6.1: Mixtures of Acids

In the previous chapter, we discussed solutions that contained only one acid or one base. In many cases, our solutions will contain a mixture of acids or bases. The equilibrium of each of the components of a system will affect the others if there are **common ions** between the equilibria. Here we discuss why common ions are important to consider for equilibrium systems, and then present strategies to determine the pH of a solution with a mixture of acids or bases.

Common Ion Effect

Consider a solution that contains both hydrochloric acid and acetic acid. Because hydrochloric acid is considered a strong acid, we expect that it will ionize completely to form hydronium ions and chloride ions.

$$\mathrm{HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-} \tag{6.1.1}$$

Acetic acid is considered a weak acid and so will only partially ionize, as shown here.

$$\mathrm{HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-} \tag{6.1.2}$$

The extent of ionization will depend on the Ka for acetic acid, 1.8 x 10^{-5}, and on the concentrations of the reactant and product species. According to Le Chatelier's principle, if we increase $\mathrm{[HC_2H_3O_2]}$, the equilibrium will shift to the right, increasing $\mathrm{[H_3O^+]}$ and decreasing the pH. If we increase the concentration of either product, the equilibrium will shift to the left and more $\mathrm{H_2C_3O_2}$ will exist in solution at equilibrium.

When multiple acids are present in a solution, the hydronium resulting from each ionization may affect other ionizations. This is termed the **common ion effect**.

Mixtures of Acids

When a solution contains a mixture of acids, the pH of the solution will be dominated by the stronger acid. Let's consider again the solution containing both HCl and $\mathrm{[HC_2H_3O_2]}$. If each of these acids were present at a concentration of 0.10 M, how could we determine the pH of the solution? We know that the HCl is a much stronger acid and so it will contribute the vast majority of hydronium ions to the solution. In this case, because HCl is strong, we expect $\mathrm{[H_3O^+]}$ from the HCl to be equal to its concentration, 0.10 M. To find the amount of hydronium contributed by the acetic acid, we can use an ICE table. However, unlike in the previous chapter, in this scenario the initial concentration of the hydronium, $\mathrm{[H_3O^+]_0}$, is 0.10 M - or the amount resulting from ionization of the HCl.

	$\mathrm{HC_2H_3O_2(aq) +}$	$\mathrm{H_2O(l) \rightleftharpoons}$	$\mathrm{H_3O^+(aq) +}$	$\mathrm{C_2H_3O_2-(aq)}$
Initial	0.10 M	excess	0.10 M	0
Change	-x	-x	+x	+x
Equilibrium	(0.10 - x)	excess	(0.10 + x)	x

Solving for x in the ICE table:

$$K_a = \frac{\mathrm{[H_3O^+][C_2H_3O_2-]}}{\mathrm{[HC_2H_3O_2]}} = 1.8 \times 10^{-5} \tag{6.1.3}$$

$$K_a = \frac{\mathrm{(0 \cdot 10 + x)(x)}}{\mathrm{(0 \cdot 10 - x)}} = 1.8 \times 10^{-5} \tag{6.1.4}$$

$$x = 1.8 \times 10^{-5} \tag{6.1.5}$$

$$\mathrm{[H_3O^+]} = (0.10 + x) \approx 0.10M \tag{6.1.6}$$

In this case, the acetic acid contributed such a small amount of hydronium to the solution that it did not contribute significantly to the overall concentration (i.e. 0.10 M). This behavior is often seen in mixtures of acids. When two acids are mixed, if one acid is much stronger than the other (e.g. the K_a values differ by at least 1000-fold), the weaker acid does not contribute significantly to the equilibrium $\mathrm{[H_3O^+]}$ and can be ignored.

Example 6.1.1 pH for a solution with HF and HBrO

What is the pH of a solution that contains $0.120\ M$ HF and $0.250\ M$ HBrO?

Solution

First we must determine which acid will contribute more protons to the solution by comparing the K_a values.

$K_a\ for\ \mathrm{HF} = 3.5 \times 10^{-4}$

$K_a\ for\ \mathrm{HBrO} = 2.8 \times 10^{-9}$

Because **HF** is much stronger, its hydronium contribution will dominate the pH. Because the Ka values differ by more than 1000-fold we can ignore the contribution from HBrO.

	$\mathrm{HF(aq)} +$	$\mathrm{H_2O(l)} \rightleftharpoons$	$\mathrm{H_3O^+(aq)} +$	$\mathrm{F^-(aq)}$
Initial	0.120 M	excess	~ 0	0
Change	-x	-x	+x	+x
Equilibrium	(0.120 - x)	excess	x	x

Solving for x,

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{F^-}]}{[\mathrm{HF}]} = 3.5 \times 10^{-4} \tag{6.1.7}$$

$$K_a = \frac{(\mathrm{x})(\mathrm{x})}{(0 \cdot 120 - \mathrm{x})} = 3.5 \times 10^{-4} \tag{6.1.8}$$

$$x = [\mathrm{H_3O^+}] = 6.5 \times 10^{-3} \tag{6.1.9}$$

$$pH = -log([\mathrm{H_3O^+}]) = -log(6.5 \times 10^{-3}) = 2.19 \tag{6.1.10}$$

Exercise 6.1.1

What is the pH of a mixture of 0.25 M HCN and 0.025 M HNO_3?

Answer

In this mixture, the HNO_3 is the stronger acid. It is one of the strong acids so it ionizes completely, resulting in $[\mathrm{H_3O^+}] = 0.025\ M$. The HCN is much weaker with a K_a value of 4.9×10^{-10}. Its contribution to the pH can be ignored.

$$pH = -log[\mathrm{H_3O^+}] = -log(0.025) \tag{6.1.11}$$

$$pH = 1.60 \tag{6.1.12}$$

Mixtures of Bases

Similar to acids, when a solution contains a mixture of bases, the pH will be dominated by the stronger base.

Exercise 6.1.2

You titrate a solution of HF with NaOH. The final concentration NaOH is 0.014 M and the final concentration of $\mathrm{F^-}$ is 0.125 M. What is the pH of the solution?

Answer

In this mixture, the NaOH is the stronger base. The $\mathrm{F^-}$ is much weaker with a K_b value of 2.9×10^{-11}. Its contribution to the pH can be ignored.

$$[\mathrm{OH^-}] = 0.014\ M \tag{6.1.13}$$

$$pOH = -log[\mathrm{OH^-}] = -log(0.014) = 1.85 \tag{6.1.14}$$

$$pH = 14.00 - 1.85 = 12.15 \tag{6.1.15}$$

Summary

When a solution contains a mixture of acids or bases, the strongest acid or base will contribute the most to the equilibrium \(\ce{[H3O^+]}. If the Ka (or Kb) values of multiple acids (or bases) differ by more than 1000-fold, the contribution of the weaker component can be ignored.
