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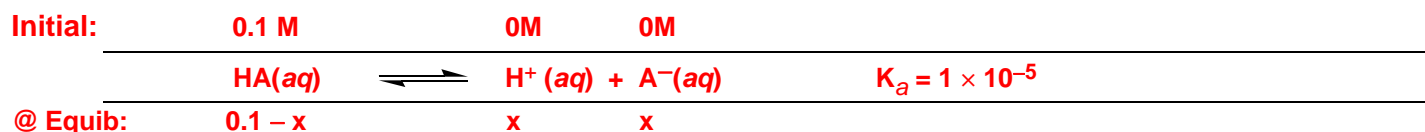


Answer Sheet -- Please Hand In! Please use CAPITAL letters for your multiple choice answers!

1. D      2. C      3. B      4. E      5. D  
 6. A      7. E      8. B      9. B      10. E  
 11. D      12. C      13. D      14. C      15. D

16. What is the pH of a 0.1 M solution of citric acid?  $pK_a = 5$ . Clearly show all your work.

Since this is an acid equilibrium, we only need to convert the  $pK_a$  listed for the conjugate acid into a  $K_a$  value.  
 $K_a = \text{antilog}(-pK_a) = \text{antilog}(-5) = 1 \times 10^{-5}$ .

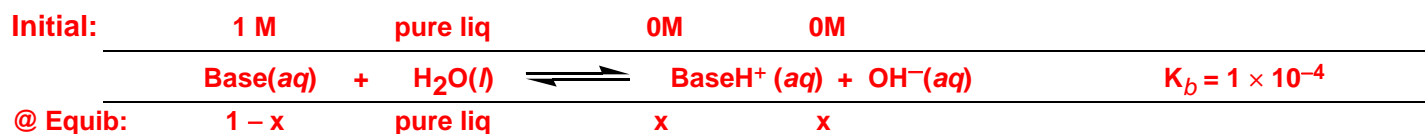


Now you can setup your equilib:  $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.1-x)} = 1 \times 10^{-5}$

assume that  $x \ll 1$  and drop  $x$ :  $\frac{(x)(x)}{(0.1)} = 1 \times 10^{-5}$  or  $x^2 = 1 \times 10^{-6}$ , or  $x = [H^+] = 1 \times 10^{-3}$  so the pH = 3

17. What is the pH of a 1 M solution of the base methyl amine?  $pK_a$  (methyl amine $H^+$ ) = 10.

Since this is a base equilibrium, we need to convert the  $pK_a$  listed for the conjugate acid into a  $K_b$  value.  
 $pK_b = 14 - pK_a = 14 - 10 = 4$ .  $K_b = \text{antilog}(-pK_b) = \text{antilog}(-4) = 1 \times 10^{-4}$ .



Now you can setup your equilib:  $K_b = \frac{[BaseH^+][OH^-]}{[Base]} = \frac{(x)(x)}{(1-x)} = 1 \times 10^{-4}$

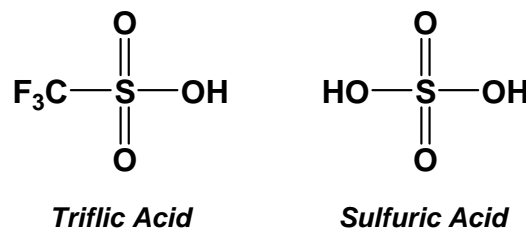
assume that  $x \ll 1$  and drop  $x$ :  $\frac{(x)(x)}{(1)} = 1 \times 10^{-4}$  or  $x^2 = 1 \times 10^{-4}$ , or  $x = [OH^-] = 1 \times 10^{-2}$

$pOH = 2$ . BUT THIS IS NOT YOUR ANSWER, since I asked for the pH!!  $pH = 14 - 2 = 12$  so the pH = 12

18. Why is triflic acid ( $\text{F}_3\text{CSO}_3\text{H}$ ) an even stronger acid than sulfuric acid ( $\text{H}_2\text{SO}_4$ )? Clearly discuss.

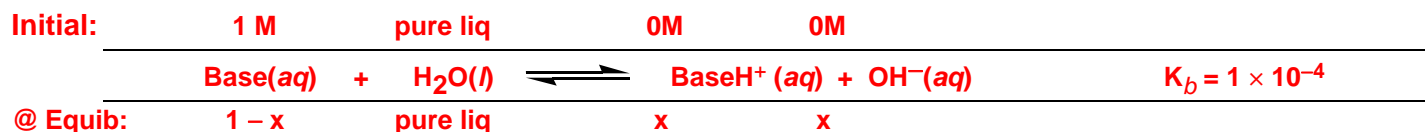
The three main reasons why triflic acid is stronger than sulfuric acid are (in order of importance):

- 1) The  $\text{CF}_3$  group has three highly electronegative and electron-withdrawing fluorine atoms. These are more effective than the OH group in sulfuric acid at pulling electrons away from the other formally negatively charged O that has the proton associated with it. The more the charge is pulled away from the O atom with the  $\text{H}^+$  attached, the easier it is for  $\text{H}^+$  to fall off.
- 2) The  $\text{CF}_3$  group is bigger than the OH that it is replacing in sulfuric acid and is actively involved (see reason #1) in delocalizing (spreading out) the negative charge once the proton dissociates. The bigger the anion and more spread out the charge, the weaker it's basic character (ability to attract the  $\text{H}^+$ ).
- 3) The charge on the triflate anion is  $-1$ , while the sulfate anion can have a  $-2$  charge. Higher negative charges on anions give higher overall negative charge to surface area ratios (more concentrated charges) that increase the basicity of the anion and its ability to hang onto or attract protons. Although you might think that this effect isn't important for the first proton dissociation in sulfuric acid, it does result in higher localized partial negative charges on the parent acid and somewhat lower acidity.



19. What is the pH of a 1 M solution of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).  $\text{p}K_b(\text{CO}_3^{2-}) = 4$

The first thing to realize is that  $\text{Na}_2\text{CO}_3$  is a **basic salt** that will generate a **basic** solution!  $\text{Na}^+$  is a “do-nothing” cation (very weak conjugate acid), while  $\text{CO}_3^{2-}$  is a **basic** anion (conjugate base) that acts as a weak base in solution. We also need to convert the  $\text{p}K_b$  listed for the conjugate acid into a  $K_b$  value.  $K_b = \text{antilog}(-\text{p}K_b) = \text{antilog}(-4) = 1 \times 10^{-4}$ .



Now you can setup your equilib:  $K_b = \frac{[\text{BaseH}^+][\text{OH}^-]}{[\text{Base}]} = \frac{(x)(x)}{(1-x)} = 1 \times 10^{-4}$

assume that  $x \ll 1$  and drop x:  $\frac{(x)(x)}{(1)} = 1 \times 10^{-4}$  or  $x^2 = 1 \times 10^{-4}$ , or  $x = [\text{OH}^-] = 1 \times 10^{-2}$  so **pOH = 2**.

**BUT THIS IS NOT YOUR ANSWER**, since I asked for the pH!!  $\text{pH} = 14 - 2 = 12$  so the **pH = 12**

**BONUS QUESTION:** Consider an acetic acid/sodium acetate buffer system.  $\text{p}K_a$  (acetic acid) = 5.

A) Assuming a 1:1 mixture of acetic acid and sodium acetate, what is the pH of this buffer system?

This will be an **acidic** buffer since the acetic acid will dominate due to it being a stronger acid than the conjugate base is basic (acetic acid  $\text{p}K_a = 5$ , acetate anion  $\text{p}K_b = 9$ ). Since there is a 1:1 mixture, the  $\text{pH} = \text{p}K_a$  of the acid. So the pH of this buffer = **5**.

B) Clearly explain how this buffer system keeps the same approximate pH when one adds small amounts of strong acid or base.

The acetic acid present will react with any strong base added to neutralize it and produce acetate anion, which is only a weak conjugate base and which is already present. Any strong acid added will react with the basic acetate anions to form acetic acid, which is already present. Thus, when one adds small amounts of acid or base, one is only changing somewhat the ratio of weak acid (acetic acid) to weak base (acetate anion, the conjugate base of acetic acid), and the overall pH of the solution stays about the same.

## CHEM 1202 – Exam # 3A

November 30, 2006

Please Answer All Questions on the Answer Sheet

1. (4 pts) What is the pH of 1 M RbOH?

- a) 1                      b) 5                      c) 9                      **d) 14**                      e) 20

Strong base,  $pOH = 0$ ,  $pH = 14 - 0 = 14$ 2. (4 pts) What is the pH of  $1 \times 10^{-10}$  M  $HNO_3$ ?

- a) 1                      b) 5                      **c) 7**                      d) 10                      e) 14

Extremely dilute acid (less than  $1 \times 10^{-7}$  M),  $pH = 7$ 3. (4 pts) What is the pH of  $1 \times 10^{-3}$  M  $HClO_4$ ?

- a) 1                      **b) 3**                      c) 5                      d) 7                      e) 11

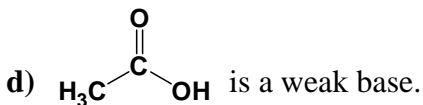
Strong acid,  $[H^+] = \text{acid concentration} = 1 \times 10^{-3}$  M,  $pH = 3$ 

4. (4 pts) Which of the following is NOT a strong acid?

- a) HCl                      b)  $HNO_3$                       c) HI                      d)  $H_2SO_4$                       **e)  $H_2S$**

The  $S^{2-}$  dianion has a concentrated 2- negative charge that strongly attracts both protons making it a weak acid.5. (4 pts) Which of the following statements is **FALSE**?

- a) Weak acids have moderately strong conjugate bases.  
 b)  $Fe^{3+}(aq)$  is considered a Lewis Acid.  
 c) HF is a weak acid in large part due to the concentrated negative charge on the small  $F^-$  anion.



This is acetic acid, which is a weak acid

- e) Compounds with nitrogen atoms that have a lone pair of electrons are weak bases.

6. (4 pts) Which of the following is NOT a strong base?

- a)  $Fe(OH)_3$**                       b) LiOH                      c) CsOH                      d)  $Ba(OH)_2$                       e) RbOH

The  $Fe^{3+}$  cation strongly attracts the  $OH^-$  anions and does not want to release them as free hydroxides.7. (4 pts) What is the  $\Delta G^\circ$  value (in KJ/mol) that corresponds to a  $pK_a = -8$  (typical for a strong acid).

$$R = 8.314 \text{ J/molK}, T = 300 \text{ K.}$$

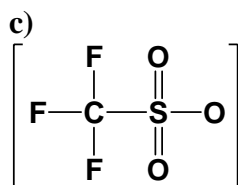
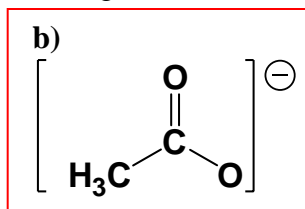
- a) 34 KJ/mol                      b) 16 KJ/mol                      c) 0 KJ/mol                      d) -2 KJ/mol                      **e) -46 KJ/mol**

 $pK_a = -8$ ; so  $K_a = 1 \times 10^8$  M; this is a very spontaneous rxn.  $\Delta G^\circ$  should be fairly negative; also calculate this using  $\Delta G^\circ = -RT \ln(K_a)$ 

8. (4 pts) Which of the following anions is the most basic?

- a)  $Cl^-$

extremely weak conjugate base, "do nothing" anion



- d)  $PF_6^-$

single negative charge spread over 6 electronegative atoms

- e)  $NO_3^-$

extremely weak conjugate base, "do nothing" anion

9. (4 pts) What is the pH of 10 M  $HPF_6$ ?  $pK_a = -10$ 

- a) -10                      **b) -1**                      c) 7                      d) 12                      e) Can't calculate from information given

 $pK_a = -10$ , this means a STRONG acid;  $[H^+] = 10$  M, so  $pH = -1$

Exam 3A – Acids/Bases (2006)

10. (4 pts) What is the pH of 0.01 M formic acid, HCOOH?

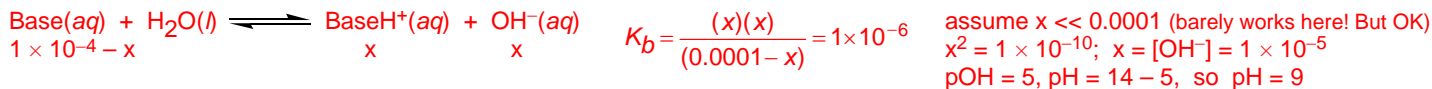
- a) -1      b) 1      c) 6      d) 9

Formic acid is a weak acid, in order to calculate a pH you need to have a  $K_a$  or  $pK_a$  value!

e) Can't calculate from information given

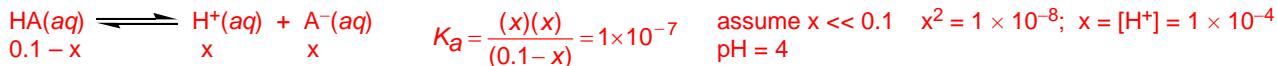
11. (4 pts) What is the pH of a  $1 \times 10^{-4}$  M solution of the weak base nicotine?  $K_b = 1 \times 10^{-6}$

- a) 0      b) 5      c) 7      **d) 9**      e) 10



12. (4 pts) Calculate the pH of a 0.1 M solution of carbonic acid,  $\text{H}_2\text{CO}_3$ .  $K_{a1} = 1 \times 10^{-7}$ ,  $K_{a2} = 1 \times 10^{-11}$ .

- a) -1      b) 2      **c) 4**      d) 5      e) 10



13. (4 pts) I react 333 mL of 0.3 M NaOH with 666 mL of 0.15 M acetic acid. Which of the following statements is **TRUE**?  $\text{p}K_a$  (acetic acid) = 5

Weak acid + equal amount of strong base = salt of weak acid which is moderately basic

- a) You will make a **very acidic** solution (pH ~ 0)      b) You will make a **moderately acidic** solution (pH ~ 4)  
 c) You will make a **very basic** solution (pH ~ 14)      **d) You will make a moderately basic solution (pH ~ 9)**  
 e) You will make a **neutral** solution

$\text{O}^{2-}$  is NOT a "do nothing" anion, it is quite basic when coordinated to an alkaline earth

14. (4 pts) Which of the following salts will produce a **basic** solution when dissolved in water?

- a)  $\text{Ga}(\text{NO}_3)_3$       b)  $\text{Li}_2\text{SO}_4$       **c) BaO**      d)  $\text{NH}_4\text{NO}_3$       e)  $\text{SrBr}_2$

15. (4 pts) Which of the following salts will produce an **acidic** solution when dissolved in water?

- a)  $\text{Ba}(\text{ClO}_4)_2$       b) CsI      c)  $\text{Rb}_2\text{CO}_3$       **d)  $\text{AlCl}_3$**       e) NaBr

$\text{Al}^{3+}$  is a small highly charged cation that is a strong Lewis acid

16. (10 pts) What is the pH of a 0.1 M solution of citric acid?  $\text{p}K_a = 5$ . Clearly show all your work. Put a box around your final answer.

17. (10 pts) What is the pH of a 1 M solution of the base methyl amine?  $\text{p}K_a$  (methyl amine $\text{H}^+$ ) = 10. Clearly show all your work. Put a box around your final answer.

18. (10 pts) Why is triflic acid ( $\text{F}_3\text{CSO}_3\text{H}$ ) an even stronger acid than sulfuric acid ( $\text{H}_2\text{SO}_4$ )? Clearly discuss. There are two or three important factors.

19. (10 pts) What is the pH of a 1 M solution of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).  $\text{p}K_b$  ( $\text{CO}_3^{2-}$ ) = 4. Clearly show all your work. Put a box around your final answer.

**Bonus Question (10 points):** Consider an acetic acid/sodium acetate buffer system.  $\text{p}K_a$  (acetic acid) = 5.

- A) Assuming a 1:1 mixture of acetic acid and sodium acetate, what is the pH of this buffer system? Briefly explain/discuss. If you don't know how to give a precise # for the pH, at least state whether this buffer will be acidic, basic, or neutral (with reasoning).
- B) Clearly explain how this buffer system keeps the same approximate pH when one adds small amounts of strong acid or base.