

ACIDS AND BASES 4

EXAMPLE 18-12 pK_a Values

The K_a values for acetic acid and hydrofluoric acid are 1.8×10^{-5} and 7.2×10^{-4} , respectively. What are their pK_a values?

Plan

pK_a is defined as the negative logarithm of K_a (i.e., $pK_a = -\log K_a$) so we take the negative logarithm of each K_a .

Solution

For CH_3COOH ,

$$pK_a = -\log K_a = -\log (1.8 \times 10^{-5}) = -(-4.74) = 4.74$$

For HF,

$$pK_a = -\log K_a = -\log (7.2 \times 10^{-4}) = -(-3.14) = 3.14$$

TABLE 18-5 Comparison of Extents of Ionization of Some Acids

Acid Solution	Ionization Constant	$[\text{H}_3\text{O}^+]$	pH	Percent Ionization
0.10 M HCl	very large	0.10 M	1.00	≈ 100
0.10 M CH_3COOH	1.8×10^{-5}	0.0013 M	2.89	1.3
0.10 M HOCl	3.5×10^{-8}	0.000059 M	4.23	0.059

From Example 18-12, we see that the stronger acid (HF in this case) has the larger K_a value and the smaller $\text{p}K_a$ value. Conversely, the weaker acid (CH_3COOH in this case) has the smaller K_a value and the larger $\text{p}K_a$ value. The generalization is

The larger the value of K_a , the smaller is the value of $\text{p}K_a$, and the stronger is the acid.

EXAMPLE 18-13 *Acid Strengths and K_a Values*

Given the following list of weak acids and their K_a values, arrange the acids in order of (a) increasing acid strength and (b) increasing $\text{p}K_a$ values.

Acid	K_a
HOCl	3.5×10^{-8}
HCN	4.0×10^{-10}
HNO_2	4.5×10^{-4}

Plan

(a) We see that HNO_2 is the strongest acid in this group because it has the largest K_a value. HCN is the weakest because it has the smallest K_a value.

(b) We do not need to calculate $\text{p}K_a$ values to answer the question. We recall that the weakest acid has the largest $\text{p}K_a$ value and the strongest acid has the smallest $\text{p}K_a$ value, so the order of increasing $\text{p}K_a$ values is just the reverse of the order in part (a).

Solution

- (a) Increasing acid strength: $\text{HCN} < \text{HOCl} < \text{HNO}_2$
(b) Increasing $\text{p}K_a$ values: $\text{HNO}_2 < \text{HOCl} < \text{HCN}$

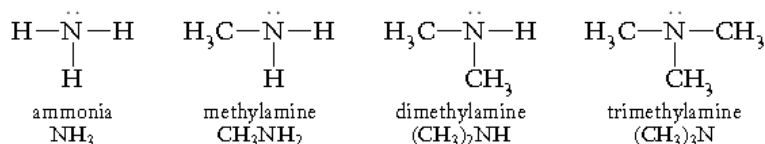
You may know that hydrofluoric acid dissolves glass. But HF is *not* a strong acid. The reaction of glass with hydrofluoric acid occurs because silicates react with HF to produce silicon tetrafluoride, SiF_4 , a very volatile compound. This reaction tells us nothing about the acid strength of hydrofluoric acid.

Thus far we have focused our attention on acids. Very few common weak bases are soluble in water. Aqueous ammonia is the most frequently encountered example

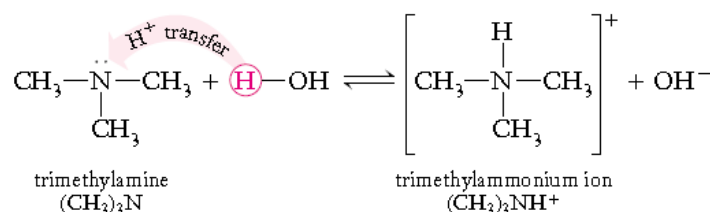
there is one unshared pair of electrons on the nitrogen atom in NH_3 . When ammonia dissolves in water, it accepts H^+ from a water molecule in a reversible reaction. We say that NH_3 ionizes slightly when it undergoes this reaction. Aqueous solutions of NH_3 are basic because OH^- ions are produced.



Amines are derivatives of NH_3 in which one or more H atoms have been replaced by organic groups, as the following structures indicate.



Thousands of amines are known, and many are very important in biochemical processes. Low-molecular-weight amines are soluble weak bases. The ionization of trimethylamine, for example, forms trimethylammonium ions and OH^- ions.



Now let us consider the behavior of ammonia in aqueous solutions. The reaction of ammonia with water and its ionization constant expression are



and

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

The fact that K_b for aqueous NH_3 has the same value as K_a for CH_3COOH is pure coincidence. It does tell us that in aqueous solutions of the same concentration, CH_3COOH and NH_3 are ionized to the same extent. Table 18-6 lists K_b and $\text{p}K_b$ values for a few common weak bases.

We use K_b 's for weak bases in the same way we used K_a 's for weak acids and $\text{p}K_b$ values for weak bases in the same way we used $\text{p}K_a$ values for weak acids.

EXAMPLE 18-14 pH of a Weak Base Solution

Calculate the $[\text{OH}^-]$, pH, and percent ionization for a 0.20 M aqueous NH_3 solution.

Plan

Write the equation for the ionization of aqueous NH_3 and represent the equilibrium concentrations algebraically. Then, substitute into the K_b expression and solve for $[\text{OH}^-]$ and $[\text{NH}_3]_{\text{ionized}}$.

TABLE 18-6 Ionization Constants and pK_b Values for Some Weak Bases

Base	Ionization Reaction	K_b at 25°C	pK_b
ammonia	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	1.8×10^{-5}	4.74
methylamine	$(\text{CH}_3)\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)\text{NH}_3^+ + \text{OH}^-$	5.0×10^{-4}	3.30
dimethylamine	$(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$	7.4×10^{-4}	3.13
trimethylamine	$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$	7.4×10^{-5}	4.13
pyridine	$\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+ + \text{OH}^-$	1.5×10^{-9}	8.82
aniline	$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	4.2×10^{-10}	9.38

Solution

The equation for the ionization of aqueous ammonia and the algebraic representations of equilibrium concentrations follow. Let $x = [\text{NH}_3]_{\text{ionized}}$.

	NH_3	+ H_2O	\rightleftharpoons	NH_4^+	+ OH^-
initial	0.20 M			0 M	$\approx 0\text{ M}$
change due to rxn	$-x\text{ M}$			$+x\text{ M}$	$+x\text{ M}$
at equil	$(0.20 - x)\text{ M}$			$x\text{ M}$	$x\text{ M}$

Substitution into the ionization constant expression gives

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.20 - x)}$$

Again, we can simplify this equation. The small value of K_b tells us that the base is only slightly ionized, so we can assume that $x \ll 0.20$, or $(0.20 - x) \approx 0.20$, and we have

$$\frac{x^2}{0.20} = 1.8 \times 10^{-5} \quad x^2 = 3.6 \times 10^{-6} \quad x = 1.9 \times 10^{-3} M$$

Then $[\text{OH}^-] = x = 1.9 \times 10^{-3} M$, $\text{pOH} = 2.72$, and $\text{pH} = 11.28$.

$[\text{NH}_3]_{\text{ionized}} = x$, so the percent ionization may be calculated.

$$\% \text{ ionization} = \frac{[\text{NH}_3]_{\text{ionized}}}{[\text{NH}_3]_{\text{initial}}} \times 100\% = \frac{1.9 \times 10^{-3}}{0.20} \times 100\% = 0.95\% \text{ ionized}$$

EXAMPLE 18-15 Household Ammonia

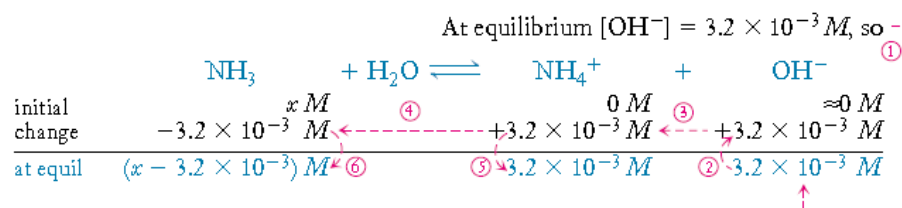
The pH of a household ammonia solution is 11.50. What is its molarity?

Plan

We are given the pH of an aqueous NH_3 solution. Use $\text{pH} + \text{pOH} = 14.00$ to find pOH, which we can convert to $[\text{OH}^-]$. Then, complete the ionization reaction summary, and substitute the representations of equilibrium concentrations into the K_b expression.

Solution

At equilibrium $\text{pH} = 11.50$; we know that $\text{pOH} = 2.50$, so $[\text{OH}^-] = 10^{-2.50} = 3.2 \times 10^{-3} M$. This $[\text{OH}^-]$ results from the reaction, so we can write the change line. Then, letting x represent the *initial* concentration of NH_3 , we can complete the reaction summary.



Substituting these values into the K_b expression for aqueous NH_3 gives

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(3.2 \times 10^{-3})(3.2 \times 10^{-3})}{(x - 3.2 \times 10^{-3})} = 1.8 \times 10^{-5}$$

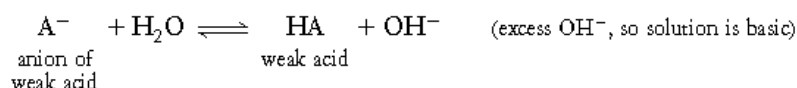
This suggests that $(x - 3.2 \times 10^{-3}) \approx x$. So we can approximate.

$$\frac{(3.2 \times 10^{-3})(3.2 \times 10^{-3})}{x} = 1.8 \times 10^{-5} \quad \text{and} \quad x = 0.57 M \text{ NH}_3$$

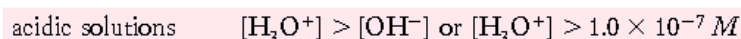
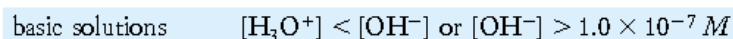
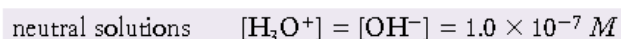
The solution is $0.57 M \text{ NH}_3$. Our assumption that $(x - 3.2 \times 10^{-3}) \approx x$ is justified.

18-6 SOLVOLYSIS

Solvolyis is the reaction of a substance with the solvent in which it is dissolved. The solvolysis reactions that we will consider in this chapter occur in aqueous solutions so they are called *hydrolysis* reactions. **Hydrolysis** is the reaction of a substance with water. Some hydrolysis reactions involve reaction with H_3O^+ or OH^- ions. One common kind of hydrolysis involves reaction of the anion of a *weak acid* with water to form *nonionized acid* molecules and OH^- ions. This upsets the $\text{H}_3\text{O}^+/\text{OH}^-$ balance in water and produces basic solutions. This reaction is usually represented as



Recall that in

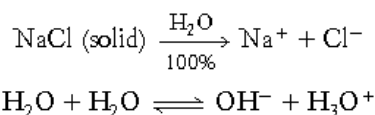


In Brønsted–Lowry terminology anions of strong acids are extremely weak bases, whereas anions of weak acids are stronger bases (Section 10-4). To refresh your memory, consider the following examples.

Nitric acid, a common strong acid, is essentially completely ionized in dilute aqueous solution. *Dilute* aqueous solutions of HNO_3 contain equal concentrations of H_3O^+ and NO_3^- ions. In dilute aqueous solution nitrate ions show almost no tendency to react with H_3O^+ ions to form nonionized HNO_3 ; thus, NO_3^- is a very weak base.

18-7 SALTS OF STRONG BASES AND STRONG ACIDS

We could also describe these as salts that contain the cation of a strong base and the anion of a strong acid. Salts derived from strong bases and strong acids give *neutral* solutions because neither the cation nor the anion reacts appreciably with H_2O . Consider an aqueous solution of NaCl , which is the salt of the strong base NaOH and the strong acid HCl . Sodium chloride is ionic even in the solid state. It dissociates into hydrated ions in H_2O . H_2O ionizes slightly to produce equal concentrations of H_3O^+ and OH^- ions.



We see that aqueous solutions of NaCl contain four ions, Na^+ , Cl^- , H_3O^+ and OH^- . The cation of the salt, Na^+ , is such a weak acid that it does not react appreciably with water. The anion of the salt, Cl^- , is such a weak base that it does not react appreciably with water. Solutions of salts of strong bases and strong acids are therefore *neutral* because neither ion of such a salt reacts to upset the $\text{H}_3\text{O}^+/\text{OH}^-$ balance in water.

EXAMPLE 18-18 K_b for the Anion of a Weak Acid

(a) Write the equation for the reaction of the base CN^- with water. (b) The value of the ionization constant for hydrocyanic acid, HCN , is 4.0×10^{-10} . What is the value of K_b for the cyanide ion, CN^- ?

Plan

(a) The base CN^- accepts H^+ from H_2O to form the weak acid HCN and OH^- ions. (b) We know that $K_a K_b = K_w$. So we solve for K_b and substitute into the equation.

Solution

(a) $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$

(b) We are given $K_a = 4.0 \times 10^{-10}$ for HCN , and we know that $K_w = 1.0 \times 10^{-14}$.

$$K_{b(\text{CN}^-)} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5}$$

EXAMPLE 18-19 Calculations Based on Hydrolysis

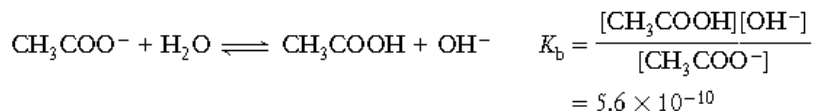
Calculate $[\text{OH}^-]$, pH, and the percent hydrolysis for 0.10 M solutions of (a) sodium acetate, NaCH_3COO , and (b) sodium cyanide, NaCN . Both NaCH_3COO and NaCN are soluble ionic salts that are completely dissociated in H_2O . From the text, K_b for $\text{CH}_3\text{COO}^- = 5.6 \times 10^{-10}$; from Example 18-18, K_b for $\text{CN}^- = 2.5 \times 10^{-5}$.

Plan

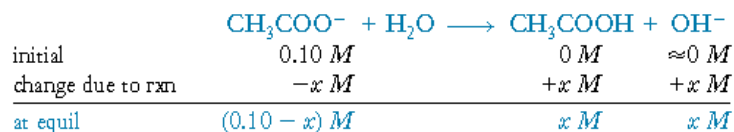
We recognize that both NaCH_3COO and NaCN are salts of strong bases and weak acids. The anions in such salts hydrolyze to give basic solutions. As we have done before, we first write the appropriate chemical equation and equilibrium constant expression. Then we complete the reaction summary, substitute the algebraic representations of equilibrium concentrations into the equilibrium constant expression, and solve for the unknown concentration(s).

Solution

(a) The overall equation for the reaction of CH_3COO^- with H_2O and its equilibrium constant expression are



Let $x = \text{mol/L}$ of CH_3COO^- that hydrolyzes. Then $x = [\text{CH}_3\text{COOH}] = [\text{OH}^-]$.



Because the value of K_b (5.6×10^{-10}) is quite small, we know that the reaction does not go very far. We can assume $x \ll 0.10$, so $(0.10 - x) \approx 0.10$; this lets us simplify the equation to

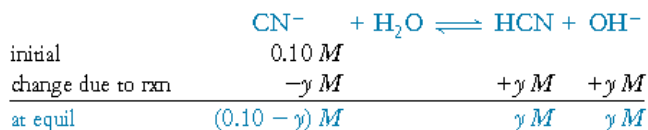
$$5.6 \times 10^{-10} = \frac{(x)(x)}{0.10} \quad \text{so} \quad x = 7.5 \times 10^{-6}$$

$$x = 7.5 \times 10^{-6}\text{ M} = [\text{OH}^-] \quad \text{pOH} = 5.12 \quad \text{and} \quad \text{pH} = 8.88$$

The 0.10 M NaCH_3COO solution is distinctly basic.

$$\begin{aligned} \% \text{ hydrolysis} &= \frac{[\text{CH}_3\text{COO}^-]_{\text{hydrolyzed}}}{[\text{CH}_3\text{COO}^-]_{\text{initial}}} \times 100\% = \frac{7.5 \times 10^{-6}\text{ M}}{0.10\text{ M}} \times 100\% \\ &= 0.0075\% \text{ hydrolysis} \end{aligned}$$

(b) Perform the same kind of calculation for 0.10 M NaCN . Let $y = \text{mol/L}$ of CN^- that hydrolyzes. Then $y = [\text{HCN}] = [\text{OH}^-]$.



$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = 2.5 \times 10^{-5}$$

Substitution into this expression gives

$$\frac{(y)(y)}{(0.10 - y)} = 2.5 \times 10^{-5} \quad \text{so} \quad y = 1.6 \times 10^{-3}\text{ M}$$

$$y = [\text{OH}^-] = 1.6 \times 10^{-3}\text{ M} \quad \text{pOH} = 2.80 \quad \text{and} \quad \text{pH} = 11.20$$

The 0.10 M NaCN solution is even more basic than the 0.10 M NaCH_3COO solution in part (a).

$$\begin{aligned} \% \text{ hydrolysis} &= \frac{[\text{CN}^-]_{\text{hydrolyzed}}}{[\text{CN}^-]_{\text{initial}}} \times 100\% = \frac{1.6 \times 10^{-3}\text{ M}}{0.10\text{ M}} \times 100\% \\ &= 1.6\% \text{ hydrolysis} \end{aligned}$$

EXAMPLE 18-20 *pH of a Soluble Salt*

Calculate the pH of a 0.20 M solution of ammonium nitrate, NH_4NO_3 . K_a for $\text{NH}_4^+ = 5.6 \times 10^{-10}$.

Plan

We recognize that NH_4NO_3 is the salt of a weak base, NH_3 , and a strong acid, HNO_3 , and that the cations of such salts hydrolyze to give acidic solutions. We proceed as we did in Example 18-19.

Solution

The cation of the weak base reacts with H_2O . Let $x = \text{mol/L}$ of NH_4^+ that hydrolyzes. Then $x = [\text{NH}_3] = [\text{H}_3\text{O}^+]$.

	NH_4^+	+ H_2O	\rightleftharpoons	NH_3	+ H_3O^+
initial	0.20 M			0 M	≈ 0 M
change due to rxn	$-x$ M			$+x$ M	$+x$ M
at equil	$(0.20 - x)$ M			x M	x M

Substituting into the K_a expression gives

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{(x)(x)}{(0.20 - x)} = 5.6 \times 10^{-10}$$

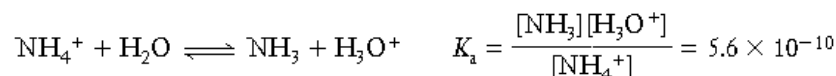
Making the usual simplifying assumption gives $x = 1.1 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$ and $\text{pH} = 4.96$. The 0.20 M NH_4NO_3 solution is distinctly acidic.

18-10 SALTS OF WEAK BASES AND WEAK ACIDS

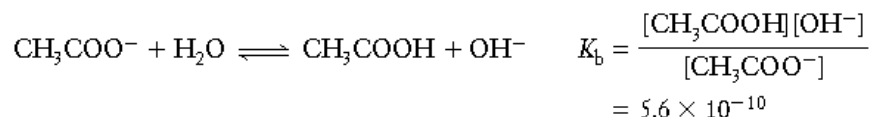
Salts of weak bases and weak acids are the fourth class of salts. Most are soluble. Salts of weak bases and weak acids contain cations that would give acidic solutions and anions that would give basic solutions. Will solutions of such salts be neutral, basic, or acidic? They may be any one of the three depending on the relative strengths of the weak molecular acid and weak molecular base from which each salt is derived. Thus, salts of this class may be divided into three types that depend on the relative strengths of their parent weak bases and weak acids.

Salts of Weak Bases and Weak Acids for Which $K_b = K_a$

The common example of a salt of this type is ammonium acetate, $\text{NH}_4\text{CH}_3\text{COO}$, the salt of aqueous NH_3 and CH_3COOH . The ionization constants for both aqueous NH_3 and CH_3COOH are 1.8×10^{-5} . We know that ammonium ions react with water to produce H_3O^+ .



We also recall that acetate ions react with water to produce OH^- .

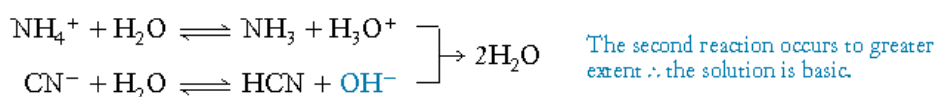


Because these K values are equal, the NH_4^+ produces just as many H_3O^+ ions as the CH_3COO^- produces OH^- ions. Thus, we predict that ammonium acetate solutions are neutral, and they are. There are very few salts that have cations and anions with equal K values.

Salts of Weak Bases and Weak Acids for Which $K_b > K_a$

Salts of weak bases and weak acids for which K_b is greater than K_a are always basic because the anion of the weaker acid hydrolyzes to a greater extent than the cation of the stronger base.

Consider NH_4CN , ammonium cyanide. K_a for HCN (4.0×10^{-10}) is much smaller than K_b for NH_3 (1.8×10^{-5}), so K_b for CN^- (2.5×10^{-5}) is much larger than K_a for NH_4^+ (5.6×10^{-10}). This tells us that the CN^- ions hydrolyze to a much greater extent than do NH_4^+ ions, and so ammonium cyanide solutions are distinctly basic. Stated differently, CN^- is much stronger as a base than NH_4^+ is as an acid.

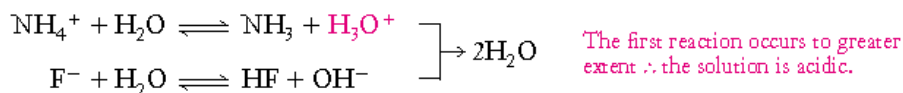


Salts of Weak Bases and Weak Acids for Which $K_b < K_a$

Salts of weak bases and weak acids for which K_b is less than K_a are acidic because the cation of the weaker base hydrolyzes to a greater extent than the anion of the stronger

acid. Consider ammonium fluoride, NH_4F , the salt of aqueous ammonia and hydrofluoric acid.

K_b for aqueous NH_3 is 1.8×10^{-5} and K_a for HF is 7.2×10^{-4} . So the K_a value for NH_4^+ (5.6×10^{-10}) is slightly larger than the K_b value for F^- (1.4×10^{-11}). This tells us that NH_4^+ ions hydrolyze to a slightly greater extent than F^- ions. In other words, NH_4^+ is slightly stronger as an acid than F^- is as a base. Ammonium fluoride solutions are slightly acidic.



[The notes are taken from General Chemistry by Whitten, Davis and Peck]