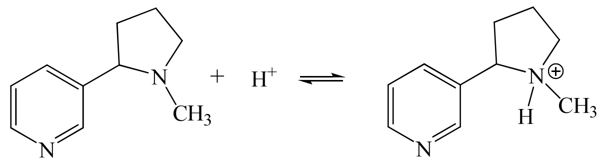
1. The Henderson–Hasselbalch (H-H) equation is a clever rearrangement of the K_a equilibrium expression that comes in very handy for certain pH calculations. So far we have focused using the H-H equation to calculate the buffer ratio ([base]/[acid]) required to prepare a buffer at a specific pH. In recitation we determined the buffer ratio required to prepare a pH 6.85 buffer we might use to study novel chemotherapy agents; however, the noble H-H equation can be used for more nefarious purposes. ***(Sp15)***

   Nicotine is the compound responsible for addiction to tobacco products. Nicotine is also a weak acid, as shown in the chemical equation. The molecular form of nicotine (left side) is more volatile than the ionic form (right side) due to the different intermolecular forces for the two forms (Chapter 11).

   Tobacco companies found that by manipulating the pH of the tobacco they could convert the ionic (protonated) form of nicotine into the neutral molecular form, increasing the amount of nicotine in cigarette smoke, making the experience more satisfying – in other words, more addictive.

   A. If you wanted to convert the ionic form of nicotine into the molecular form, would you increase the pH of the tobacco or decrease the pH of the tobacco? ______________________

      Explain your reasoning.

   B. Suppose you wanted a nicotine:nicotine-H^+ ratio of 20:1; that is, you want $\frac{[\text{nicotine}]}{[\text{nicotine-H}^+]} = 20$. What would the pH of the tobacco mixture need to be? (The K_b for nicotine is 1.0×10^{-6}.)

   C. Now think about your answer to Part B. Does it make sense considering your answer to Part A. If not, look back over work in Part B to see if you made a dumb mistake on an easy calculation.

2. Most bacteria can only survive in an environment with a narrow pH range centered around pH 7; however, some bacteria require acidic conditions (acidophiles) or basic conditions (alkalinophiles). A new species of alkaliphilic bacteria isolated from mica mines in the Nellore district of Andhra Pradesh, India, was recently reported (*Research and Reviews: Journal of Microbiology and Biotechnology*, **2013**, *2*, 1-7). This strain of bacteria exhibited optimum growth at pH 10.0, but it continued to grow at up to pH 12.0. ***(Sp14)***

   The paper reported that "sodium acetate, sodium phosphate and calcium carbonate were used to adjust pH," but very little information was provided on how this was done. The relevant K_a and pK_a values for the conjugate acids associated with these compounds are given in the able on the right.

	K_a	pK_a
H_3PO_4	7.5×10^{-3}	2.12
CH_3COOH	1.8×10^{-5}	4.74
H_2CO_3	4.2×10^{-7}	6.38
$H_2PO_4^-$	6.2×10^{-8}	7.21
HCO_3^-	4.8×10^{-11}	10.32
HPO_4^{2-}	4.8×10^{-13}	12.32

   Suppose you wanted to study this strain of bacteria at pH 11.65.

   A. What conjugate acid-base pair would you use for your buffer?

      Why?

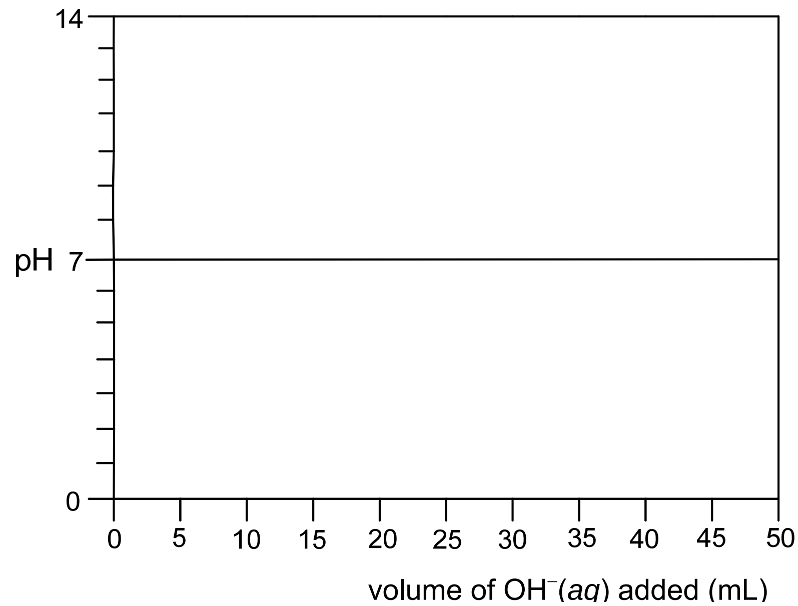
   B. What concentrations of acid and base would you use to make the buffer?

   C. *"sodium acetate, sodium phosphate and calcium carbonate were used to adjust pH"*

      Anything seem weird about this? Calculate the maximum solubility of $CaCO_3(s)$. The K_{sp} of $CaCO_3$ is 8.7×10^{-9}.

3. Thioglycolic acid, $HC_2H_3O_2S(aq)$, was originally developed as a chemical depilatory, but it is primary used to make ammonium thioglycolate, the chemical that breaks disulfide bonds in the hair permanent process, as most of us learned in the 2001 documentary *Legally Blonde* that chronicled the life and early career of Elle Woods. A 25.0 mL sample of 0.20 *M* $HC_2H_3O_2S(aq)$ was titrated with 0.20 *M* $NaOH(aq)$. The K_a and pK_a of thioglycolic acid are 2.1×10^{-4} and 3.68, respectively. ***(Sp14)***

   A. Sketch the shape of the curve that you expect to result from this titration from 0 to 50 mL, using reasonable estimates for the initial and final pH values. Label the half-equivalence and equivalence points, and be sure to place these points at the correct volumes and a reasonable pH value.



   B. Calculate the pH after the following volumes of 0.20 M $NaOH(aq)$ are added:

      1. 10.0 mL

      2. 25.0 mL

      3. 40.0 mL

4. ***(Note: This is more of an "Exam 2" question, but it sets up the next two problems*.)** Hydrazoic acid, $HN_3(aq)$, is interesting for several reasons we will consider over the next three weeks. So let's warm up by looking at the acid-base chemistry. ***(Sp16)***

   A. The K_a for $HN_3(aq)$ is 1.9×10^{-5}. Calculate the pH of a 0.015 M solution of $HN_3(aq)$.

   B. Calculate the pH of a 0.015 M solution of $LiN_3(aq)$, but first...

      Write a chemical equation showing the acid-base chemistry of $LiN_3(aq)$ in water.

      Now calculate the pH.

   C. Suppose we used $Be(N_3)_2(aq)$ instead. Give two reasons your pH will be different than the value you calculated in Part B. You do not have to do any calculations.

5. Now suppose you add 10 mL of 0.020 M $NaOH(aq)$ to 20 mL of 0.015 M $HN_3(aq)$. ***(Sp16)***

   A. Write a chemical equation for the reaction that occurs.

   B. What kind of problem are you going to solve to find the pH of the final solution?

   C. Find the pH.

6. This time let's add 20 mL of 0.020 M $NaOH(aq)$ to 20 mL of 0.015 M $HN_3(aq)$. ***(Sp16)***

   A. Write a chemical equation for the reaction that occurs.

   B. What kind of problem are you going to solve to find the pH of the final solution?

   C. Find the pH.

7. Acids and bases. ***(Sp16)***

TABLE 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

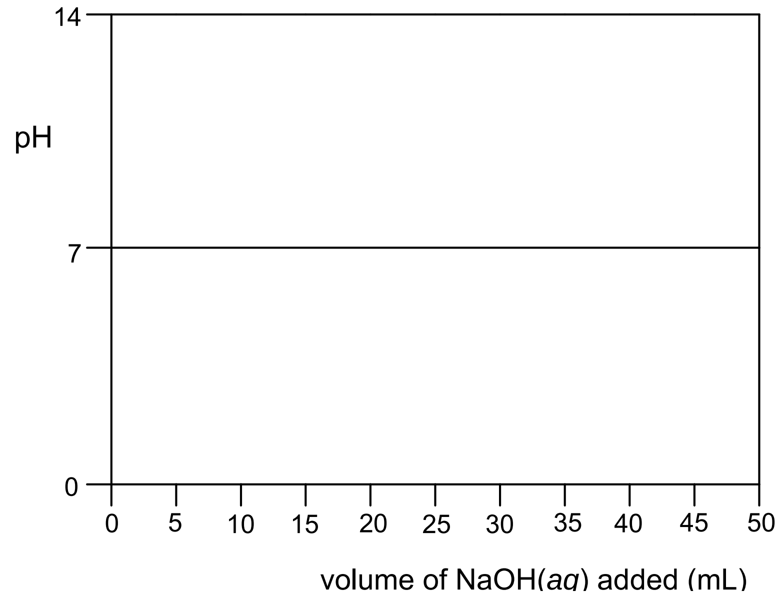
A. Citric acid, $H_3C_6H_5O_7(aq)$ is the official weak acid for the State of Florida. (Okay, I made that up.)

Would a solution of $NaH_2C_6H_5O_7(aq)$ be acidic, basic, or essentially neutral? (Show your work or explain your reasoning.)

8. One more dance with our favorite weak acid, hydrogen cyanate (HOCN, $K_a = 3.3 \times 10^{-4}$). A 30.0 mL sample of 0.20 M HOCN(*aq*) was titrated with 0.20 M NaOH(*aq*). ***(Sp15)***

A. Write a balanced chemical equation for the neutralization reaction between HOCN(*aq*) and NaOH(*aq*).

B. Before you do any calculations, sketch the shape of the curve that you expect to result from this titration, and label the equivalence point (eq pt) and the half-equivalence point (1/2 eq pt) on the curve.

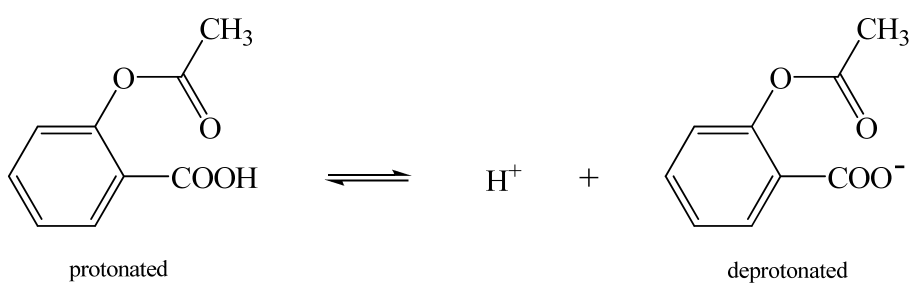


C. Calculate the pH after the following volumes of 0.20 M NaOH(*aq*) are added:

1. 20 mL

2. 40 mL

9. On the last exam we looked at the kinetics for the hydrolysis of aspirin. The chemical name of aspirin is acetylsalicylic acid (you will synthesize this compound if you take organic lab), and it is a weak acid with $K_a = 2.8 \times 10^{-4}$. The acid ionization of acetylsalicylic acid is shown in the following chemical equation:



The ratio of neutral (protonated) to deprotonated aspirin varies with the pH of the body fluid in which it is dissolved. Such variations can be important when considering the active form of drugs and their transport between the blood stream and other biological tissues. ***(Sp12)***

What is the ratio of neutral (protonated) aspirin to deprotonated aspirin in…

A. gastric juices in the stomach; pH = 1.0–2.0, so let's assume pH = 1.5.

B. the duodenum (small intestine). The pH in the small intestine generally ranges from 7.0 to 9.0; assume 8.0.

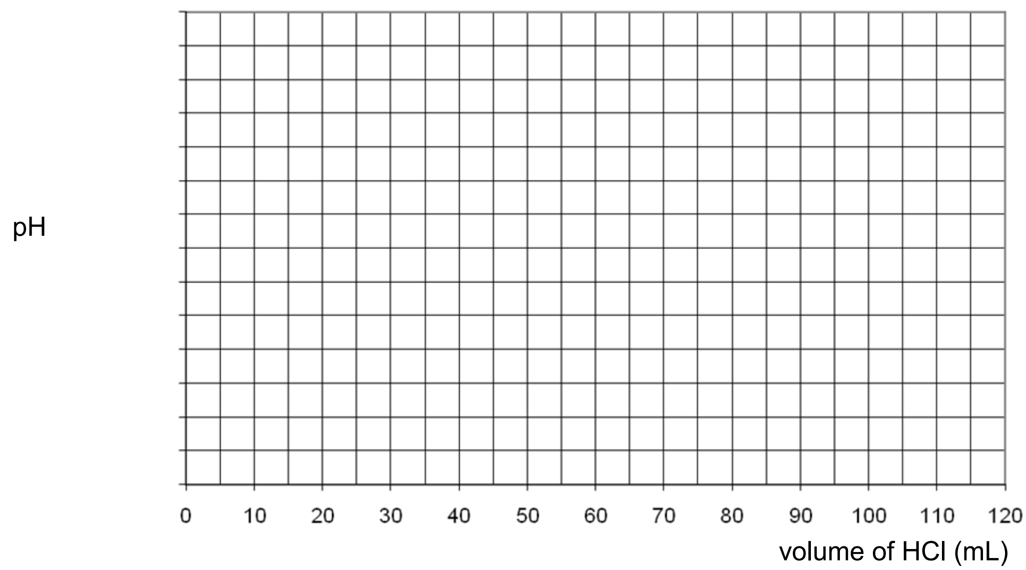
10. Weak base B is titrated with HCl(aq). ***(Fa12)***

$$B + HCl \rightarrow HB^+ + Cl^-$$

A. Real titration: It required 34.19 mL of 0.1052 M HCl(aq) to reach the end point when titrating 21.01 mL of a solution containing an unknown amount of B(aq). Determine the concentration of the weak base.

B. Fake titration: 50 mL of 0.10 M B(aq) with 0.10 M HCl (aq). So the equivalence will be 50 mL.

Sketch the expected appearance of the titration curve. What kind of problem are you solving in each region?



Calculate the pH at…

0 mL of 0.10 M HCl (aq)

35 mL of 0.10 M HCl (aq)

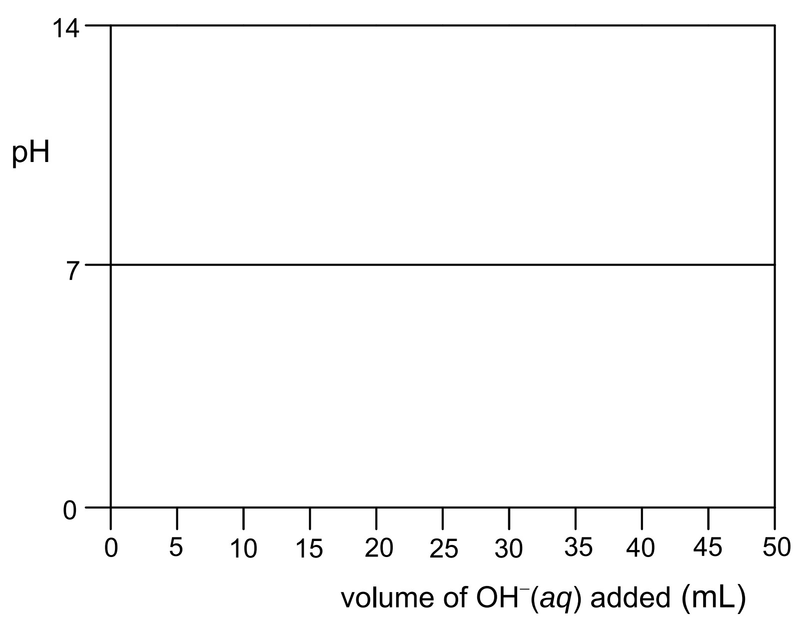
50 mL of 0.10 M HCl (aq)

11. Because HF(aq) is a weak acid, it can be titrated with a strong base such as NaOH(aq). A 0.10 M solution of HF was prepared and checked by titrating a 30.0 mL sample of the solution with 0.10 M NaOH(aq). The K_a of hydrofluoric acid is 7.1×10^{-4}. ***(Sp11)***

A. Sketch the shape of the curve that you expect to result from this titration. Label the equivalence point, and be sure to place it at the correct volume and in the correct pH range.

B. Calculate the pH after the following volumes of 0.10 M NaOH(aq) are added:

1. 15.0 mL
2. 25.0 mL
3. 30.0 mL
4. 40.0 mL



12. One liter (1.00 L) of an acetate buffer was prepared with the following concentrations: $[HC_2H_3O_2] = 0.050$ M and $[NaC_2H_3O_2] = 0.040$ M. The pK_a of acetic acid is 4.74. ***(Sp10)***

   A. Calculate the pH of the buffer.

   B. You wish to adjust the pH of this buffer to 5.00 by adding either 1.0 M HCl(aq) or 1.0 M NaOH(aq). Which should you add?

   (In the original version of the exam, I went on to ask: How much of the solution that you selected in part B will you need to add to adjust the pH to 5.00? Turns out this problem is doable – and kind of fun if it is not on an exam – but it actually takes a fair bit of work. So I pulled it at the last minute, and instead I will give it as a homework problem. You're welcome.)

13. Malachite Green, the dye used to make dark green paper, is actually a weak base ($K_b = 2.2 \times 10^{-2}$). A 0.150 M solution of the dye was prepared, and the concentration was checked by titrating a 40.0 mL sample of the dye with 0.300 M HNO_3(aq). ***(Su09,4)***

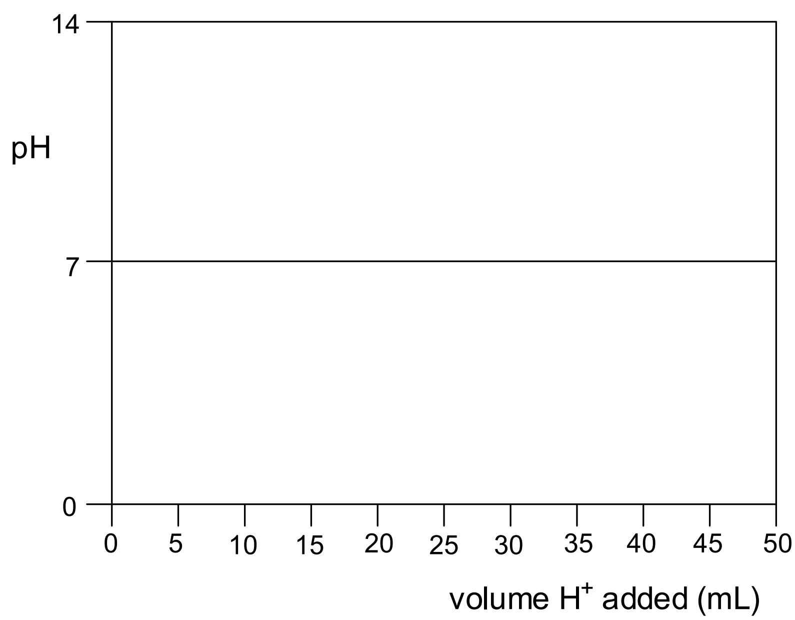
   A. Sketch the shape of the curve that you expect to result from this titration.

   B. Calculate the pH after the following volumes of 0.300 M HNO_3(aq) are added:

      1. 10.0 mL

      2. 15.0 mL

      3. 20.0 mL



14. A 50.0 mL sample of 0.20 M HA(aq) with $K_a = 8.6 \times 10^{-5}$ is titrated with 0.10 M NaOH(aq). ***(Su09)***

   A. What is the volume of 0.10 M NaOH(aq) that must be added to reach the equivalence point?

   B. Write a chemical equation that describes the titration reaction.

   C. Which of the following statements best describes the equivalence point? (circle one)

      1. mostly HA and very little A^- in solution at the equivalence point
      2. significant amounts of HA and A^- in solution at the equivalence point
      3. mostly A^- and very little HA in solution at the equivalence point
      4. essentially no HA or A^- in solution at the equivalence point

   D. Based on your answer to part C, do you expect the pH to be less than 7, roughly 7, or greater than 7?

   E. Calculate the pH at the equivalence point. Be sure to show your work clearly for partial credit.

15. A 0.100 M solution of NaOH(aq) was used to titrate 20.0 mL of a 0.200 M solution of phenylacetic acid, $HC_8H_7O_2$ (only the first hydrogen is acidic). The K_a for phenylacetic acid is 4.9 x 10^{-5}. ***(Sp08)***

    Calculate the pH of the solution being titrated at the following volumes of added NaOH(aq):

    A. 0 mL of 0.100 M NaOH(aq) added (i.e. calculate the pH of 0.200 M [$HC_8H_7O_2$])

    B. 20.0 mL of 0.100 M NaOH(aq) added

    C. 30.0 mL of 0.100 M NaOH(aq) added

    D. 40.0 mL of 0.100 M NaOH(aq) added

16. Fluoride is an interesting anion. For example, HCl(aq), HBr(aq), and HI(aq) are all strong acids, but HF(aq) is a weak acid with K_a given with the data at the end of the exam. ***(Sp05)***

    A. Calculate the pH of 0.40 M HF(aq).

    B. Calculate the pH of 0.20 M NaF(aq).

    C. Calculate the pH of a solution formed by mixing equal volumes of the solutions in parts A and B. (Note: You do not need your answers from part A or B to do this calculation.)

    D. What would be the optimal pH of a buffer formed from HF(aq) and F^-(aq)? In other words, what is the pH at the center of the buffer region?

    E. Name something about fluoride that makes it chemically interesting or unique.