

Unit6 Day8 RAQ
CH302
Spring 2013
LaBrake/Vanden Bout

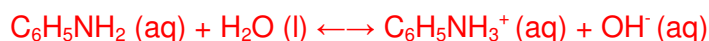
Name: _____ KEY _____

EID: _____

KNOW YOUR ACIDS AND BASES: For each problem:

- I. Identify what is in the final solution (acid, base, salt, combination).
- II. Identify whether or not a neutralization reaction is occurring.
- III. Set up how you would solve the for pH of the problem.
- IV. Don't actually solve for the pH until you have all the set up of all the problems completed.
- V. Explain why you set up the problem as you did.

1 Calculate the pH of a solution containing 1.0 M aniline, $C_6H_5NH_2$.
($K_b = 3.8 \times 10^{-10}$)



- I. The final solution will have a mix of base and its conjugate acid. Since we start off with just base, we also expect some OH^- at the end
- II. There is no neutralization occurring (only a weak base equilibria)
- III. To solve for the pH, we will use a RICE table



I	1M	0	0
C	-x	+x	+x
E	1-x	x	x

$$K_b = [C_6H_5NH_3^+][OH^-]/[C_6H_5NH_2]$$

$$3.8 \times 10^{-10} = (x)(x)/(1-x)$$

Since K_b is less than 1×10^{-3} , we can ignore the "x" in the denominator and will solve using the quadratic equation that we memorized in high school

$$3.8 \times 10^{-10} = x^2/(1-x)$$

$$3.8 \times 10^{-10} = x^2/1$$

$$3.8 \times 10^{-11} = x^2$$

$$x = 1.95 \times 10^{-5}$$

$$x = [OH^-] = 1.95 \times 10^{-5} M$$

IV. We can then find the pOH

$$pOH = -\log(1.95 \times 10^{-5}) = 4.71$$

$$pH = 14 - pOH$$

$$pH = 14 - 4.71$$

$$pH = 9.29$$

V. We set up this problem with only one RICE table because it is a weak base equilibrium problem. Once we used RICE to find the OH^- concentration, we knew that the negative

logarithm of this value would give pOH. At room temperature, the sum of pOH and pH is 14, so to find pH we simply subtract pOH from 14.

2. Calculate the pH of a solution containing 0.25 M anilinium chloride, $C_6H_5NH_3Cl$.

What is $C_6H_5NH_3Cl$?

Since it has a Cl in the formula, we know this is a type of salt. We know Cl^- is a spectator ion.

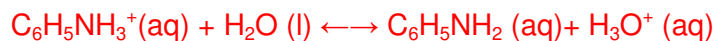
What kind of salt is it? Let's look at how it will break down in water:



We know Cl^- has a negative charge, thus the other part of the molecule must have a positive charge since the original salt has a neutral (no) charge. Cl^- would be the conjugate base of HCl, but we know HCl is a STRONG acid, and dissociates completely. Therefore, Cl^- does NOT spontaneously pick up an H^+ to form HCl in solution.

$C_6H_5NH_3^+$ now looks like a derivative of the ammonium ion! This is a weak acid.

How does the weak acid interact with water?



I. The final solution has a weak acid with some of its conjugate base. Since we start with a weak acid, we expect some H_3O^+ in solution at the end

II. There is no neutralization happening, only a weak acid equilibria

III. We can solve this using a RICE table! Since this is a weak acid problem, we will need the K_a of $C_6H_5NH_3^+$.

We know that $K_w = K_a \times K_b$

so $K_a = K_w/K_b$

$$K_a = 1 \times 10^{-14} \div 3.8 \times 10^{-10} = 2.63 \times 10^{-5}$$



I	0.25M	0	0
C	-x	+x	+x
E	0.25-x	x	x

$$K_a = [C_6H_5NH_2][H_3O^+]/[C_6H_5NH_3^+]$$

$$2.63 \times 10^{-5} = (x)(x)/(0.25-x)$$

Here, the K_a value is small (much less than 1×10^{-3}), so we can ignore the "x" in the "0.25-x"

$$2.63 \times 10^{-5} = x^2/0.25$$

$$(2.63 \times 10^{-5})0.25 = x^2$$

$$x = 2.56 \times 10^{-3}$$

IV. What does x mean? We look back at our RICE table to find that

$$x = [H_3O^+] = 2.56 \times 10^{-3}$$

$$pH = -\log[H_3O^+] = -\log(2.56 \times 10^{-3})$$

pH = 2.59

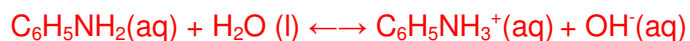
V. We set up this problem with only one RICE table because it is a weak acid equilibrium problem. Once we used RICE to find the H_3O^+ concentration, we knew that the negative logarithm of this value would give pH.

3. Calculate the pH of a solution containing 0.10 M aniline, $\text{C}_6\text{H}_5\text{NH}_2$, and 0.25 M anilinium chloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$.

From the previous problems, we have identified $\text{C}_6\text{H}_5\text{NH}_2$ to be a weak base and have seen that when in water, the salt anilinium chloride breaks into $\text{C}_6\text{H}_5\text{NH}_3^+$ and Cl^- .



I. So this is a weak base with its conjugate acid!



Since we KNOW we have both a base and its conjugate acid AND since there is about the same amount of each (we have twice as much conjugate acid, but we do not have 10,000 times as much acid)...even in our final, equilibrium solution, we will have roughly equal amounts!!

II. There is no neutralization occurring. Equilibrium between weak base and its conjugate acid

III. Based on what we have in solution, we have a BUFFER

We can use the Henderson Hasselbalch equation!

$$\text{IV. } \text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

OR

$$\text{pOH} = \text{pK}_b + \log\left(\frac{[\text{HB}^+]}{[\text{B}]}\right)$$

It may be preferable to work with the second equation because we set up our equation as a weak base dissociation in water.

$$\text{pK}_b = -\log(K_b) = -\log(3.8 \times 10^{-10}) = 9.42$$

$[\text{HB}^+]$ is the conjugate acid or the protonated form of the base - $\text{C}_6\text{H}_5\text{NH}_3^+$

$[\text{B}]$ is the unprotonated weak base - $\text{C}_6\text{H}_5\text{NH}_2$

$$\text{pOH} = 9.42 + \log(0.25\text{M}/0.10\text{M}) = 9.82$$

$$\text{pH} = 14 - \text{pOH} = 14 - 9.82 = 4.18$$

If using the other equation:

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$\text{pH} = 4.58 + \log(0.1\text{M}/0.25\text{M})$$

$$\text{pH} = 4.58 + (-0.398) = 4.18$$

BOTH versions of the equation get the same final pH!

V. We recognized that we had both a weak species and its conjugate pair in solution together in roughly equivalent magnitudes. There was no strong acid or strong base for the weak species to react with, so we knew that we only had to set up an aqueous equilibrium between the conjugate acid/base pair and use Henderson Hasselbalch to find pH.

4. Calculate the pH of a solution containing the result of the addition of 0.5 moles HCl to a solution of 1 liter from problem 1.

I. We have a strong acid, HCl, being added to a weak base aniline, $C_6H_5NH_2$ ($K_b = 3.8 \times 10^{-10}$). When combined, the strong acid donates its proton to the weak base until one of the two species is exhausted! This is a completion reaction so we would write the equation:



In one liter of 1.0M of aniline, there are 1.0 moles of the base ($1.0 \text{ mol/L} \times 1L = 1.0 \text{ moles}$). We are adding 0.5 moles of HCl. the weak base and HCl react in a 1:1 ratio, so we will be left with excess base reactant and no remaining HCl!

With leftover weak base reactant and with the conjugate acid salt that was created, we will have a BUFFER solution (provided that the two species have concentrations of roughly the same magnitude - we will find out).

II. A neutralization reaction is occurring. The strong acid reacts with the weak base to form water and a salt.

III. We will use a RICE table to solve for the strong reaction with HCl. Then, we will have a mixture of weak base and its conjugate acid so we can use Henderson Hasselbalch.

RICE tables that go to completion are best done in moles!

R	$C_6H_5NH_2 (aq)$	+	$HCl (aq)$	\rightarrow	$C_6H_5NH_3Cl(aq)$	+	$H_2O (l)$
I	1 mol		0.5 mol		0 mol		----
C	-0.5 mol		-0.5 mol		+0.5 mol		----
E	0.5 mol		0 mol		0.5 mol		----

Now we have equal amounts of $C_6H_5NH_2$ and $C_6H_5NH_3Cl$ which is a weak base and its conjugate acid! In one liter, they have equal concentrations of 0.5M each. We can use Henderson Hasselbalch.

IV. $pOH = pK_b + \log([HB^+]/[B])$

$pK_b = -\log(K_b) = -\log(3.8 \times 10^{-10}) = 9.42$

$[HB^+]$ is the conjugate acid or the protonated form of the base - $C_6H_5NH_3^+$

$[B]$ is the unprotonated weak base - $C_6H_5NH_2$

$pOH = 9.42 + \log(0.5M/0.5M) = 9.42 + 0$

$pH = 14 - pOH = 14 - 9.42 = 4.58$

V. We knew that the strong acid would react completely with any base first. When we ran this reaction, there was excess weak base in solution with its conjugate acid. They had concentrations of equivalent magnitude so we could use Henderson Hasselbalch to evaluate the pH. We selected the pOH version of Henderson Hasselbalch because its easier to think of aniline species in terms of bases. At room temperature, the sum of pOH and pH is 14, so to find pH we simply subtracted pOH from 14.

5. Calculate the pH of a solution containing the result of the addition of .01 moles of HCl to 1 liter of the solution from problem 3.

In problem 3 we found we had a buffer with 0.10 M of the base, $C_6H_5NH_2$ and 0.25 M of its conjugate acid $C_6H_5NH_3^+$

I. Since we start with a buffer and add a strong acid to it, we will have some salt left over, and a buffer solution if the strong acid does not exhaust the buffer (and since the amount of HCl being added is less than the moles of base present, it will not exhaust the buffer)

II. A neutralization reaction IS happening since we have a strong acid and a weak base present reacting to form water and a salt.

III. We will use a RICE table to determine the new concentrations of our buffer components

Since we have 1 L of our solution from #3, we will have 0.1 moles of $C_6H_5NH_2$ ($0.1 \text{ M} \times 1 \text{ L} = 0.1$ moles) and 0.25 moles of $C_6H_5NH_3^+$ ($0.25 \text{ M} \times 1 \text{ L} = 0.25$ moles)

RICE tables for completion reactions are best done in moles.



I	0.1mol	0.01mol	0.25mol
C	-0.01mol	-0.01mol	+0.01mol
E	0.09mol	0mol	0.26mol

From here, we can use our Henderson Hasselbalch equation, since we still have similar concentrations of our buffer components. We were told a number of moles of HCl have been added, we will assume that the volume did not change.

Therefore, our final concentrations are just the number of moles divided by 1L:

$$[C_6H_5NH_2] = 0.09M$$

$$[C_6H_5NH_3^+] = 0.26M$$

$$IV. \text{pOH} = \text{pK}_b + \log\left(\frac{[HB^+]}{[B]}\right)$$

$$\text{pK}_b = -\log(K_b) = -\log(3.8 \times 10^{-10}) = 9.42$$

$[HB^+]$ is the conjugate acid or the protonated form of the base - $C_6H_5NH_3^+$

$[B]$ is the unprotonated weak base - $C_6H_5NH_2$

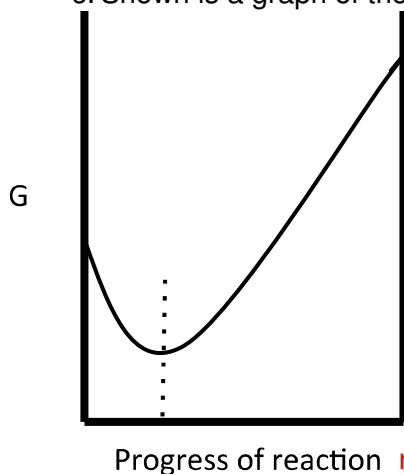
$$\text{pOH} = 9.42 + \log(0.26M/0.09M)$$

$$\text{pOH} = 9.42 + 0.46 = 9.88$$

$$\text{pH} = 14 - \text{pOH} = 14 - 9.88 = 4.12$$

V. We knew that the strong acid would react completely with any base first. When we ran this reaction, there was excess weak acid in solution with its conjugate base. They had concentrations of equivalent magnitude so we could use Henderson Hasselbalch to evaluate the pH. We selected the pOH version of Henderson Hasselbalch because its easier to think of aniline species in terms of bases. At room temperature, the sum of pOH and pH is 14, so to find pH we simply subtracted pOH from 14.

6. Shown is a graph of the free energy as function of reaction progress for a chemical reaction.



For this reaction is $\Delta_R G^\circ$ positive, negative, or zero? Explain why.

$\Delta_R G^\circ$ is positive for this reaction. There are a number of explanations for this.

$$\Delta_R G^\circ = G_{\text{final}} - G_{\text{initial}}$$

It can be seen from the graph that G_{final}° is greater than G_{initial}° , so $\Delta_R G^\circ$ should be positive

By looking at the graph, the products side (the end of the reaction) has a higher G° than the reactants side. This means that this reaction is “uphill” and is nonspontaneous. Again, a positive $\Delta_R G^\circ$

Why is the position marked with the dashed line the equilibrium point?

The equilibrium point is that when the reactions reaches its minimum free energy. This is not necessarily at the beginning or the end of the reaction, but is wherever the Gibbs free energy is at its lowest value. This position on the graph is the location of the dashed line, at the bottom of the curve, or the bottom of the energy well. Notice that for this reaction, the equilibrium point (point of lowest free energy) occurs after the reaction has only progressed partially (less than halfway). This means that the reaction is “reactant heavy” or “lies toward the reactants.” This makes sense for a non-spontaneous reaction!

Would you expect the graph of the free energy vs progress of the reaction to look like this for an ionization reaction of a weak acid or weak base? Why?

Yes. A weak acid or a weak base does NOT ionize completely. In fact, they barely ionize at all. Which means that they are reactant favored. This equilibrium curve is reactant favored as the equilibrium point is closer to the reactants than the products.

Also, the products are of higher free energy than the reactants, showing that it is not likely that there will be 100% products. Again, looking at the equilibrium of salts made of the conjugate pair of the acid or base, we again find this to be logical.

Reactant favored also means that $K < 1$, true for weak acids and weak bases. If $K < 1$, $\Delta G^\circ > 0$. That is, if it reactant favored, it is a nonspontaneous process. $\Delta G^\circ = -RT \ln K$

Would you expect the graph of the free energy vs progress of the reaction to look like this for a neutralization reaction between a strong acid and strong base? What about a weak acid and a strong base?

NO. A strong acid or a strong base does ionize completely - 100%. Their ions would completely react with one another leaving only a neutral salt and liquid water. The equilibrium curve would show essentially 100% products. The neutralization between a strong acid or base is spontaneous so the free energy of the products would be lower than the free energy of the reactants. Its equilibrium point would show after the reaction had progressed essentially completely.

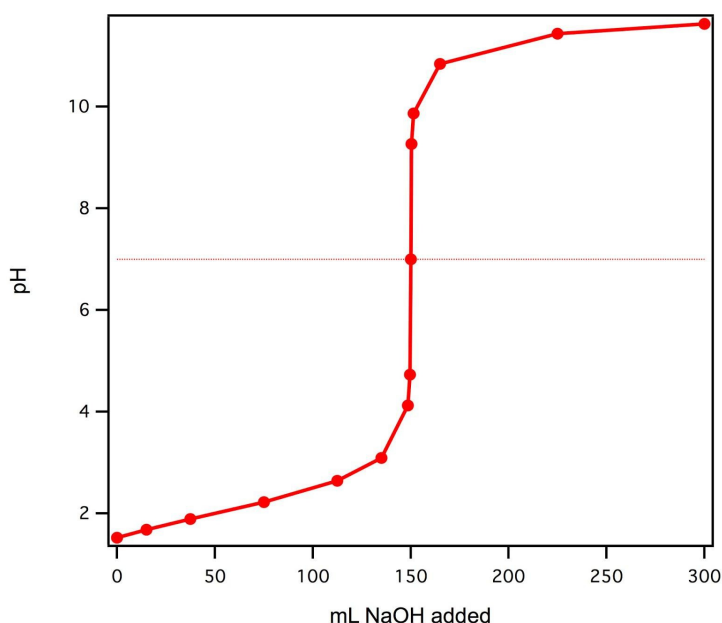
Here, $K \gg 1$, so our ΔG° should be negative.

NO. A weak acid and a strong base equilibrium would have a similar structure to the strong-strong neutralization in that the strong base would react completely with the weak acid to form the basic salt and liquid water. The strong base still ionizes completely and its OH^- groups combine with the acidic protons of the weak acid. The weak acid has really NOT ionized much and is mostly still the acid form (with its acidic proton still on). So the strong base has a lot of acidic protons to react with! The equilibrium curve would show essentially 100% products. The neutralization between a strong base and weak acid is spontaneous so the free energy of the products would be lower than the free energy of the reactants. Its equilibrium point would show after the reaction had progressed essentially completely.

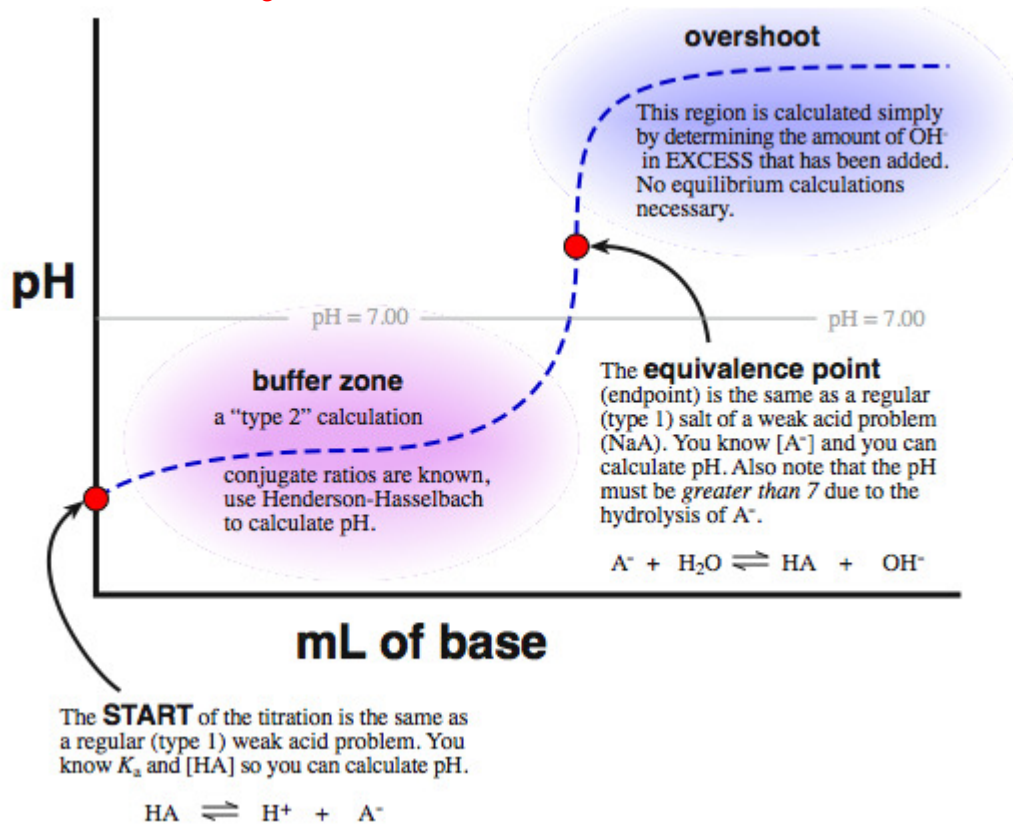
Here again, $K > 1$, the reaction is product favored since we have a neutralization reaction.

7. Sketch a titration curve of a strong acid and a strong base. Then sketch and fully label the titration curve of a strong base and a weak acid.

Strong acid titrated with strong base (NaOH in this example):



Weak acid titrated with a strong base:



Note that in the middle of the "BUFFER ZONE" there is a place where the concentration of conjugate acid is equal to the concentration of conjugate base

AND

The pH = pKa!