



## Titration and Buffers – Supplemental Worksheet **KEY**

HINT: When calculating the pH of a solution use the following 3 steps

Step 1: What is left in solution?

Step 2: What are the equilibrium concentrations of the species in solution?

Step 3: What is the pH of the solution?

### **Titration**

The next six problems represent many points along a titration curve of a weak base with a strong acid. This is a helpful exercise in understanding neutralization reactions and exactly what is going on at each step of a titration. Note this titration is opposite the titration problem we did in class where we did a titration of a weak acid with a strong base.

The titration is of 100 mL of a 0.1 M solution of ammonia. We titrate this solution with a 0.1 M solution of HBr. The  $K_b$  of ammonia is  $1.8 \times 10^{-5}$ .

#### **1. What is the pH when no HBr is added to 100 mL of a 0.1 M solution of ammonia?**

Ammonia is the only thing in solution so ,



This reaction does not go to completion because ammonia is a weak base. So this reaction will reach an equilibrium state associated with  $K_b$  of ammonia.  $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$ .

#### Moles or Concentration in RICE tables?

RICE tables provide a convenient way for us to track shifts in reactants and products as a system shifts to a new equilibrium state. Stoichiometry is traditionally solved in moles and you can use moles in a RICE table.

\*\*\* You just have to remember to convert those moles back into concentration before you solve the equilibrium expression and solve for  $x$ . Sometimes moles and concentration are the same number – like when your volume is exactly 1 liter.

#### Step 1: What is left in solution?

For the first step, the concentration has not been changed yet so we can directly put concentration into the RICE table and solve.



R	NH <sub>3</sub> (l) +	H <sub>2</sub> O(l) ↔	NH <sub>4</sub> <sup>+</sup> (aq) +	OH <sup>-</sup> (aq)
I	0.1	-	0	0
C	-x	-	+x	+x
E	0.1-x	-	x	x

Step 2: What are the equilibrium concentrations of the species in solution?

We calculate the equilibrium concentrations using  $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$ . The equilibrium concentration of  $\text{NH}_3$  is about equal to 0.1. We can ignore the  $-x$  because it is so small which we know due to the very small  $K_b$  value.

$$K_b(\text{NH}_3) = 1.8 \times 10^{-5} = \frac{x^2}{0.1} \Rightarrow x = \sqrt{(1.8 \times 10^{-5}) * (0.1)} = 1.34 \times 10^{-3}$$

So here we have  $[\text{OH}^-] = 1.34 \times 10^{-3} \text{ M}$

Step 3: What is the pH of the solution?

$$\text{pH} = 14 - \text{pOH} = 14 - (-\log[\text{OH}^-]) = 14 - (-\log[1.34 \times 10^{-3} \text{ M}]) = 14 - 2.87 = 11.13$$

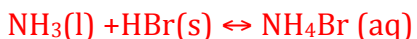
The pH of the solution is 11.13.

**Note the pH of the solution is basic. This makes sense because we have a weak base solution.**

**2. What is the pH when 20 mL of HBr is added to 100 mL of a 0.1 M solution of ammonia?**

Step 1: What is left in solution?

The following neutralization reaction occurs



This reaction goes to completion because HBr is a strong acid and dissociates fully. The  $\text{H}^+$  ions react with the  $\text{NH}_3$  to produce  $\text{NH}_4^+$  ions.

However, there is a limiting reactant in this neutralization reaction, in this case it is the HBr. Some  $\text{NH}_3$  is left over since it is not the limiting reactant and some  $\text{NH}_4\text{Br}$  is produced.

In the following RICE tables, we will convert all concentrations into moles. We will track the volume separately and combine it to get concentration when we need it.



Remember that  $\text{conc} * \text{volume} = \text{amount (moles)}$ . The total volume after this step is 120 mL or 0.12 L.

$$n(\text{NH}_3) = c * V = 0.1 \text{ mol/L} * 0.1 \text{ L} = 0.01 \text{ moles}$$

$$n(\text{HBr}) = c * V = 0.1 \text{ mol/L} * 0.02 \text{ L} = 0.002 \text{ moles}$$

R	$\text{NH}_3(\text{l}) +$	$\text{HBr}(\text{s}) \leftrightarrow$	$\text{NH}_4\text{Br}(\text{aq})$
I	0.01	0.002	0
C	-0.002	-0.002	+0.002
End	0.008	0	0.002

The  $\text{NH}_4\text{Br}$  is a soluble salt that will dissociate 100% into the following ions.

R	$\text{NH}_4\text{Br}(\text{s}) \rightarrow$	$\text{NH}_4^+(\text{aq}) +$	$\text{Br}^-(\text{aq})$
I	0.002	0	0
C	-0.002	+0.002	+0.002
E	0	0.002	0.002

We are then left with  $\text{NH}_4^+$  ions in solution. Now, both the  $\text{NH}_3$  and the  $\text{NH}_4^+$  initial concentrations are set in our RICE table. We now bring back the total volume to set up our final RICE table for the problem.

$$[\text{NH}_4^+] = n/V = 0.002 \text{ moles}/0.12 \text{ L} = 0.017 \text{ M.}$$

$$[\text{NH}_3] = n/V = 0.008 \text{ moles}/0.12 \text{ L} = 0.067 \text{ M.}$$

Also, because we now have the very definition of a buffer we can use either equilibria to solve the problem (either of the two conjugate equilibria). Since we almost always want a pH, it is better to just use the acid-based equilibria based on  $\text{NH}_4^+$  with a  $K_a = K_w/K_b = 5.56 * 10^{-10}$  :

R	$\text{NH}_4^+(\text{aq}) +$	$\text{H}_2\text{O}(\text{l}) \leftrightarrow$	$\text{NH}_3(\text{aq}) +$	$\text{H}_3\text{O}^+(\text{aq})$
I	0.017	-	0.067	0
C	-x	-	+x	+x
E	0.017-x	-	0.067+x	x

Step 2: What are the equilibrium concentrations of the species in solution?

The RICE table shows us that the equilibrium concentration of  $\text{NH}_4^+$  is about equal to 0.017 M and the  $\text{NH}_3$  concentration is about equal to 0.067 M. We can ignore the -x in each case because it is so incredibly small which we know due to the very small  $K_a$  value ( $5.56 * 10^{-10}$ ).

Step 3: What is the pH of the solution?



Since we have both of the weak base and its conjugate acid in solution, we have a buffer solution and will use the Henderson-Hasselbach equation to calculate the pH of the solution.

Once again, we can choose to use either the pH or pOH form of the Henderson-Hasselbach equation. Here we choose to use the pH version, since that is what we are trying to calculate.

$$\text{Remember that } K_a = K_w/K_b = 10^{-14}/1.8 \times 10^{-5} = 5.56 \times 10^{-10}$$

$$\text{p}K_a = -\log(K_a) = 9.26$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{\text{conjugate base}}{\text{acid}}\right) = 9.26 + \log\left(\frac{0.067}{0.017}\right) = 9.86$$

**Note at this point of the titration  $\text{pH} > \text{p}K_a$**

### 3. What is the pH when 50 mL of HBr is added to 100 mL of a 0.1 M solution of ammonia?

Step 1: What is left in solution?

This is exactly the same as in #2 above with the only difference being the amount of acid added which will force a new ratio of the conjugates,  $\text{NH}_3$  and  $\text{NH}_4^+$ . Also, our total volume is now 150 mL or 0.15 L.

$$n(\text{NH}_3) = c \cdot V = 0.1 \text{ mol/L} \cdot 0.1 \text{ L} = 0.01 \text{ moles}$$

$$n(\text{HBr}) = c \cdot V = 0.1 \text{ mol/L} \cdot 0.05 \text{ L} = 0.005 \text{ moles}$$

R	$\text{NH}_3(\text{l}) +$	$\text{HBr}(\text{s}) \leftrightarrow$	$\text{NH}_4\text{Br}(\text{aq})$
I	0.01	0.005	0
C	-0.005	-0.005	+0.005
End	0.005	0	0.005

Notice how this time we have EQUAL amounts of  $\text{NH}_3$  and  $\text{NH}_4^+$ . Convert the moles to concentrations:

$$[\text{NH}_4^+] = n/V = 0.005 \text{ moles}/0.15 \text{ L} = 0.033 \text{ M.}$$

$$[\text{NH}_3] = n/V = 0.005 \text{ moles}/0.15 \text{ L} = 0.033 \text{ M.}$$

Now plug those into the RICE table for the acid equilibria:

R	$\text{NH}_4^+(\text{aq}) +$	$\text{H}_2\text{O}(\text{l}) \leftrightarrow$	$\text{NH}_3(\text{aq}) +$	$\text{H}_3\text{O}^+(\text{aq})$
I	0.033	-	0.033	0
C	-x	-	+x	+x



Step 2: What are the equilibrium concentrations of the species in solution?

Once again, we can ignore the very small values of x and just assume the final concentration of both species is 0.033 M.

Step 3: What is the pH of the solution?

We once again use the acid version of the Henderson-Hasselbach equation to calculate the pH of the solution.

$$pH = pK_a + \log\left(\frac{\text{conjugate base}}{\text{acid}}\right) = 9.26 + \log\left(\frac{0.033}{0.033}\right) = 9.26$$

**Note at this point of the titration pH = pKa. This is the half equivalence point. When doing a titration in lab, you can use this point to predict the pKa of an unknown acid.**

**4. What is the pH when 70 mL of HBr is added to 100 mL of a 0.1 M solution of ammonia?**

Step 1: What is left in solution?

This is exactly the same as in #2 and #3 above with the only difference being the amount of acid added which will force a new ratio of the conjugates, NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>. Also, our total volume is now 170 mL or 0.17 L.

$$n(\text{NH}_3) = c \cdot V = 0.1 \text{ mol/L} \cdot 0.1 \text{ L} = 0.01 \text{ moles}$$

$$n(\text{HBr}) = c \cdot V = 0.1 \text{ mol/L} \cdot 0.07 \text{ L} = 0.007 \text{ moles}$$

R	NH <sub>3</sub> (l) +	HBr(s) ↔	NH <sub>4</sub> Br (aq)
I	0.01	0.007	0
C	-0.007	-0.007	+0.007
End	0.003	0	0.007

Notice how this time we have EQUAL amounts of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>. Convert the moles to concentrations:

$$[\text{NH}_4^+] = n/V = 0.007 \text{ moles}/0.15 \text{ L} = 0.0412 \text{ M.}$$

$$[\text{NH}_3] = n/V = 0.003 \text{ moles}/0.15 \text{ L} = 0.0176 \text{ M.}$$

Now plug those into the RICE table for the acid equilibria:



R	$\text{NH}_4^+(\text{aq}) +$	$\text{H}_2\text{O}(\text{l}) \leftrightarrow$	$\text{NH}_3(\text{aq}) +$	$\text{H}_3\text{O}^+(\text{aq})$
I	0.0412	-	0.0176	0
C	-x	-	+x	+x
E	0.0412-x	-	0.0176+x	x

Step 2: What are the equilibrium concentrations of the species in solution?

Once again, we can ignore the very small values of x as it relates to the concentrations of  $\text{NH}_3$  and  $\text{NH}_4^+$ .

Step 3: What is the pH of the solution?

We once again use the acid version of the Henderson-Hasselbach equation to calculate the pH of the solution.

$$\text{pH} = \text{pK}_a + \log\left(\frac{\text{conjugate base}}{\text{acid}}\right) = 9.26 + \log\left(\frac{0.0176}{0.0412}\right) = 8.89$$

**Note at this point of the titration  $\text{pH} < \text{pK}_a$**

**5. What is the pH when 100 mL of HBr is added to 100 mL of a 0.1 M solution of ammonia?**

Step 1: What is left in solution?

The following neutralization reaction occurs



This reaction goes to completion because HBr is a strong acid and dissociates fully. The  $\text{H}^+$  ions react with the  $\text{NH}_3$  to produce  $\text{NH}_4^+$  ions.

There is no limiting reactant in this problem because both reactants are added in stoichiometric amounts. No  $\text{NH}_3$  is left over. All the  $\text{NH}_3$  and HBr is converted into  $\text{NH}_4\text{Br}$ . The total volume is now 200mL or 0.20 L.

$$N(\text{NH}_4^+) = c \cdot V = 0.01 \text{ moles} \quad \text{divide by volume (.2L)} = 0.05 \text{ M } \text{NH}_4^+$$



Now this is just a weak acid ionization problem with the following RICE table:

R	$\text{NH}_4^+(\text{aq}) +$	$\text{H}_2\text{O}(\text{l}) \leftrightarrow$	$\text{NH}_3(\text{aq}) +$	$\text{H}_3\text{O}^+(\text{aq})$
I	0.05	-	0	0
C	-x	-	+x	+x
E	0.05-x	-	x	x

Step 2: What are the equilibrium concentrations of the species in solution?

This is no longer a buffer problem because we have run out of the base,  $\text{NH}_3$ . We calculate the equilibrium concentrations using on  $K_a(\text{NH}_4^+) = 5.56 \times 10^{-10}$  and the concentration of  $\text{NH}_4^+$ . We can still ignore the  $-x$  because it is so small which we know due to the very small  $K_b$  value.

$$K_a(\text{NH}_4^+) = 5.56 \times 10^{-10} = \frac{x^2}{0.05} \Rightarrow x = \sqrt{(5.56 \times 10^{-10}) * (0.05)} = 5.27 \times 10^{-6}$$

So here we have  $[\text{H}_3\text{O}^+] = 5.27 \times 10^{-6} \text{ M}$

Step 3: What is the pH of the solution?

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[5.27 \times 10^{-6} \text{ M}] = 5.28$$

The pH of the solution is 5.28.

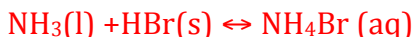
**Note the pH of the solution is acidic. This makes sense because essentially we have a weak acid solution. Also, not that at this point  $n(\text{HBr added}) = n(\text{NH}_3 \text{ initial})$ . This is the equivalence point and can be used in the lab to calculate the initial concentration of the starting weak base if it is unknown.**



**6. What is the pH when 140 mL of HBr is added to 100 mL of a 0.1 M solution of ammonia?**

Step 1: What is left in solution?

The following neutralization reaction occurs



This reaction goes to completion because HBr is a strong acid and dissociates fully. The  $\text{H}^+$  ions react with the  $\text{NH}_3$  to produce  $\text{NH}_4^+$  ions.

The limiting reactant is  $\text{NH}_3$ . All the  $\text{NH}_3$  is used up. Some HBr is left over. All the  $\text{NH}_3$  and some of the HBr is converted into  $\text{NH}_4\text{Br}$ .

$$\begin{aligned} n(\text{NH}_3) &= c \cdot V = 0.1 \text{ mol/L} \cdot 0.1 \text{ L} = 0.01 \text{ moles} \\ n(\text{HBr}) &= c \cdot V = 0.1 \text{ mol/L} \cdot 0.14 \text{ L} = 0.014 \text{ moles (excess!!)} \\ \text{total volume is now } &240 \text{ mL or } 0.24 \text{ L} \end{aligned}$$

R	$\text{NH}_3(\text{l}) +$	$\text{HBr}(\text{s}) \leftrightarrow$	$\text{NH}_4\text{Br}(\text{aq})$
I	0.01	0.014	0
C	-0.01	-0.01	+0.01
E	0	0.004	0.01

The  $\text{NH}_4\text{Br}$  is a salt that is soluble in water and so will dissociate into the following ions 100%. However the effect of the weak acid produced in this reaction is negligible compared to the effect of the excess strong acid that is left in solution. So, we only need to concern ourselves with the 100% dissociation of the strong acid left in solution. Think: the pH is SET by the excess strong acid.

R	$\text{HBr}(\text{s}) +$	$\text{H}_2\text{O} \rightarrow$	$\text{H}_3\text{O}^+(\text{aq}) +$	$\text{Br}^-(\text{aq})$
I	0.004	-	0	0
C	-0.004	-	+0.004	+0.004
End	0	-	0.004	0.004

Step 2: What are the equilibrium concentrations of the species in solution?

When calculating the pH of a solution with strong acid and weak acid, we can ignore the effect of the weak acid on the pH since its contribution compared to the contribution of the strong acid is so small.

So here we have  $n(\text{H}_3\text{O}^+) = 0.004$  moles

$$[\text{H}_3\text{O}^+] = n/V = 0.004 \text{ moles}/0.24\text{L} = 0.0167 \text{ M}$$





Step 3: What is the pH of the solution?

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[0.0167 \text{ M}] = 1.77$$

**The pH of the solution is 1.78.**

**Note the pH of the solution is very acidic. This makes sense because essentially we have a strong acid solution.**



## Buffers

The next three problems represent experimenting with a given buffer system. How much strong acid can you add without exhausting the buffer capacity? In class, we experimented with a buffer system to see how much acid it took to change the pH of the solution dramatically. Remember, it took adding a lot of acid to change the pH in the buffer solution than what we had to add to change the pH of pure water.

The buffer system we will use for this problems is: 100 mL of 0.5 M  $\text{NH}_3$  and 100 mL of 0.5 M  $\text{NH}_4\text{Br}$ . The  $K_b$  of ammonia is  $1.8 \times 10^{-5}$ .

### 9. What is the pH of this buffer system?

We first have to calculate the concentration of  $\text{NH}_3$  and  $\text{NH}_4^+$ .

$$n(\text{NH}_3) = c \cdot V = 0.5 \text{ mol/L} \cdot 0.1 \text{ L} = 0.05 \text{ moles}$$
$$[\text{NH}_3] = n/V = 0.05 \text{ mol} / 0.2 \text{ L} = 0.25 \text{ M}$$

$$n(\text{NH}_4^+) = c \cdot V = 0.5 \text{ mol/L} \cdot 0.1 \text{ L} = 0.05 \text{ moles}$$
$$[\text{NH}_4^+] = n/V = 0.05 \text{ mol} / 0.2 \text{ L} = 0.25 \text{ M}$$

Since this is a buffer system, we use the Henderson-Hasselbach equation to calculate the pH of the solution.

We can choose to use either the pH or pOH form of the Henderson-Hasselbach equation. Here we choose to use the pH version, since that is what we are trying to calculate.

However, in order to do this we need to calculate the  $pK_a$  of  $\text{NH}_4^+$  knowing the  $K_b$  of ammonia is  $1.8 \times 10^{-5}$ .

$$K_a = K_w/K_b = 10^{-14}/1.8 \times 10^{-5} = 5.56 \times 10^{-10}$$

$$pK_a = -\log(K_a) = 9.26$$

$$pH = pK_a + \log\left(\frac{\text{conjugate base}}{\text{acid}}\right) = 9.26 + \log\left(\frac{0.25}{0.25}\right) = 9.26$$

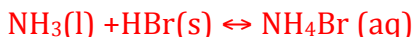
The pH of a solution with equal concentrations of weak acid and conjugate base is equal to the  $pK_a$  of the weak acid.



**10. What is the pH when 100 mL of 0.1 M HBr is added to this buffer system?  
Have you exhausted the buffer capacity?**

Step 1: What is left in solution?

The following neutralization reaction occurs



This reaction goes to completion because HBr is a strong acid and dissociates fully. The  $\text{H}^+$  ions react with the  $\text{NH}_3$  to produce  $\text{NH}_4^+$  ions.

However, the HBr is the limiting reactant in this problem. Some  $\text{NH}_3$  is left over since it is not the limiting reactant and some  $\text{NH}_4\text{Br}$  is produced.

In RICE tables, we need to convert all concentrations into moles.

$$n(\text{NH}_3) = c \cdot V = 0.5 \text{ mol/L} \cdot 0.1 \text{ L} = 0.05 \text{ moles}$$

$$n(\text{HBr}) = c \cdot V = 0.1 \text{ mol/L} \cdot 0.1 \text{ L} = 0.01 \text{ moles}$$

R	$\text{NH}_3(\text{l}) +$	$\text{HBr}(\text{s}) \leftrightarrow$	$\text{NH}_4\text{Br}(\text{aq})$
I	0.05	0.01	0
C	-0.01	-0.01	+0.01
End	0.04	0	0.01

Step 2: What are the equilibrium concentrations of the species in solution?

We now have new concentrations of  $\text{NH}_3$  and  $\text{NH}_4^+$  in solution.

$n(\text{NH}_4^+) = 0.01 \text{ moles} + 0.05 \text{ moles} = 0.06 \text{ moles}$  because 0.05 moles of  $\text{NH}_4^+$  are in the buffer system initially and 0.01 moles are formed from the  $\text{NH}_4\text{Br}$  salt formed in the neutralization reaction.

$$[\text{NH}_3] = n/V = 0.04 \text{ mol} / 0.3 \text{ L} = 0.133 \text{ M}$$

$$[\text{NH}_4^+] = n/V = 0.06 \text{ mol} / 0.3 \text{ L} = 0.2 \text{ M}$$

Step 3: What is the pH of the solution?

Since this is a buffer system, we use the Henderson-Hasselbach equation to calculate the pH of the solution.

$$\text{pH} = \text{pK}_a + \log\left(\frac{\text{conjugate base}}{\text{acid}}\right) = 9.26 + \log\left(\frac{0.133}{0.2}\right) = 9.08$$

**This is not a substantial change in the pH for adding 100 mL of 0.1 M HBr solution. So we have not exhausted the buffer capacity.**



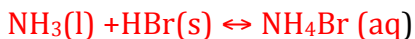
**Note: If we were to add this to pure water, the ending solution would definitely be acidic and would have a pH of 1.30.**



**11. What is the pH when 700 mL of 0.1 M HBr is added to this buffer system?  
Have you exhausted the buffer capacity?**

Step 1: What is left in solution?

The following neutralization reaction occurs



This reaction goes to completion because HBr is a strong acid and dissociates fully. The  $\text{H}^+$  ions react with the  $\text{NH}_3$  to produce  $\text{NH}_4^+$  ions.

The limiting reactant is  $\text{NH}_3$ . All the  $\text{NH}_3$  is used up. Some HBr is left over. All the  $\text{NH}_3$  and some of the HBr is converted into  $\text{NH}_4\text{Br}$ .

In RICE tables, we need to convert all concentrations into moles.

$$n(\text{NH}_3) = c \cdot V = 0.5 \text{ mol/L} \cdot 0.1 \text{ L} = 0.05 \text{ moles}$$

$$n(\text{HBr}) = c \cdot V = 0.1 \text{ mol/L} \cdot 0.7 \text{ L} = 0.07 \text{ moles}$$

R	$\text{NH}_3(\text{l}) +$	$\text{HBr}(\text{s}) \leftrightarrow$	$\text{NH}_4\text{Br}(\text{aq})$
I	0.05	0.07	0
C	-0.05	-0.05	+0.05
End	0	0.02	0.05

Step 2: What are the equilibrium concentrations of the species in solution?

When calculating the pH of a solution with strong acid and weak acid, we can ignore the effect of the weak acid on the pH since its contribution compared to the contribution of the strong acid is so small.

So here we have  $n(\text{H}_3\text{O}^+) = 0.02$  moles

$$[\text{H}_3\text{O}^+] = n/V = 0.02 \text{ moles}/0.9\text{L} = 0.022 \text{ M}$$

Step 3: What is the pH of the solution?

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[0.022 \text{ M}] = 1.65$$

The pH of the solution is 1.65.

**This is a substantial change in the pH. We have exhausted the buffer capacity here. The buffer capacity of this buffer system is 0.05 moles for both acid and base because that is how many of weak acid and weak base the buffer system contains initially.**