

# Chapter 17

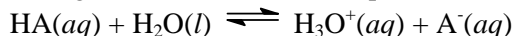
## Acid-Base Equilibria

### Concept Check 17.1

You have prepared dilute solutions of equal molar concentrations of  $\text{HC}_2\text{H}_3\text{O}_2$  (acetic acid),  $\text{HNO}_2$ ,  $\text{HF}$ , and  $\text{HCN}$ . Rank the solutions from the highest pH to the lowest pH.

#### Solution

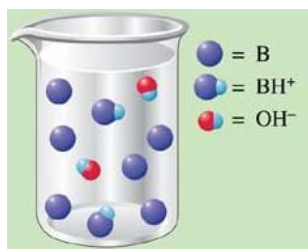
You would probably guess that the pH's of the acid solutions depend on their respective  $K_a$ 's: the larger the  $K_a$ , the greater the acidity or the lower the pH. We can put this on a firm basis by looking at the acid ionization equilibrium. An acid HA ionizes in water as follows:



The corresponding equilibrium constant  $K_a$  equals  $[\text{H}_3\text{O}^+][\text{A}^-]/[\text{HA}]$ . When you start with the same concentration of HA, the concentration of HA in solution is essentially the same for each acid. Also,  $[\text{H}_3\text{O}^+] = [\text{A}^-]$ . This means that  $K_a$  is proportional to  $[\text{H}_3\text{O}^+]^2$ . Or,  $\text{pH} = -\log [\text{H}_3\text{O}^+]$  is proportional to  $-\log K_a$ . Therefore, the larger the  $K_a$ , the lower the pH. As an example, compare two acids, one with  $K_a = 10^{-5}$  and the other with  $K_a$  equal to  $10^{-4}$ . The corresponding  $-\log K_a$  values are 5 and 4, respectively. The second acid (the one with the greater  $K_a$ ) would have the lower pH. If you look at Table 17.1, the acid with the largest  $K_a$  of those listed in the problem statement is HF. So the ranking from lowest to highest pH is:  $\text{HCN} < \text{HC}_2\text{H}_3\text{O}_2 < \text{HNO}_2, \text{HF}$ .

### Concept Check 17.2

A base B is placed into a beaker of water with the result depicted below (water molecules have been omitted for clarity). Write the ionization reaction for this base and classify the base as being strong or weak.



### Solutions

By examining the contents of the beaker, you see there are three different species present, the ions BH<sup>+</sup> and OH<sup>-</sup> as well as unreacted B molecules. This represents a weak base. The ionization reaction for this base is



### Concept Check 17.3

Which of the following aqueous solutions has the highest pH and which has the lowest?

- a. 0.1 M NH<sub>3</sub>
- b. 0.1 M NH<sub>4</sub>Br
- c. 0.1 M NaF
- d. 0.1 M NaCl

### Solution

Ammonia, NH<sub>3</sub>, is a weak base; the other compounds are salts. You can decide the acidity or basicity of salt solutions by noting whether the corresponding acid and base are strong or weak. For example, NH<sub>4</sub>Br is the salt of a weak base (NH<sub>3</sub>) and a strong acid (HBr), so the salt is acidic. Similarly, NaF is basic (it is the salt of a strong base, NaOH, and a weak acid, HF). NaCl is neutral. This means that two of the solutions are basic (NH<sub>3</sub> and NaF), one solution is neutral (NaCl), and the other is acidic (NH<sub>4</sub>Br). Although a salt might be as basic as NH<sub>3</sub>, this occurs only when the acid from which the salt formed is quite weak (for example, NaCN is quite basic). So the solution with highest pH is 0.1 M NH<sub>3</sub> (a), and the solution of lowest pH is 0.1 M NH<sub>4</sub>Br (b).

### Concept Check 17.4

You add 1.5 mL of 1 M HCl to each of the following solutions. Which one will show the least change of pH?

- a. 15 mL of 0.1 M NaOH
- b. 15 mL of 0.1 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

- c. 30 mL of 0.1 *M* NaOH and 30 mL of 0.1 *M* HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>
- d. 30 mL of 0.1 *M* NaOH and 60 mL of 0.1 *M* HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

### Solution

The amount of any substance in the solution is proportional to the volume times molarity. Let's look at each solution.

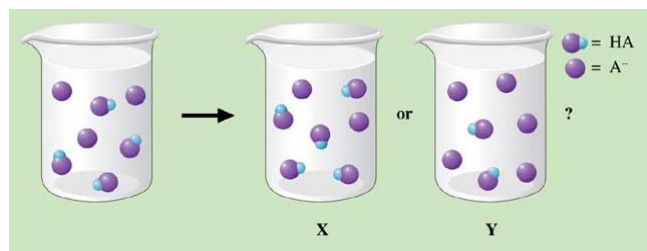
- a. The 1.5 mL of 1 *M* HCl just neutralizes 15 mL of 0.1 *M* NaOH, giving a solution of NaCl. Thus, the pH of the original solution changes from very basic to neutral (pH = 7) after the addition of HCl.
- b. The solution of acetic acid changes from weakly acidic to strongly acidic with the addition of HCl.
- c. Equal amounts of NaOH and HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> in the original solution exactly neutralize each other to produce the salt NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, which is slightly basic. The addition of the strong acid HCl gives an acidic solution.
- d. The 30 mL of NaOH reacts with 30 mL of HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> to give the salt NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, leaving an equal amount of the corresponding acid HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>. The result is a buffer solution. The addition of HCl to the buffer does not change the pH appreciably. (This is true as long as the amount of added acid does not overwhelm the capacity of the buffer. In this case, it does not. The amount of acid and base conjugates in the buffer are twice the amount of added acid.)

Only d. does not change appreciably in pH.

### Concept Check 17.5

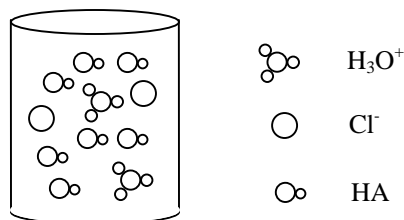
The beaker on the left below represents a buffer solution of a weak acid HA and its conjugate base A<sup>-</sup>. (Water molecules and spectator ions have been omitted for clarity.)

- a. Which beaker on the right, X or Y, depicts the solution after the addition of two formula units of NaOH?
- b. How many HCl molecules can be added to the original buffer solution before the buffer capacity is exceeded?
- c. Draw a picture of the solution where the buffer capacity has been exceeded by the addition of HCl.



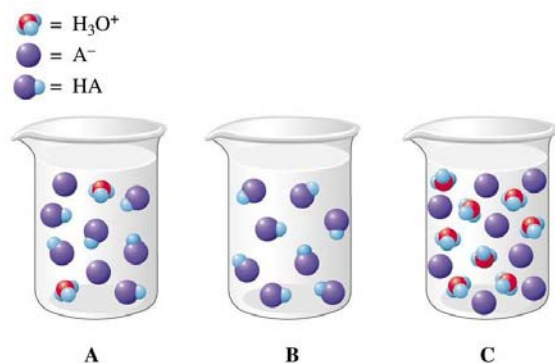
### Solution

- When two formula units of NaOH are added to the beaker on the left, a reaction occurs consuming two HA molecules and forming two  $A^-$  ions. This results in a solution with two HA molecules and five  $A^-$  ions, which is depicted in beaker Y.
- Since the original buffer contains three  $A^-$  ions, three HCl molecules could be added before the buffer capacity would be exceeded.
- The beaker would contain seven HA molecules. In addition, the extra HCl molecules would dissociate into  $H_3O^+$  and  $Cl^-$  ions. This could be represented by the following:



### Conceptual Problem 17.17

Which of the following beakers best represents a container of a weak acid, HA, in water?  
(Water molecules have been omitted for clarity.)

**Solution**

A solution of the weak acid, HA, will contain hydronium ions ( $\text{H}_3\text{O}^+$ ) and anions ( $\text{A}^-$ ) in equal amounts as well as some undissociated acid (HA) molecules. This is represented by the solution in container A, which contains six HA molecules, two  $\text{H}_3\text{O}^+$  and two  $\text{A}^-$  ions. The solution in container B contains eight HA molecules and represents an undissociated acid. In container C, all of the HA molecules have dissociated, so this represents a strong acid.

**Conceptual Problem 17.18**

You have 0.10-mol samples of three acids identified simply as HX, HY, and HZ. For each acid, you make up a 0.10 M solution by adding sufficient water to each of the acid samples. When you measure the pH of these samples, you find that the pH of HX is greater than the pH of HY, which in turn is greater than the pH of HZ.

- Which of the acids is the least ionized in its solution?
- Which acid has the largest  $K_a$ ?

**Solution**

- The greater the pH of the solution, the less  $\text{H}_3\text{O}^+$  present in solution. When comparing the three acid solutions of equal concentration, the HX produced the least amount of  $\text{H}_3\text{O}^+$  in solution (highest pH); therefore, it must be the least ionized.
- When comparing the three acids, HZ was the most ionized in solution (lowest pH) producing the greatest concentration of  $\text{H}_3\text{O}^+$ . Therefore, HZ must be the strongest acid with the largest  $K_a$ .

### Conceptual Problem 17.19

What reaction occurs when each of the following is dissolved in water?

- HF
- NaF
- $\text{C}_6\text{H}_5\text{NH}_2$
- $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$

#### Solution

- When HF is dissolved in water, the  $\text{F}^-$  hydrolyzes. The reaction is  
$$\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq).$$
- When NaF is dissolved in water,  $\text{F}^-$  hydrolyzes. The reaction is  
$$\text{F}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HF}(aq) + \text{OH}^-(aq).$$
- When  $\text{C}_6\text{H}_5\text{NH}_2$  is dissolved in water, the following reaction occurs:  
$$\text{C}_6\text{H}_5\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(aq) + \text{OH}^-(aq).$$
- When  $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$  is dissolved in water,  $\text{C}_6\text{H}_5\text{NH}_3^+$  hydrolyzes. The reaction is  
$$\text{C}_6\text{H}_5\text{NH}_3^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_2(aq) + \text{OH}^-(aq).$$

### Conceptual Problem 17.20

You have the following solutions, all of the same molar concentrations: KBr, HBr,  $\text{CH}_3\text{NH}_2$ , and  $\text{NH}_4\text{Cl}$ . Rank them from the lowest to the highest hydroxide-ion concentrations.

#### Solution

The KBr solution is made from a neutral salt. Thus, it should have a pH of 7.0. The HBr solution is a strong acid, with  $\text{pH} < 7.0$ . The  $\text{CH}_3\text{NH}_2$  solution is a weak base, with  $\text{pH} > 7.0$ . The  $\text{NH}_4\text{Cl}$  solution is made from a salt with a weak acid cation,  $\text{NH}_4^+$ , with  $\text{pH} < 7.0$ . Therefore, the ranking from lowest to highest hydroxide concentrations is:  $\text{HBr} < \text{NH}_4\text{Cl} < \text{KBr} < \text{CH}_3\text{NH}_2$ .

### Conceptual Problem 17.21

Rantidine is a nitrogen base that is used to control stomach acidity by suppressing the stomach's production of hydrochloric acid. The compound is present in Zantac<sup>®</sup> as the chloride salt (rantidinium chloride; also called rantidine hydrochloride). Do you expect a solution of rantidine hydrochloride to be acidic, basic, or neutral? Explain by means of a general chemical equation.

**Solution**

A solution of rantidine hydrochloride should be acidic. Let Ran represent rantidine. Then RanHCl is the chloride salt, rantidinium chloride. The cation rantidinium, RanH<sup>+</sup>, should hydrolyze according to the following equation.

**Conceptual Problem 17.22**

A chemist prepares dilute solutions of equal molar concentrations of NH<sub>3</sub>, NH<sub>4</sub>Br, NaF, and NaCl. Rank these solutions from highest to lowest pH.

**Solution**

NH<sub>3</sub> is a weak base; therefore, the solution would have pH > 7. The NH<sub>4</sub>Br solution is made from a salt with a weak acid cation, NH<sub>4</sub><sup>+</sup>, with pH < 7.0. The NaF solution is made from a salt with a basic anion, F<sup>-</sup>, with a pH > 7. The NaCl solution is made from a neutral salt; therefore, it should have a pH = 7. In order to rank the relative strengths of the F<sup>-</sup> and NH<sub>3</sub>, you should estimate *K<sub>b</sub>* for each. Using data from Appendices E and F of your text, *K<sub>b</sub>* for NH<sub>3</sub> is about 10<sup>-5</sup> and about 10<sup>-10</sup> for F<sup>-</sup>, which indicates NH<sub>3</sub> is a stronger base than F<sup>-</sup>. Therefore, the ranking from highest to lowest pH is: NH<sub>3</sub> > F<sup>-</sup> > NaCl > NH<sub>4</sub>Br.

**Conceptual Problem 17.23**

You want to prepare a buffer solution that has a pH equal to the p*K<sub>a</sub>* of the acid component of the buffer. If you have 100 mL of a 0.10 *M* solution of the acid HA, what volume and concentration of NaA solution could you use in order to prepare the buffer?

**Solution**

To prepare a buffer solution that has a pH equal to the p*K<sub>a</sub>* of the acid, you need equal amounts of acid and conjugate base in the solution. The easiest way to make the buffer is to mix equal volumes of equal molar solutions of HA and NaA. Thus, mix 100 mL of 0.10 *M* NaA with the 100 mL of 0.10 *M* HA to prepare the buffer.

**Conceptual Problem 17.24**

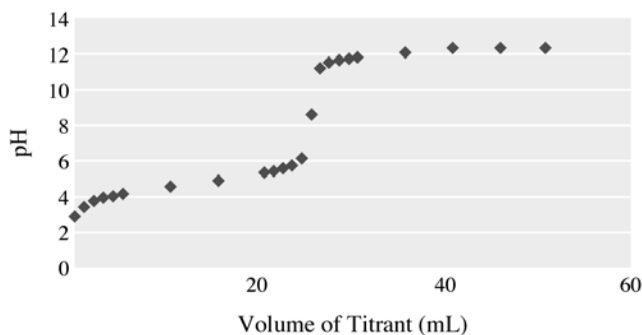
A friend of yours has performed three titrations: strong acid with a strong base, weak acid with a strong base, and a weak base with a strong acid. He hands you the three titration curves, saying he has forgotten which is which. What attributes of the curves would you look at to correctly identify each curve?

### Solution

Of the three titrations, the weak base-strong acid titration is easiest to identify. The attributes to look for are a high pH at the start, and a gradual decrease in pH as the titration proceeds. The other two titrations both start with low pH and increase in pH as the titration proceeds. Of the two, the strong acid-strong base titration should show a more rapid increase in pH before the endpoint is reached, and a well-defined, sharp equivalence point at pH 7. The weak acid-strong base titration will show a more gradual change in pH before the equivalence point, which should be less sharply defined, and occur at a pH above 7.

### Conceptual Problem 17.25

You are given the following acid-base titration data, where each point on the graph represents the pH after adding a given volume of titrant (substance being added during the titration).



- What substance is being titrated, a strong acid, strong base, weak acid, or weak base?
- What is the pH at the equivalence point of the titration?
- What indicator might you use to perform this titration? Explain.

### Solution

There are several features of the curve that indicate the type of titration that is being performed.

- First, since the pH of the solution is less than 7 at the beginning of the titration, you can conclude that an acid is being titrated with a base.
- The pH of the equivalence point is about 8.5. Therefore, the acid that is being titrated is a weak acid.

- c. You need to pick an indicator that changes color in the pH range of about 7-10. Therefore, Thymol blue or phenolphthalein would work fine for this titration.