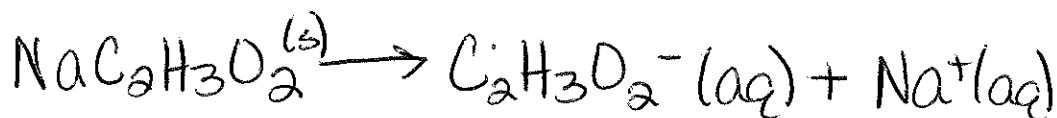


# Common Ion Effect

- If the solution contains two dissolved solutes that contain the same ion, the common ion will suppress the ionization of a weak acid or weak base

ex.  $\text{NaC}_2\text{H}_3\text{O}_2$  and  $\text{HC}_2\text{H}_3\text{O}_2$  in soln.



\* Completely dissociates since it's a strong electrolyte



\* Incompletely dissociates since it's a weak acid

\* Le Chatelier's principle - adding the sodium acetate increases the acetate ions, pushing the system more left and decreasing  $[\text{H}^+]$  ∴ pH increases

Henderson Hasselbalch Equation:  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

$$\text{pH} = \underset{\substack{\uparrow \\ -\log K_a}}{\text{p}K_a} + \log \frac{[\text{A}^-] \leftarrow \text{conjugate base}}{[\text{HA}] \leftarrow \text{acid}}$$

- For a solution containing a weak base adding a common ion makes the solution less base ∴ pH decreases

## Common Ion Effect Example

ex. Find pH of a soln. containing 0.20M

Two  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.30M  $\text{NaC}_2\text{H}_3\text{O}_2$ .

Two ways to solve:

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$1.8 \times 10^{-5} = \frac{[\text{H}^+][.30]}{[.20]}$$

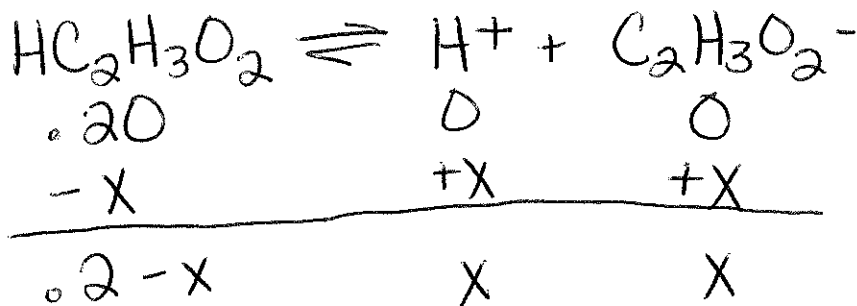
$$[\text{H}^+] = 1.2 \times 10^{-5} \text{M}$$

$$\text{pH} = -\log 1.2 \times 10^{-5} \text{M} = 4.92$$

$$\text{pH} = -\log[1.8 \times 10^{-5}] + \log\left[\frac{.3 \text{M}}{.2 \text{M}}\right] = 4.92$$

or  
use  
Henderson  
Hasselbach

Follow up: What is the pH of the 0.20M acetic acid solution if no salt were present?



$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x^2}{.2 - x} = 1.8 \times 10^{-5}$$

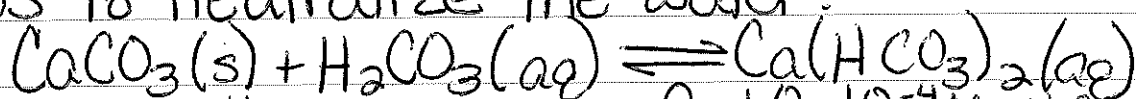
$$x = .0019 = [\text{H}^+]$$

$$\text{pH} = -\log .0019 = 2.72$$

so pH increased with adding the ion

Common ion effect - the rxn that produces an ion is suppressed when another source of the ion is added to the system

Calcium carbonate from river sediments helps to neutralize the water:



How does the addition of  $1.0 \times 10^{-4} \text{ M HCO}_3^-$  salts affect the pH, assuming that the water also contains  $1.3 \times 10^{-5} \text{ M H}_2\text{CO}_3$ ?



$$K_a = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$$

$$4.3 \times 10^{-7} = \frac{[1.0 \times 10^{-4}][\text{H}^+]}{[1.3 \times 10^{-5}]}$$

$$[\text{H}^+] = 5.6 \times 10^{-8} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(5.6 \times 10^{-8} \text{ M}) = \boxed{7.25}$$

\*Note pH of  $1.3 \times 10^{-5} \text{ M H}_2\text{CO}_3$  is 5.63, so nearly a 100x decrease in pH! Adding  $\text{HCO}_3^-$  pushes rxn. left.

or Henderson Hasselbach:

$$\text{pH} = \text{p}K_a + \frac{\log[X^-]}{[HX]}$$

$$\text{pH} = -\log(4.3 \times 10^{-7}) + \log \frac{1.0 \times 10^{-4}}{1.3 \times 10^{-5}} = \boxed{7.26}$$

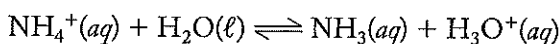
## Common Ion Effect: Weak Base/Acid

ex Find pH of a solution that is 0.200M  $\text{NH}_3$  and 0.300M  $\text{NH}_4\text{Cl}$ . ( $\text{p}K_b = 4.75$ )

$$\text{p}K_a = 14 - 4.75 = 9.25$$
$$\text{pH} = 9.25 + \log \left[ \frac{0.200}{0.300} \right] = 9.07$$

bonds of the other halogens are all weaker than the O—H bonds in  $\text{H}_2\text{O}$ , which helps explain why the other halide ions do not react with water. Solutions of  $\text{NaF}$  are weakly basic.

If salts that contain the conjugate bases of weak acids are basic, then it is logical that salts that contain the conjugate acids of weak bases are acidic. An example of such a salt is  $\text{NH}_4\text{Cl}$ . We have seen that the  $\text{Cl}^-$  ions that are produced when  $\text{NH}_4\text{Cl}$  dissolves have negligible strength as Brønsted–Lowry bases. However,  $\text{NH}_4^+$  ions are the conjugate acid of a weak base,  $\text{NH}_3$ . Therefore,  $\text{NH}_4^+$  ions should be weakly acidic, producing at least some  $\text{H}_3\text{O}^+$  ions:



As with the hydrolysis of fluoride ions, differences in bond energies also drive this reaction: the O—H bonds in the  $\text{H}_3\text{O}^+$  ions that are formed are stronger than the N—H bonds in  $\text{NH}_4^+$  ions that must be broken. Consequently, solutions of  $\text{NH}_4\text{Cl}$  are weakly acidic.

Table 15.7 summarizes how salts can be acidic, basic, or neutral depending on whether they include cations that are the conjugate acids of weak bases, or anions that are the conjugate bases of weak acids, or both. Note that salts that contain both the conjugate base of a weak acid *and* the conjugate acid of a weak base may be acidic, basic, or neutral, depending on the relative strengths of the acid and base. Ammonium acetate represents the rare example of a salt in which the strengths of the acid (acetic acid) and the base (ammonia) happen to be *exactly the same* [ $K_a$  (acetic acid) =  $K_b$  (ammonia) =  $1.8 \times 10^{-5}$ ]. As a result, ammonium acetate is a neutral salt.

**TABLE 15.7 Acid–Base Properties of Some Common Salts**

Anion Is Derived from a	Cation Is Derived from a	pH of Aqueous Solutions	Example
Strong acid	Strong base	7	$\text{NaCl}$
Strong acid	Weak base	$\leq 7$	$\text{NH}_4\text{Cl}$
Weak acid	Strong base	$\geq 7$	$\text{NaF}$
Weak acid	Weak base	Depends on relative values of $\text{p}K_a$ and $\text{p}K_b$	$\text{p}K_a > \text{p}K_b$ , acidic; $\text{NH}_4\text{F}$ $\text{p}K_b > \text{p}K_a$ , basic; $\text{NH}_4\text{HCO}_3$ $\text{p}K_a = \text{p}K_b$ , neutral; $\text{NH}_4\text{CH}_3\text{COO}$

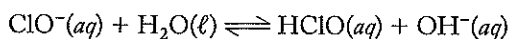
**SAMPLE EXERCISE 15.7 Distinguishing Acidic, Basic, and Neutral Salts**

105

Is an aqueous solution of  $\text{NaClO}$  acidic, basic, or neutral?

**COLLECT AND ORGANIZE** We are asked whether a solution of  $\text{NaClO}$  is acidic, basic, or neutral. When this salt dissolves in water, it dissociates into  $\text{Na}^+$  ions and  $\text{ClO}^-$  ions.

**ANALYZE** Sodium ions do not hydrolyze and hence do not produce acidic solutions in water. However,  $\text{ClO}^-$  ions are the conjugate base of  $\text{HClO}$ , which is a weak acid (Table 15.2). Therefore,  $\text{ClO}^-$  ions should partially hydrolyze in water, forming  $\text{OH}^-$  ions:



basic

**SOLVE B**  
weakly bas

**THINK AE**  
a weak aci

**Practice E**  
why an aq

Having e  
a strategy fo  
is much like  
of weak acid  
 $\text{Na}_2\text{CO}_3$ . W  
as well as bic  
conjugate ac  
second ioniz

$\text{HCO}_3^-(\text{aq})$

Carbona  
the carbonat

None of the  
tion in Equa  
constant exp

We have lat  
reactions th:  
the first reac

We give the

To calculate  
constant exp

Now compa  
carbonic aci

$K_b$

Solving for  $x$ ,

$$K_{b_1} = 2.1 \times 10^{-4} = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]} = \frac{(x)(x)}{(0.100 - x)}$$

$$x = 4.5 \times 10^{-3} \text{ M} = [\text{OH}^-]$$

The calculated  $[\text{OH}^-]$  is much greater than  $[\text{OH}^-]$  in pure water ( $1.0 \times 10^{-7} \text{ M}$ ), so the assumption that water autoionization is unimportant in this calculation is valid. To calculate pH from  $[\text{OH}^-]$ , we first calculate pOH:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(4.5 \times 10^{-3}) = 2.35$$

and then use Equation 15.13 to calculate pH:

$$\text{pH} = \text{p}K_w - \text{pOH} = 14.00 - 2.35 = 11.65$$

A pH of 11.65 is quite basic. If you swam in a pool of water at that pH, you would experience skin irritation and painful burning in your eyes. Sodium carbonate is often used to adjust the pH of pools, but to make sure just the right amount is used, the pH of the water is tested to ensure that the pool is not too basic. We will see how this is done later in this chapter.

**SAMPLE EXERCISE 15.B Calculating the pH of a Solution of an Acidic Salt**

**LO4**

What is the pH of a 0.25 M solution of  $\text{NH}_4\text{Cl}$ ?

**COLLECT AND ORGANIZE** We are asked to calculate the pH of a solution of  $\text{NH}_4\text{Cl}$ . When  $\text{NH}_4\text{Cl}$  dissolves in water,  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions are released into solution. The  $\text{NH}_4^+$  ion is the conjugate acid of  $\text{NH}_3$ ; the  $\text{Cl}^-$  ion is the conjugate base of  $\text{HCl}$ .

**ANALYZE** We have seen that the  $\text{Cl}^-$  ion has negligible strength as a Brønsted-Lowry base, so it does not contribute to the acid-base properties of  $\text{NH}_4\text{Cl}$ . Ammonia is a weak base, which means that its conjugate acid,  $\text{NH}_4^+$ , is a weak acid. Therefore some of the ammonium ions in solution donate  $\text{H}^+$  ions to molecules of water:



The  $K_a$  value of  $\text{NH}_4^+$  is not given in the problem and is not listed in Appendix 5. However, the  $K_b$  value of its conjugate base,  $\text{NH}_3$ , is in Appendix 5 (Table A5.3):  $1.8 \times 10^{-5}$ . The value of  $K_a$  can be calculated from  $K_b$  using Equation 15.21.

The  $K_b$  value of ammonia is close to  $10^{-5}$ . The product of  $K_a \times K_b$  of a conjugate acid-base pair is  $10^{-14}$ ; therefore, the  $K_a$  value of the ammonium ion will be close to  $10^{-9}$ . Because the ammonium ion is a very weak acid, we can anticipate a pH value that is less than 7 but probably closer to 7 than to 0.

**SOLVE** The simplified  $K_a$  expression for the  $\text{NH}_4^+$  ion is

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

Rearranging Equation 15.21 to solve for  $K_a$ :

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^]}$$

We set up a RICE table in which we make the usual assumptions that the reaction is the only significant source of  $\text{H}^+$  and that  $x = [\text{H}^+] = [\text{NH}_3]$  at equilibrium:

Reaction	$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$		
	$[\text{NH}_4^+]$ (M)	$[\text{NH}_3]$ (M)	$[\text{H}^+]$ (M)
Initial	0.25	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.25 - x$	$x$	$x$

$$K_a = 5.56 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = \frac{(x)(x)}{0.25 - (x)}$$

Given the very small value of  $K_a$ , we can make the simplifying assumption that  $0.25 \text{ M} - x \approx 0.25 \text{ M}$ , which gives us


$$\frac{x^2}{0.25} = 5.56 \times 10^{-10}$$

$$x^2 = 1.39 \times 10^{-10}$$

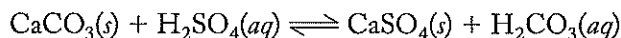
$$x = 1.18 \times 10^{-5} = [\text{H}^+]$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.18 \times 10^{-5}) = 4.93$$

**THINK ABOUT IT** This result matches our prediction: the pH of the solution is less than 7, but closer to 7 than to 0. The calculated  $[\text{H}^+]$  is less than 5% of the initial concentration of  $\text{NH}_4^+$ , so our simplifying assumption was valid.

**Practice Exercise** What is the pH of a 0.25 M solution of sodium acetate? (*Hint:* The acetate ion is the conjugate base of acetic acid.) 


The reactions of carbonate minerals in soils and rocks with acidic groundwater are critically important in mitigating the effects of acidic precipitation. When, for example, rain containing dilute sulfuric acid soaks into soil containing  $\text{CaCO}_3$  in the form of limestone, marble, or shellfish shells, the acid is converted either into environmentally more benign carbonic acid,



or, if enough  $\text{CaCO}_3$  is available, into calcium sulfate and soluble calcium bicarbonate:



As long as carbonates and other basic substances are present in soils and in the sediments of rivers and lakes, nature has the capacity to neutralize the acid in acid rain and maintain pH in a range that supports aquatic life. Unfortunately these minerals are scarce in the soils and sediments of some watersheds, and severe acidification and loss of aquatic life has occurred as a result.

 **CONNECTION** The reaction of acidic groundwater with calcium carbonate and its connection to the formation of limestone caves are described in Chapter 8.

## 15.7 The Common-Ion Effect

Thus far in this chapter we have worked with reactions consisting of a single acidic or basic reactant. Natural systems are often more complicated than that: they typically have multiple reactants that can influence pH or resist a pH change. Suppose, for example, that a sample of river water contains  $1.3 \times 10^{-5} \text{ M H}_2\text{CO}_3$  as a result of atmospheric carbon dioxide dissolving in the water. Suppose also