 4x^3 = 0.0769 \]

\[ x = 0.268 \text{ atm} \]

\[ y = 0.636 \text{ atm} \]

\[ K_c = \frac{1}{(x)^4 n} = \frac{7.69 (\text{atm})}{(0.08206 \text{ L atm mol}^{-1} \text{K}^{-1})} = 0.0849 \text{ (m)} \]

\[ 830 + 273.15 = 1103.15 \text{ degrees C} \]
3. Titrations and Amino Acids (40 pts)

Acid-Base Titrations

Added volume of Base

(a; 9 pts) The graphs above show five titrations of the same weak acid, at the same concentration, using bases with pKb's of 0, 2, 4, 6, and 8, all at the same concentration. Explain why the five curves all coincide on the left and diverge on the right. Estimate the pKa of the weak acid.

- On the left, the added base neutralizes the weak acid. Even for weak acids and bases, this reaction proceeds nearly to completion, so the identity of the base does not matter—it is just giving us A⁻.

- On the right, all of the H⁺ is titrated so added base reacts with water, to an extent dictated by the strength of the base, so stronger base gives higher pH.

The pKa of the weak acid is about 3.6. (3.4 - 3.8 OK)
(b; 9 pts) Consider the right hand edge of the graph, where 2 equivalents of base have been added. What is the ratio of $[\text{BH}^+]/[\text{B}]$ at this point for titration with a weak base? Derive the relationship apparent from the graph that $\text{pH} = 14 - \text{pK}_b$ at this point, for weak bases. In class we sometimes described the titration curve after the equivalence point as "adding base to salt." This is accurate only for titration with a strong base, for which the final pH is the same as the pH of 100 ml of base diluted to 200 ml. Qualitatively explain why this is not true as for weak bases: the pH at the end is less than the pH of pure diluted base.

(e; 10 pts) The structure of fully-protonated arginine is shown below. Draw the predominant ionic form at pH 10.75. What is the special name/symbol we give to this particular pH, for Arg? Why is the pKa for the guanidino group at the left so much higher than the pKa for the protonated amine group?

\[
\text{pKa} = 12.5 \quad \text{pKa} = 1.8
\]

\[
\text{pKa} = 9.0
\]

\[
10.75 = \frac{12.5 + 9.0}{2} = \text{pH at the 2nd equivalence point}
\]

\[
\text{Dominant form} = \quad \text{pH} < \text{pK}_a
\]

\[
\text{Net charge} = 0 \quad \text{so} \quad 10.75 \quad \text{is} \quad \text{pD}
\]

\[
\text{The guanidino group is a very weak acid because the charge is delocalized by resonance.}
\]

Score for the page 11/9
(c; 12 pts) Sketch a titration curve for titrating 100 ml of 0.1 M sulfurous acid, H$_2$SO$_3$ with 0.1 M NaOH.

The first pKa of H$_2$SO$_3$ is 1.77 and the second is 7.21. The initial pH is 1.34. Write in the pH values at the three indicated volumes of NaOH.

\[
\frac{1.77 + 7.21}{2} = \frac{8.98}{2} = 4.49
\]

2nd eq. pt is at $\left[H_2O^-\right] \approx \sqrt{K_w \cdot C_0} = \sqrt{\frac{10^{-14}}{10^{-7.21} \cdot 0.1}} = \sqrt{10^{-3.71}} = 10^{-1.85}$

\[
\text{pH} = 14 - 3.85 = 10.105
\]

\[
\text{pOH} = 3.89
\]

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