

Chemistry 271, Section 22xx

Your Name: _____

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Your SID #: _____

General Chemistry and Energetics

Your Section # or day+time: _____

Exam I (100 points total)

October 16, 2013

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:

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

$$\text{pH} = -\log([\text{H}^+])$$

$$K_b = [\text{BH}^+][\text{HO}^-]/[\text{B}]$$

$$F = ma$$

$$e^{i\pi} + 1 = 0$$

$$PV = nRT$$

$$K_w = [\text{H}^+][\text{HO}^-] = 10^{-14}$$

$$\text{pH} = \text{p}K_a + \log([\text{A}^-]/[\text{HA}])$$

$$\text{pH (e.p.)} = (\text{p}K_{a1} + \text{p}K_{a2})/2$$

$$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mole K}$$

$$0 \text{ }^\circ\text{C} = 273.15 \text{ K}$$

$$\text{p}K_a = -\log(K_a)$$

$$K_p = K_c(\text{RT})^{\Delta n}$$

$$P^2/a^3 = 4\pi^2/MG$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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. (25 pts) Short Answers

(a; 4 pts) Circle the best answer below: The pK_a of $H_2PO_4^-$ {written $pK_a(H_2PO_4^-)$ } is equal to

(i) $14 - pK_b(H_2PO_4^-)$

(ii) $14 - pK_b(HPO_4^{2-})$

(iii) $1/pK_b(HPO_4^{2-})$

(iv) $14 - pK_a(H_3PO_4)$

(b; 6 pts) Explain your reasoning for (a), in words or equations.

(c; 5 pts) The ideal gas is a useful model system, even though it doesn't exist. Mark each of the statements below true or false:

Ideal gases do not have rotational or vibrational energy. T F

Real gases always show $P_{\text{real}} > P_{\text{ideal}}$. T F

Ideal gases exert pressure on the container independently of each other. T F

Ideal gases have zero volume at $T = 0$ K. T F

Ideal gases are still considered to have nonzero excluded volume. T F

(d; 6 pts) Under what conditions does the behavior of real gases approach that of an ideal gas?

(e; 4 pts) Circle the best answer below: "Dynamic equilibrium" means that

(i) the equilibrium state has equal amounts of reactant and product.

(ii) the equilibrium constant always increases as temperature increases.

(iii) at equilibrium, all forward rates are equal to the corresponding reverse rates.

(iv) None of the above.

2. (20 pts) LeChatelier and Dynamic Equilibrium

Consider the reaction $A + B \rightleftharpoons 2 C$, initially at equilibrium

(a; 4 pts) When A is added, what is the LeChatelier's principle stress on the equilibrium, and what is the response?

(b; 8 pts) Use the change in the reaction quotient Q to verify the prediction from LeChatelier, and also demonstrate that the stress on the system will not be completely removed when it returns to equilibrium.

(c; 4 pts) Explain the shift in the equilibrium in terms of changes in the rates of the forward and reverse reactions.

(d; 4 pts) How does the equilibrium shift if the reaction mix is diluted 10-fold, and why?

3. (25 pts) Acid-Base Equilibria

We will derive a general expression for the pH of a solution of the salt of weak base and a strong acid, like ammonium chloride, NH_4Cl . We assume that the concentration C_0 is large enough so that we can ignore water self-dissociation as a source of protons or hydroxide. We also assume that we know that the weak base $K_b = 10^{-Y}$, so the $\text{p}K_b = Y$. We assume as usual that we can dissolve the species of interest instantaneously, at zero $[\text{H}^+]$ and $[\text{HO}^-]$, and figure out the equilibrium composition starting from there.

(a; 4 pts) Logic first: Should your answer be < 7 or > 7 , and why? How should your answer depend on “ Y ,” and why?

(b; 3 pts) Write the base dissociation equilibrium for ammonia in water.

(c; 5 pts) In a solution that initially contains only NH_4^+ ions and Cl^- ions, what is the dominant acid-base equilibrium reaction that determines the pH? Calculate its equilibrium constant in terms of Y .

(d; 8 pts) Write down the ICE table that gives us $[\text{H}^+]$, and solve for $[\text{H}^+]$ assuming that the concentration C_0 of ammonium chloride is large with respect to “ x ”. Give an expression for the pH.

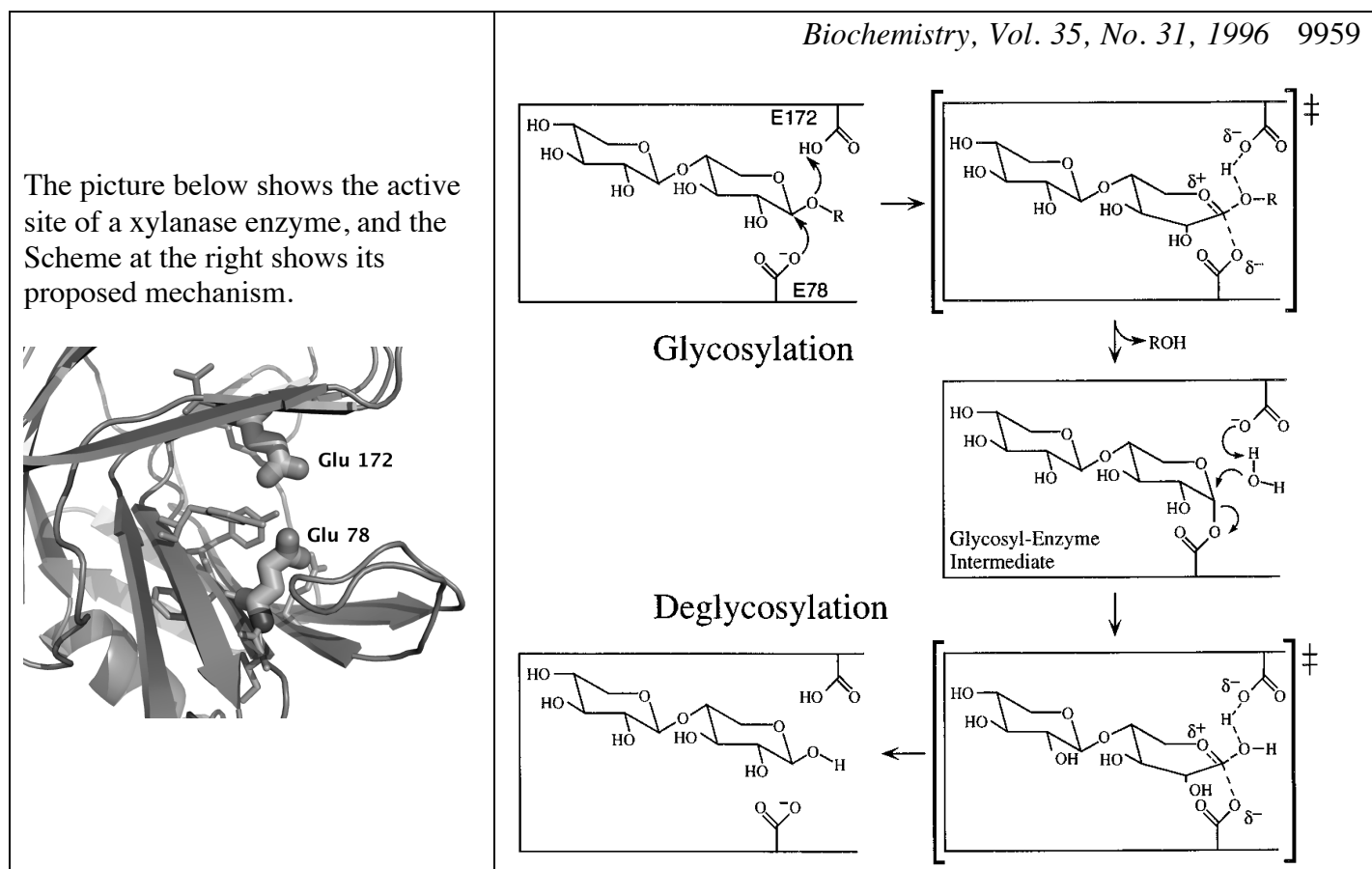
(e; 3 pts) Calculate the pH of a 125 mM solution of a salt with $Y = 4.8$ according to your formula.

(f; 2 pts) Do your answers to (d) and (e) agree with your predictions from (a)?

4. (15 pts) Buffers

(a; 6 pts) Explain when the Henderson-Hasselbach can be used to predict the pH of a solution. Why does it break down at the very beginning or the very end of a titration (a separate answer for each)?

(b; 9 pts) Consider a benzoic acid/sodium benzoate buffer made from 60 mM NaOH + 80 mM benzoic acid ($pK_a = 4.2$). What is the pH? What is the pH if an additional 10 mM NaOH is added? A further additional 30 mM of NaOH?

5. (15 pts) The effect of pH on enzymatic reactions

- (a; 6 pts) Glutamic acid 78 (Glu78 or E78) and Glu172 (E172) have been shown to have pK_a 's of 4.6 and 6.7, respectively, in the ES complex shown at the top left of the scheme. (The pK_a of the Glu side chain is 3.9 for the free amino acid in solution.) How can you tell from the scheme above that which pK_a goes with which residue? What is a likely cause for the elevated pK_a of 6.7 for Glu172?

(b; 5 pts) The pK_a of Glu172 drops to 4.2 in the covalent Glycosyl-enzyme intermediate shown in the middle on the right side of the Scheme. This “pH cycling” has been proposed to assist in the enzymatic reaction. Explain how the pK_a drops in this intermediate.

(c; 4 pts) Why does the enzymatic activity drop off markedly at basic pH?

Page	Score
2	/25
3	/20
4	/20
5	/20
6	/6
7	/9
Total	/100

Score for the page _____