Dr. Zellmer | Chemistry 1220 | All Sections
Time: 7 PM Sun. | Spring Semester 2023 | March 5, 2023
40 min | Quiz VII

Name KEY Rec. Instr. ____________________

1. (3 pts) Which of the following is the **weakest** acid? **Explain!**

a)* **H_2TeO_3** b) H_2TeO_4 c) H_2SeO_3 d) H_2SeO_4

The acids have the **same structure** (**same** # of **O** atoms) but **diff**. **central atom**

- **acidity inc**. as electronegativity (**EN**) of **central atom inc**.

$EN_{Se} > EN_{Te}$

$\therefore$ **H_2SeO_3** $> H_2TeO_3$ and **H_2SeO_4** $> H_2TeO_4$

The acids have the **same central atom** but **diff**. # of **O** atoms

- **acidity inc**. as **number** of **O** atoms **inc**.

$\therefore$ **H_2TeO_4** $> H_2TeO_3$ and **H_2SeO_4** $> H_2SeO_3$

Thus, **H_2SeO_4** is the **strongest** acid & **H_2TeO_3** is the **weakest** acid

2. (2 pts) Based on their structure and composition, select the member of the following pair of acids that is the **stronger acid**. Briefly **explain** (but more than just any periodic trends).

a) H_2S b)* **H_2Se** c) PH_3 d) SiH_4

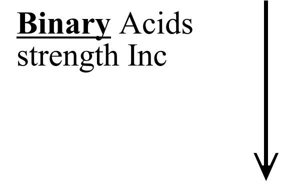
H_2Se & H_2S :

H_2Se is the stronger acid. Even though S is more EN than Se the H-Se bond is longer and weaker so it is broken more easily (easily ionized). Since H_2Se is stronger acid its conj bases, HSe^-.

Also, from standpoint of bases, HTe^- is much larger than HSe^- so it can distribute (-) chg better & stabilize the (-) chg making it a weaker base and thus its conj. acid, H_2Te, is stronger.

$H_2Se <$ **H_2Te**

H_2S, PH_3 & SiH_4: H_2S is the strongest acid. In a period (row) the size of the atom the H is attached to doesn't change much so the bond polarity is most important, which depends on the electronegativity of the central atom. Since S is more EN than P, H_2S is a stronger acid than PH_3 (and its conj base, HS^-, is weaker than H_2P^-). Since P is more EN than Si, PH_3 is a stronger acid than SiH_4. SiH_4 is a nonpolar neutral molecule it isn't going to act as an acid.



Binary Acids strength Inc

3. (2 pts) Identify the Lewis acid and Lewis base in the following reactions. **Explain!**

a) $CN^-(aq) + H_2O(l) \longrightarrow HCN(aq) + OH^-(aq)$
LB LA LA LB

Lewis Acid : e^- pair acceptor (something that is electron deficient: H^+ is technically the Lewis Acid)

Lewis Base : e^- pair donor (something with a lone-pair of electrons -
does not have to have a negative chg)

Bronsted-Lowry theory involves a proton transfer from an acid to a base. The H^+ literally is pulled off the acid by the base (the H^+ is transferred, actually moves, from the acid to the base).

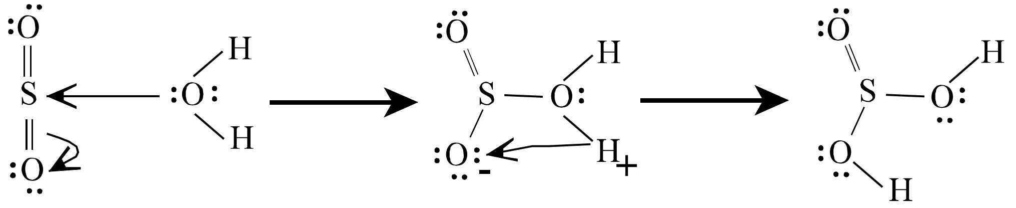
In Lewis theory the e- pair does not actually move from one atom to another. Instead the LA combines with the LB and in so doing the LA is accepting a pair of e^- from the LB (the LB is donating the e^- pair) to form a new bond between the two. A good example is the reaction between BF_3 with NH_3. The BF_3 molecule is overall e- deficient (even though there's electrons on the F atoms the B has only 6 e- around it making it and the molecule e- deficient). The NH_3 has an e- pair on the N. Thus, the N atom in NH_3 can donate the e- pair to the B in the BF_3 to form a new bond and new molecule, $H_3N\text{-}BF_3$.

The CN^- would also be considered a B-L base and the H_2O would be a B-L acid. Remember, Arrhenius acids and bases are B-L acids and bases and B-L acids and bases are Lewis acids and bases. However, it doesn't necessarily go the other way.

b) $SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$
LA LB

Lewis Acid : e^- pair acceptor (something that is electron deficient: the S is "electron deficient" -
double bonded to the O atoms)

Lewis Base : e^- pair donor (something with a lone-pair of electrons - like O atom)



Nonmetal central atoms with double bonds to them are somewhat electron deficient and can accept a pair of electrons. Thus, the molecule can act as a Lewis acid.

4. (2 pts) Which of the following solutions would be a common-ion system?

a) HCN and NaCl

b)* HF and NaF

c) NH_3 and NaF

d) HCl and NaBr

e) HNO_2 and KCl

What constitutes a common-ion system for a weak acid or weak base system?

$$\begin{array}{ccccccc} CH_3CO_2H & + & H_2O & \rightleftarrows & CH_3CO_2^- & + & H_3O^+ \\ 0.10\text{ M} & & & & 0.02\text{ M} & & 0 \end{array}$$

OR

$$\begin{array}{ccccccc} CH_3CO_2H & + & H_2O & \rightleftarrows & CH_3CO_2^- & + & H_3O^+ \\ 0.10\text{ M} & & & & 0 & & 0.02\text{ M} \end{array}$$

A common-ion (CI) system involves a weak acid or weak base equilibrium where you not only start with the WA (or WB) but also with one of the products. Most often you start with a WA and it's conjugate base (as shown in the first reaction above). You can also think of it as adding the conj. base to the WA equil. which causes it to go back in the reverse direction. Either way you think about it, the CI prevents the WA (or WB) from ionizing as much as it would if it were all by itself (you had just the WA or WB in solution).

You could also start with the WA and some H^+ (H_3O^+) from a strong acid (starting with acetic acid as above if you add HCl you're adding some H^+ which causes the reaction to go back in the reverse direction).

The same applies to a weak base equil. such as NH_3. If you have both NH_3 and NH_4^+ you have a CI problem. If you have both NH_3 and OH^- you have a CI problem.

$$\begin{array}{ccccccc} NH_3 & + & H_2O & \rightleftarrows & OH^- & + & NH_4^+ \\ 0.10\text{ M} & & & & 0\text{ M} & & 0.02\text{ M} \end{array}$$

OR

$$\begin{array}{ccccccc} NH_3 & + & H_2O & \rightleftarrows & OH^- & + & NH_4^+ \\ 0.10\text{ M} & & & & 0.02\text{ M} & & 0\text{ M} \end{array}$$

Also, buffers are just special CI problems.

5. (3 pts) What change will occur for the following reaction if $NaCH_3CO_2$ is added to a solution of CH_3CO_2H? **Explain!**

$$CH_3CO_2H + H_2O \rightleftarrows CH_3CO_2^- + H_3O^+$$

a)* a decrease in the fraction of acid dissociated
b) an increase in the fraction of acid dissociated
c) no change in the fraction of acid dissociated

Add $CH_3CO_2^-$, a product. The reaction shifts AWAY from added. Thus, it shifts in the reverse direction. As it does you get MORE CH_3CO_2H. That means the fraction of the CH_3CO_2H which dissociates decreases.

The same thing would occur if strong acid is added. That would increase the conc. of H_3O^+ and shift the reaction in th reverse direction. As it does you get MORE CH_3CO_2H. That means the fraction of the CH_3CO_2H which dissociates decreases.

6. (2 pts) Which of the following would be the best choice to make a buffer system around a pH of 4.3?

How do you chose a buffer system? You have both conjugate members of a weak acid or base (a weak acid-conjugate base or weak base-conjugate acid pair). A buffer system is a special case of a CI problem. The conc. of the two components should be between 10 and 0.1 and the conc. of each component should be relatively large compared to the K_a (or K_b) to have a decent buffer system. This means the pH of the buffer should be in the range of $pK_a \pm 1$. For a buffer with pH = 4.3 you want $pK_a = 4.3 \pm 1$.

You could set up an ICE table and do the CI problem or since you know it's a buffer you can use the **Henderson-Hasselbalch** eqn.

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

$$pH = pK_a + \log\left(\frac{10}{1}\right) = pK_a + 1$$

$$pH = pK_a + \log\left(\frac{1}{10}\right) = pK_a - 1$$

$$pH = pK_a \pm 1$$

So, if you want a buffer around pH = 4.3 you need a system with a pK_a between 3.3 and 5.3, ideally the closer to the desired pH the better.

a) $HClO_2/NaClO_2$	K_a for $HClO_2 = 1.1 \times 10^{-2}$	$pK_a = 1.96$
b) HF/NaF	K_a for HF $= 6.8 \times 10^{-4}$	$pK_a = 3.17$
c)* $HC_2H_3O_2/NaC_2H_3O_2$	K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$	$pK_a = 4.74$
d) $HNO_2/NaNO_2$	K_a for $HNO_2 = 4.5 \times 10^{-4}$	$pK_a = 3.35$
e) $H_2CO_3/NaHCO_3$	K_a for $H_2CO_3 = 4.3 \times 10^{-7}$	$pK_a = 6.37$

Thus, system C with a pK_a of 4.74 would be the best choice since it is within ± 1 of the desired pH of 4.3 and the closest to 4.3. The easiest thing to do would be to make a buffer with equal amounts of $HC_2H_3O_2$ and $NaC_2H_3O_2$ ($C_2H_3O_2^-$). Then since the desired pH of 4.3 is less than the pK_a strong acid would be added to adjust the amounts of the $HC_2H_3O_2$ and $C_2H_3O_2^-$. Some of the $C_2H_3O_2^-$ would react with the strong acid to form $HC_2H_3O_2$ until the amount of $HC_2H_3O_2$ is slightly larger than the amount of $C_2H_3O_2^-$ to make the pH = 4.3.

7. (8 pts) You have a 0.20 M solution of acetic acid, $HC_2H_3O_2$. You add enough sodium acetate, $NaC_2H_3O_2$, to make the solution 0.010 M in $NaC_2H_3O_2$. What is the **pH** of the solution? ($HC_2H_3O_2$: $K_a = 1.8 \times 10^{-5}$) (**Show all work**, including ICE tables, assumptions & check for % error.)

$HC_2H_3O_2$ is a weak acid & $C_2H_3O_2^-$ is its conj base

- common ion problem - **Use ICE (equil). table** (in Molarity)

NOT a buffer system (conc of $C_2H_3O_2^-$ may be too small for this solution to be a buffer, the ratio of base/acid is 0.05 which is less than 0.1; should be between 0.1 and 10).

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^- \qquad (\text{or } HC_2H_3O_2 + H_2O \rightleftarrows C_2H_3O_2^- + H_3O^+)$$

	$HC_2H_3O_2$	H^+	$C_2H_3O_2^-$
initial	0.20	0	0.010
change	- x	+ x	+ x
equil	0.20 - x	x	0.010 + x

$$K_a = \frac{[H^+]\,[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5} \qquad \frac{x\,(0.010 + x)}{0.20 - x} = 1.8 \times 10^{-5}$$

Assume 0.20 >> x, so (0.20 - x) ≈ 0.20
Assume 0.010 >> x, so (0.010 + x) ≈ 0.010

$$\frac{(0.010)\,x}{0.20} = 1.8 \times 10^{-5} \; ; \quad x = \mathbf{[H^+] = 3.\underline{6} \times 10^{-4}}$$

(2 s.f.)

$$\%\ \text{error} = \frac{3.6 \times 10^{-4}}{0.20} \times 100\% = 0.18\ \%\ \text{error (assumption above is okay)}$$

$$\%\ \text{error} = \frac{3.6 \times 10^{-4}}{0.01} \times 100\% = 3.6\ \%\ \text{error (assumption above is okay - barely)}$$

$x = \mathbf{[H^+]} = 3.\underline{\mathbf{6}} \times 10^{-4}$ (2 s.f.)

pH = - log ($3.\underline{\mathbf{6}} \times 10^{-4}$) = $3.4\underline{\mathbf{4}}3$ = **3.44** (2 decimal place; only 2 s.f., the two digits to rt of decimal)

Compare this to a pH of 2.72 for 0.20 M $HC_2H_3O_2$. When you add the base $C_2H_3O_2^-$ to a solution of $HC_2H_3O_2$ the solution becomes more basic. In this case, since the ratio of base to acid was 0.05 and just outside the normal range I mentioned for a buffer system it might not be safe to use the Henderson-Hasselbalch eqn. **It turned out the error in ignoring "x" was ok and thus you could have used the HH eqn. and you would get pH = 3.44.**

Is it allowable to ignore the "x" in one instance and not another? Yes. For example, you could maybe ignore the "x" compared to 0.20 and not ignore it compared to the 0.010 since it's much small than the 0.20, giving $(x)(0.010 + x)/0.20 = 1.8 \times 10^{-5}$ and solving this simplified quadratic. Doing this, ignoring "x" compared to 0.20 but not ignoring the "x" compared to the 0.010 above, would give $[H^+] = 3.478 \times 10^{-4}$ and a pH = 3.458.

Not ignoring the "x" at all in either place and doing the more complicated algebra to wind up with a quadratic eqn. would give $[H^+] = 3.473 \times 10^{-4}$ and a pH = 3.459. Either would give a pH = 3.46 (to 2 decimal places) compared to the 3.44 obtained above by ignoring the "x" in both numerator and denominator.

8. (11 pts) A buffer solution is 0.15 M in HNO_2 and 0.10 M in $NaNO_2$. (HNO_2: $K_a = 4.5 \times 10^{-4}$) **Explain or show work!**

a) (4 pts) What is the **pH** of this buffer solution?

Since this a solution of a conjugate acid-base pair and the ratio of the concentrations is between 0.1 & 10 you have a buffer (as it stated in the problem) - use the **Henderson-Hasselbalch** eqn.

$$pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \qquad pK_a = -\log(4.5 \times 10^{-4}) = 3.3\underline{4}6$$

$$pH = pK_a + \log\left(\frac{[NO_2^-]}{[HNO_2]}\right) = 3.3\underline{4}6 + \log\left(\frac{0.10\text{ M}}{0.15\text{ M}}\right) = 3.1\underline{7}0 = 3.17 \quad \text{(actually only 2 s.f.)}$$

b) (9 pts) You have 100.0 mL of this buffer solution. What is the **pH** of the buffer solution after adding 15.0 mL of 0.30 M of NaOH? (**Show all work, including ICE tables, assumptions & check for % error.**)

Must first do a stoichiometric calculation involving the reaction of NaOH with HNO_2.

Stoich. (neutralization) calc. - in **moles**

$$?\text{ mol } NO_2^- = 0.1000\text{ L} \times \frac{0.10\text{ mol } NO_2^-}{1\text{ L}} = 0.010\text{ mol } NO_2^-$$

$$?\text{ mol } HNO_2 = 0.1000\text{ L} \times \frac{0.15\text{ mol } HNO_2}{1\text{ L}} = 0.015\text{ mol } HNO_2$$

$$?\text{ mol NaOH} = 0.0150\text{ L} \times \frac{0.30\text{ mol NaOH}}{1\text{ L}} = 0.0045\text{ mol NaOH} = 0.0045\text{ mol } OH^-$$

	HNO_2	+	OH^-	$\longrightarrow$	NO_2^-	+	H_2O
initial	0.015		0.0045		0.010		
change	- 0.0045		- 0.0045		+ 0.0045		
comp.	0.0105		0		0.0145		

Find the pH of the solution:

Since the ratio of moles of NO_2^- to HNO_2 (0.0145/0.0105) = 1.3809 is still between 0.1 & 10 and the number of moles of each component is still reasonably large this solution can still be considered a buffer solution - can still use the Henderson-Hasselbalch eqn.

Also, since you are using a ratio of conc. ($[NO_2^-]/[HNO_2]$) you can actually just use a ratio of moles (since the volume of solution cancels).

$$\frac{[NO_2^-]}{[HNO_2]} = \frac{(0.01\underline{4}5\text{ mol } NO_2^- / 0.115\text{ L})}{(0.01\underline{0}5\text{ mol } HNO_2 / 0.115\text{ L})} = \frac{0.1\underline{2}60\text{ M}}{0.09\underline{1}30\text{ M}} = \frac{0.01\underline{4}5\text{ mol}}{0.01\underline{0}5\text{ mol}} = 1.\underline{3}809$$

$$pH = pK_a + \log\left(\frac{[NO_2^-]}{[HNO_2]}\right) = 3.3\underline{4}6 + \log\left(\frac{0.01\underline{4}5}{0.01\underline{0}5}\right) = 3.4\underline{8}6 = 3.49 \quad \text{(actually only 2 s.f.)}$$

9. (11 pts) A buffer solution is 0.10 M in HCN and 0.15 M in NaCN. (HCN: $K_a = 4.9 \times 10^{-10}$)

a) (3 pts) What is the **pH** of this buffer solution?

Since this a solution of a conjugate acid-base pair and the ratio of the concentrations is between 0.1 & 10 you have a buffer (as it stated in the problem) - use the **Henderson-Hasselbalch** eqn.

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \qquad pK_a = -\log(4.9 \times 10^{-10}) = 9.3\underline{\mathbf{0}}9$$

$$pH = pK_a + \log\left(\frac{[CN^-]}{[HCN]}\right) = 9.3\underline{\mathbf{0}}9 + \log\left(\frac{0.15\ M}{0.10\ M}\right) = 9.4\underline{\mathbf{8}}5 = 9.\underline{\mathbf{49}}$$

(only 2 s.f.)
(2 decimal places)

b) (8 pts) You have 100.0 mL of this buffer solution. What is the pH of the buffer solution after adding 15.0 mL of 0.200 M of HCl? (**Show all work**, including ICE tables, assumptions & check for % error.)

Must first do a stoichiometric calculation involving the reaction of HCl with CN^-

<u>**Stoich**. (neurtralization) calc. - in moles</u>

$$?\ mol\ CN^- = 0.1000\ L \times \frac{0.15\ mol\ CN^-}{1\ L} = 0.015\ mol\ CN^-$$

$$?\ mol\ HCN = 0.1000\ L \times \frac{0.10\ mol\ HCN}{1\ L} = 0.010\ mol\ HCN$$

$$?\ mol\ HCl = 0.0150\ L \times \frac{0.20\ mol\ HCl}{1\ L} = 0.0030\ mol\ HCl = 0.0030\ mol\ H^+$$

	CN^-	+	H^+	$\rightarrow$	HCN
initial	0.015		0.0030		0.010
change	- 0.0030		- 0.0030		+ 0.0030
comp.	0.012		0		0.013

Find the pH of the solution:

***** continued on next page *****

9. (Cont.)

Since the ratio of moles of CN^- to HCN (0.012/0.013 = 0.9231 is still between 0.1 & 10 and the number of moles of each component is still reasonably large this solution can still be considered a buffer solution - can still use the Henderson-Hasselbalch eqn.

Also, since you are using a ratio of conc. ($[CN^-]/[HCN]$) you can actually just use a ratio of moles (since the volume of solution cancels).

$$\frac{[CN^-]}{[HCN]} = \frac{(0.01\underline{2}\text{ mol } CN^- / 0.115\text{ L})}{(0.01\underline{3}\text{ mol HCN} / 0.115\text{ L})} = \frac{0.1\underline{0}43\text{ M}}{0.1\underline{1}30\text{ M}} = \frac{0.01\underline{2}\text{ mol}}{0.01\underline{3}\text{ mol}} = 0.9\underline{2}307$$

$$pH = pK_a + \log\left(\frac{[CN^-]}{[HCN]}\right) = 9.3\underline{0}9 + \log\left(\frac{0.01\underline{2}}{0.01\underline{3}}\right) = 9.2\underline{7}5 = 9.28 \quad (\text{“3" s.f.})$$

(2 decimal places)

10. (6 pts) You have 0.101 L of a 1.367 M solution of NH_3. How many grams of an NH_4Cl salt should be added to prepare a buffer solution with a pH = 10.05? Neglect the small volume change that occurs when the NH_4Cl salt is added. (Molar Mass of NH_4Cl = 53.49 g/mol; K_b of $NH_3 = 1.80 \times 10^{-5}$).

This is similar to EOCE 17.25 and 17.26.

This can be done by using an ICE table and the K_b for NH_3 or using the Henderson-Hasselbalch equation. I will use the HH eqn for this.

Using the HH eqn you would first solve for the [base]/[acid] ratio. You need the pK_a for NH_4^+.

For NH_3 the $pK_b = -\log(1.80 \times 10^{-5}) = 4.74\underline{4}7$

For NH_4^+ the $pK_a = 14.000 - 4.74\underline{4}7 = 9.25\underline{5}2$

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

$$pH = pK_a + \log\left(\frac{[NH_3]}{[NH_4^+]}\right)$$

$$10.05 = 9.25\underline{5}2 + \log\left(\frac{[NH_3]}{[NH_4^+]}\right)$$

$$0.7\underline{9}47 = \log\left(\frac{[NH_3]}{[NH_4^+]}\right)$$

$$\frac{[NH_3]}{[NH_4^+]} = 6.\underline{2}334$$

$[NH_4^+] = [NH_3] / 6.\underline{2}334 = (1.367\text{ M}) / 6.\underline{2}334 = 0.219\text{ M}$

? mol NH_4^+ = 0.101 L * 0.219 mol/L = 0.02$\underline{2}$14 mol

? mol NH_4Cl = mol NH_4^+

? g NH_4Cl = 0.02$\underline{2}$14 mol x (53.49 g/mol) = 1.$\underline{1}$84 g = 1.2 g NH_4Cl