

## 1.3: Acid Strength and the Acid Dissociation Constant ( $K_a$ )

### Learning Objectives

- To know the relationship between acid or base strength and the magnitude of  $K_a$ ,  $K_b$ ,  $pK_a$ , and  $pK_b$ .
- To understand the leveling effect.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and  $A^-$  is its conjugate base, is as follows:



The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \quad (1.3.2)$$

As we noted earlier, because water is the solvent, it has an activity equal to 1, so the  $[H_2O]$  term in Equation 1.3.2 is actually the  $a_{H_2O}$ , which is equal to 1.

Again, for simplicity,  $H_3O^+$  can be written as  $H^+$  in Equation 1.3.3.



Keep in mind, though, that free  $H^+$  does not exist in aqueous solutions and that a proton is transferred to  $H_2O$  in all acid ionization reactions to form hydronium ions,  $H_3O^+$ . The larger the  $K_a$ , the stronger the acid and the higher the  $H^+$  concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of  $H^+$  or  $OH^-$ , thus making them unitless. The values of  $K_a$  for a number of common acids are given in Table 1.3.1.

Table 1.3.1: Values of  $K_a$ ,  $pK_a$ ,  $K_b$ , and  $pK_b$  for Selected Acids (HA and Their Conjugate Bases ( $A^-$ ))

| Acid               | HA            | $K_a$                 | $pK_a$ | $A^-$          | $K_b$                 | $pK_b$ |
|--------------------|---------------|-----------------------|--------|----------------|-----------------------|--------|
| hydroiodic acid    | HI            | $2 \times 10^9$       | -9.3   | $I^-$          | $5.5 \times 10^{-24}$ | 23.26  |
| sulfuric acid (1)* | $H_2SO_4$     | $1 \times 10^2$       | -2.0   | $HSO_4^-$      | $1 \times 10^{-16}$   | 16.0   |
| nitric acid        | $HNO_3$       | $2.3 \times 10^1$     | -1.37  | $NO_3^-$       | $4.3 \times 10^{-16}$ | 15.37  |
| hydronium ion      | $H_3O^+$      | 1.0                   | 0.00   | $H_2O$         | $1.0 \times 10^{-14}$ | 14.00  |
| sulfuric acid (2)* | $HSO_4^-$     | $1.0 \times 10^{-2}$  | 1.99   | $SO_4^{2-}$    | $9.8 \times 10^{-13}$ | 12.01  |
| hydrofluoric acid  | HF            | $6.3 \times 10^{-4}$  | 3.20   | $F^-$          | $1.6 \times 10^{-11}$ | 10.80  |
| nitrous acid       | $HNO_2$       | $5.6 \times 10^{-4}$  | 3.25   | $NO_2^-$       | $1.8 \times 10^{-11}$ | 10.75  |
| formic acid        | $HCO_2H$      | $1.78 \times 10^{-4}$ | 3.750  | $HCO_2^-$      | $5.6 \times 10^{-11}$ | 10.25  |
| benzoic acid       | $C_6H_5CO_2H$ | $6.3 \times 10^{-5}$  | 4.20   | $C_6H_5CO_2^-$ | $1.6 \times 10^{-10}$ | 9.80   |
| acetic acid        | $CH_3CO_2H$   | $1.7 \times 10^{-5}$  | 4.76   | $CH_3CO_2^-$   | $5.8 \times 10^{-10}$ | 9.24   |
| pyridinium ion     | $C_5H_5NH^+$  | $5.9 \times 10^{-6}$  | 5.23   | $C_5H_5N$      | $1.7 \times 10^{-9}$  | 8.77   |
| hypochlorous acid  | HOCl          | $4.0 \times 10^{-8}$  | 7.40   | $OCl^-$        | $2.5 \times 10^{-7}$  | 6.60   |
| hydrocyanic acid   | HCN           | $6.2 \times 10^{-10}$ | 9.21   | $CN^-$         | $1.6 \times 10^{-5}$  | 4.79   |
| ammonium ion       | $NH_4^+$      | $5.6 \times 10^{-10}$ | 9.25   | $NH_3$         | $1.8 \times 10^{-5}$  | 4.75   |
| water              | $H_2O$        | $1.0 \times 10^{-14}$ | 14.00  | $OH^-$         | 1.00                  | 0.00   |
| acetylene          | $C_2H_2$      | $1 \times 10^{-26}$   | 26.0   | $HC_2^-$       | $1 \times 10^{12}$    | -12.0  |

\*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

| Acid    | $HA$   | $K_a$               | $pK_a$ | $A^-$    | $K_b$              | $pK_b$ |
|---------|--------|---------------------|--------|----------|--------------------|--------|
| ammonia | $NH_3$ | $1 \times 10^{-35}$ | 35.0   | $NH_2^-$ | $1 \times 10^{21}$ | -21.0  |

\*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and  $BH^+$  is its conjugate acid:



The equilibrium constant for this reaction is the base ionization constant ( $K_b$ ), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \quad (1.3.5)$$

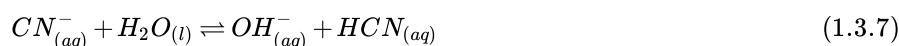
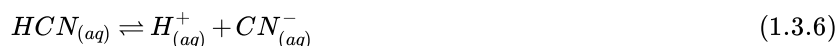
Once again, the activity of water has a value of 1, so water does not appear in the equilibrium constant expression. The larger the  $K_b$ , the stronger the base and the higher the  $OH^-$  concentration at equilibrium. The values of  $K_b$  for a number of common weak bases are given in Table 1.3.2.

Table 1.3.2: Values of  $K_b$ ,  $pK_b$ ,  $K_a$ , and  $pK_a$  for Selected Weak Bases (B) and Their Conjugate Acids ( $BH^+$ )

| Base           | $B$          | $K_b$                 | $pK_b$ | $BH^+$           | $K_a$                 | $pK_a$ |
|----------------|--------------|-----------------------|--------|------------------|-----------------------|--------|
| hydroxide ion  | $OH^-$       | 1.0                   | 0.00*  | $H_2O$           | $1.0 \times 10^{-14}$ | 14.00  |
| phosphate ion  | $PO_4^{3-}$  | $2.1 \times 10^{-2}$  | 1.68   | $HPO_4^{2-}$     | $4.8 \times 10^{-13}$ | 12.32  |
| dimethylamine  | $(CH_3)_2NH$ | $5.4 \times 10^{-4}$  | 3.27   | $(CH_3)_2NH_2^+$ | $1.9 \times 10^{-11}$ | 10.73  |
| methylamine    | $CH_3NH_2$   | $4.6 \times 10^{-4}$  | 3.34   | $CH_3NH_3^+$     | $2.2 \times 10^{-11}$ | 10.66  |
| trimethylamine | $(CH_3)_3N$  | $6.3 \times 10^{-5}$  | 4.20   | $(CH_3)_3NH^+$   | $1.6 \times 10^{-10}$ | 9.80   |
| ammonia        | $NH_3$       | $1.8 \times 10^{-5}$  | 4.75   | $NH_4^+$         | $5.6 \times 10^{-10}$ | 9.25   |
| pyridine       | $C_5H_5N$    | $1.7 \times 10^{-9}$  | 8.77   | $C_5H_5NH^+$     | $5.9 \times 10^{-6}$  | 5.23   |
| aniline        | $C_6H_5NH_2$ | $7.4 \times 10^{-10}$ | 9.13   | $C_6H_5NH_3^+$   | $1.3 \times 10^{-5}$  | 4.87   |
| water          | $H_2O$       | $1.0 \times 10^{-14}$ | 14.00  | $H_3O^+$         | 1.0*                  | 0.00   |

\*As in Table 1.3.1.

There is a simple relationship between the magnitude of  $K_a$  for an acid and  $K_b$  for its conjugate base. Consider, for example, the ionization of hydrocyanic acid ( $HCN$ ) in water to produce an acidic solution, and the reaction of  $CN^-$  with water to produce a basic solution:



The equilibrium constant expression for the ionization of  $HCN$  is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \quad (1.3.8)$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \quad (1.3.9)$$

If we add Equations 1.3.6 and 1.3.7, we obtain the following:

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| Reaction | Equilibrium Constants |
|----------|-----------------------|
|----------|-----------------------|

| Reaction  | Equilibrium Constants                              |
|---|--|
| $\text{HCN}_{(aq)} \rightleftharpoons \text{H}_{(aq)}^+ + \text{CN}_{(aq)}^-$                             | $K_a = [\text{H}^+] [\text{CN}^-] / [\text{HCN}]$  |
| $\text{CN}_{(aq)}^- + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{OH}_{(aq)}^- + \text{HCN}_{(aq)}$ | $K_b = [\text{OH}^-] [\text{HCN}] / [\text{CN}^-]$ |
| $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_{(aq)}^+ + \text{OH}_{(aq)}^-$                      | $K = K_a \times K_b = [\text{H}^+][\text{OH}^-]$   |

In this case, the sum of the reactions described by  $K_a$  and  $K_b$  is the equation for the autoionization of water, and the product of the two equilibrium constants is  $K_w$ :

$$K_a K_b = K_w \quad (1.3.10)$$

Thus if we know either  $K_a$  for an acid or  $K_b$  for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with  $pH$ ,  $pOH$ , and  $pK_w$ , we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining  $pK_a$  as follows:

$$pK_a = -\log_{10} K_a \quad (1.3.11)$$

$$K_a = 10^{-pK_a} \quad (1.3.12)$$

and  $pK_b$  as

$$pK_b = -\log_{10} K_b \quad (1.3.13)$$

$$K_b = 10^{-pK_b} \quad (1.3.14)$$

Similarly, Equation 1.3.10, which expresses the relationship between  $K_a$  and  $K_b$ , can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \quad (1.3.15)$$

At 25 °C, this becomes

$$pK_a + pK_b = 14.00 \quad (1.3.16)$$

The values of  $pK_a$  and  $pK_b$  are given for several common acids and bases in Tables 1.3.1 and 1.3.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of  $pK_a$  correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid ( $\text{HNO}_2$ ), with a  $pK_a$  of 3.25, is about a million times stronger acid than hydrocyanic acid (HCN), with a  $pK_a$  of 9.21. Conversely, smaller values of  $pK_b$  correspond to larger base ionization constants and hence stronger bases.

| ACID       |                                   | BASE                           |            |
|------------|-----------------------------------|--------------------------------|------------|
| negligible | $\text{OH}^-$                     | $\text{O}^{2-}$                | strong     |
|            | $\text{HS}^-$                     | $\text{S}^{2-}$                |            |
| weak       | $\text{H}_2\text{O}$              | $\text{OH}^-$                  | weak       |
|            | $\text{HPO}_4^{2-}$               | $\text{PO}_4^{3-}$             |            |
|            | $\text{HCO}_3^-$                  | $\text{CO}_3^{2-}$             |            |
|            | $\text{NH}_4^+$                   | $\text{NH}_3$                  |            |
|            | $\text{HCN}$                      | $\text{CN}^-$                  |            |
|            | $\text{H}_2\text{PO}_4^-$         | $\text{HPO}_4^{2-}$            |            |
|            | $\text{HSO}_3^-$                  | $\text{SO}_3^{2-}$             |            |
|            | $\text{H}_2\text{S}$              | $\text{HS}^-$                  |            |
|            | $\text{H}_2\text{CO}_3$           | $\text{HCO}_3^-$               |            |
|            | $\text{C}_5\text{H}_5\text{NH}^+$ | $\text{C}_5\text{H}_5\text{N}$ |            |
|            | $\text{CH}_3\text{CO}_2\text{H}$  | $\text{CH}_3\text{CO}_2^-$     |            |
|            | $\text{HF}$                       | $\text{F}^-$                   |            |
|            | $\text{H}_3\text{PO}_4$           | $\text{H}_2\text{PO}_4^-$      |            |
|            | $\text{H}_2\text{SO}_3$           | $\text{HSO}_3^-$               |            |
| strong     | $\text{HSO}_4^-$                  | $\text{SO}_4^{2-}$             | negligible |
|            | $\text{H}_3\text{O}^+$            | $\text{H}_2\text{O}$           |            |
|            | $\text{HNO}_3$                    | $\text{NO}_3^-$                |            |
|            | $\text{H}_2\text{SO}_4$           | $\text{HSO}_4^-$               |            |
|            | $\text{HCl}$                      | $\text{Cl}^-$                  |            |
|            | $\text{HBr}$                      | $\text{Br}^-$                  |            |

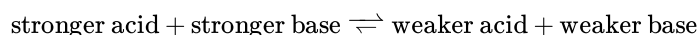
Figure 1.3.1: The Relative Strengths of Some Common Conjugate Acid–Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Strong acids are  $\text{H}_3\text{O}^+$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{HBr}$ . Negligible acids are  $\text{HS}^-$  and  $\text{OH}^-$ . Strong bases are  $\text{O}^{2-}$ ,  $\text{S}^{2-}$ . Negligible bases are  $\text{NO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ .

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 1.3.1. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of  $pK_a$ . This order corresponds to decreasing strength of the conjugate base or increasing values of  $pK_b$ . At the bottom left of Figure 1.3.2 are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

*The conjugate base of a strong acid is a weak base and vice versa.*

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

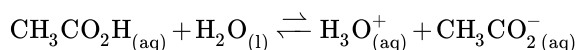


In an acid–base reaction, the proton always reacts with the stronger base.

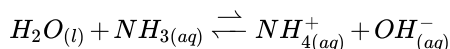
For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$ ; only negligible amounts of  $\text{HCl}$  molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:



In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of  $\text{H}_3\text{O}^+$  and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:



Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:



*All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.*

### ✓ Example 1.3.1: Butyrate and Dimethylammonium Ions

- Calculate  $K_b$  and  $pK_b$  of the butyrate ion ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2^-$ ). The  $pK_a$  of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.
- Calculate  $K_a$  and  $pK_a$  of the dimethylammonium ion ( $(\text{CH}_3)_2\text{NH}_2^+$ ). The base ionization constant  $K_b$  of dimethylamine ( $(\text{CH}_3)_2\text{NH}$ ) is  $5.4 \times 10^{-4}$  at 25°C.

**Given:**  $pK_a$  and  $K_b$

**Asked for:** corresponding  $K_b$  and  $pK_b$ ,  $K_a$  and  $pK_a$

**Strategy:**

The constants  $K_a$  and  $K_b$  are related as shown in Equation 1.3.10. The  $pK_a$  and  $pK_b$  for an acid and its conjugate base are related as shown in Equations 1.3.15 and 1.3.16. Use the relationships  $pK = -\log K$  and  $K = 10^{-pK}$  (Equations 1.3.11 and 1.3.13) to convert between  $K_a$  and  $pK_a$  or  $K_b$  and  $pK_b$ .

**Solution:**

We are given the  $pK_a$  for butyric acid and asked to calculate the  $K_b$  and the  $pK_b$  for its conjugate base, the butyrate ion. Because the  $pK_a$  value cited is for a temperature of 25°C, we can use Equation 1.3.16:  $pK_a + pK_b = pK_w = 14.00$ . Substituting the  $pK_a$  and solving for the  $pK_b$ ,

$$4.83 + pK_b = 14.00$$

$$pK_b = 14.00 - 4.83 = 9.17$$

Because  $pK_b = -\log K_b$ ,  $K_b$  is  $10^{-9.17} = 6.8 \times 10^{-10}$ .

In this case, we are given  $K_b$  for a base (dimethylamine) and asked to calculate  $K_a$  and  $pK_a$  for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is  $K_b$  rather than  $pK_b$ , we can use Equation 1.3.10:  $K_a K_b = K_w$ . Substituting the values of  $K_b$  and  $K_w$  at 25°C and solving for  $K_a$ ,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14}$$

$$K_a = 1.9 \times 10^{-11}$$

Because  $pK_a = -\log K_a$ , we have  $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$ . We could also have converted  $K_b$  to  $pK_b$  to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27$$

$$pK_a + pK_b = 14.00$$

$$pK_a = 10.73$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11}$$

If we are given any one of these four quantities for an acid or a base ( $K_a$ ,  $pK_a$ ,  $K_b$ , or  $pK_b$ ), we can calculate the other three.

### ? Exercise 1.3.1: Lactic Acid

Lactic acid ( $CH_3CH(OH)CO_2H$ ) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its  $pK_a$  is 3.86 at 25°C. Calculate  $K_a$  for lactic acid and  $pK_b$  and  $K_b$  for the lactate ion.

#### Answer

- $K_a = 1.4 \times 10^{-4}$  for lactic acid;
- $pK_b = 10.14$  and
- $K_b = 7.2 \times 10^{-11}$  for the lactate ion



A Video Calculating pH in Strong Acid or Strong Base Solutions: [Calculating pH in Strong Acid or Strong Base Solutions](https://youtu.be/) [youtu.be]

### Solutions of Strong Acids and Bases: The Leveling Effect

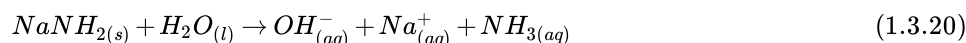
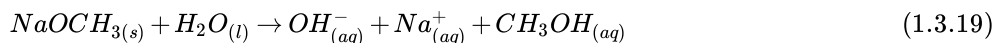
You will notice in Table 1.3.1 that acids like  $H_2SO_4$  and  $HNO_3$  lie above the hydronium ion, meaning that they have  $pK_a$  values less than zero and are stronger acids than the  $H_3O^+$  ion. Recall from Chapter 4 that the acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as  $HONO_2$ . Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving  $HNO_3$  instead. In fact, all six of the common strong acids that we first encountered in Chapter 4 have  $pK_a$  values less than zero, which means that they have a greater tendency to lose a proton than does the  $H_3O^+$  ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibria for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the  $H_3O^+$  ion and the conjugate base of the acid.

Although  $K_a$  for  $HI$  is about 108 greater than  $K_a$  for  $HNO_3$ , the reaction of either  $HI$  or  $HNO_3$  with water gives an essentially stoichiometric solution of  $H_3O^+$  and  $I^-$  or  $NO_3^-$ . In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M  $H_3O^+$ , regardless of the identity of the strong acid. This phenomenon is called the leveling effect: any species that is a stronger acid than the conjugate acid of water ( $H_3O^+$ ) is leveled to the strength of  $H_3O^+$  in aqueous solution because  $H_3O^+$  is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as  $HI$  and  $HNO_3$  in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than  $H_2O$ . Measurements of the conductivity of 0.1 M solutions of both  $HI$  and  $HNO_3$  in acetic acid show that  $HI$  is completely dissociated, but  $HNO_3$  is only partially dissociated and behaves like a weak acid in this solvent. This result clearly tells us that  $HI$  is a stronger acid than  $HNO_3$ . The relative order of acid strengths and approximate  $K_a$  and  $pK_a$  values for the strong acids at the top of Table 1.3.1 were determined using measurements like this and different nonaqueous solvents.

*In aqueous solutions,  $H_3O^+$  is the strongest acid and  $OH^-$  is the strongest base that can exist in equilibrium with  $H_2O$ .*

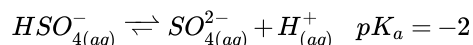
The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than  $\text{OH}^-$  is leveled to the strength of  $\text{OH}^-$  because  $\text{OH}^-$  is the strongest base that can exist in equilibrium with water. Salts such as  $\text{K}_2\text{O}$ ,  $\text{NaOCH}_3$  (sodium methoxide), and  $\text{NaNH}_2$  (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table 1.3.2, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of  $\text{OH}^-$  and the corresponding cation:



Other examples that you may encounter are potassium hydride ( $\text{KH}$ ) and organometallic compounds such as methyl lithium ( $\text{CH}_3\text{Li}$ ).

## Polyprotic Acids and Bases

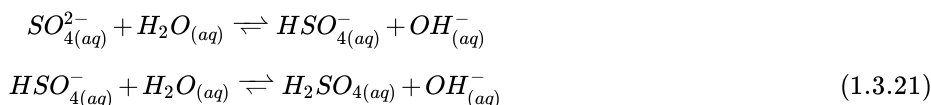
As you learned, polyprotic acids such as  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{H}_2\text{CO}_3$  contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the  $pK_a$  increases. Consider  $\text{H}_2\text{SO}_4$ , for example:



The equilibrium in the first reaction lies far to the right, consistent with  $\text{H}_2\text{SO}_4$  being a strong acid. In contrast, in the second reaction, appreciable quantities of both  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  are present at equilibrium.

*For a polyprotic acid, acid strength decreases and the  $pK_a$  increases with the sequential loss of each proton.*

The hydrogen sulfate ion ( $\text{HSO}_4^-$ ) is both the conjugate base of  $\text{H}_2\text{SO}_4$  and the conjugate acid of  $\text{SO}_4^{2-}$ . Just like water,  $\text{HSO}_4^-$  can therefore act as either an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion ( $\text{SO}_4^{2-}$ ) is a polyprotic base that is capable of accepting two protons in a stepwise manner:



Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by  $pK_a + pK_b = pK_w$ . Consider, for example, the  $\text{HSO}_4^- / \text{SO}_4^{2-}$  conjugate acid–base pair. From Table 1.3.1, we see that the  $pK_a$  of  $\text{HSO}_4^-$  is 1.99. Hence the  $pK_b$  of  $\text{SO}_4^{2-}$  is  $14.00 - 1.99 = 12.01$ . Thus sulfate is a rather weak base, whereas  $\text{OH}^-$  is a strong base, so the equilibrium shown in Equation 1.3.21 lies to the left. The  $\text{HSO}_4^-$  ion is also a very weak base ( $pK_a$  of  $\text{H}_2\text{SO}_4 = 2.0$ ,  $pK_b$  of  $\text{HSO}_4^- = 14 - (-2.0) = 16$ ), which is consistent with what we expect for the conjugate base of a strong acid.

### ✓ Example 1.3.2

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $\text{NH}_{4(aq)}^+ + \text{PO}_{4(aq)}^{3-} \rightleftharpoons \text{NH}_{3(aq)} + \text{HPO}_{4(aq)}^{2-}$
- $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}_{(aq)} + \text{CN}_{(aq)}^- \rightleftharpoons \text{CH}_3\text{CH}_2\text{CO}_2^-(aq) + \text{HCN}_{(aq)}$

**Given:** balanced chemical equation

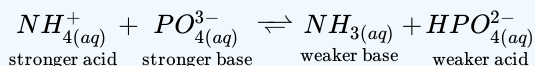
**Asked for:** equilibrium position

**Strategy:**

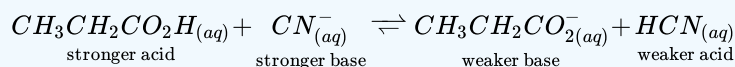
Identify the conjugate acid–base pairs in each reaction. Then refer to Tables 1.3.1 and 1.3.2 and Figure 1.3.2 to determine which is the stronger acid and base. Equilibrium **always** favors the formation of the weaker acid–base pair.

**Solution:**

The conjugate acid–base pairs are  $NH_4^+/NH_3$  and  $HPO_4^{2-}/PO_4^{3-}$ . According to Tables 1.3.1 and 1.3.2,  $NH_4^+$  is a stronger acid ( $pK_a = 9.25$ ) than  $HPO_4^{2-}$  ( $pK_a = 12.32$ ), and  $PO_4^{3-}$  is a stronger base ( $pK_b = 1.68$ ) than  $NH_3$  ( $pK_b = 4.75$ ). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:



The conjugate acid–base pairs are  $CH_3CH_2CO_2H/CH_3CH_2CO_2^-$  and  $HCN/CN^-$ . According to Table 1.3.1, HCN is a weak acid ( $pK_a = 9.21$ ) and  $CN^-$  is a moderately weak base ( $pK_b = 4.79$ ). Propionic acid ( $CH_3CH_2CO_2H$ ) is not listed in Table 1.3.1, however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties are listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid ( $-CH_2CH_3$  versus  $-CH_3$ ), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the  $pK_a$  of propionic acid to be similar in magnitude to the  $pK_a$  of acetic acid. (In fact, the  $pK_a$  of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:



### ? Exercise 1.3.1

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $H_2O_{(l)} + HS_{(aq)}^- \rightleftharpoons OH_{(aq)}^- + H_2S_{(aq)}$
- $HCO_2^-(aq) + HSO_4^-(aq) \rightleftharpoons HCO_2H_{(aq)} + SO_4^{2-}(aq)$

**Answer a**

left

**Answer b**

left



A Video Discussing Polyprotic Acids: [Polyprotic Acids](https://youtu.be/) [youtu.be]

### Summary

Acid–base reactions always contain two conjugate acid–base pairs. Each acid and each base has an associated ionization constant that corresponds to its acid or base strength. Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases.

For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant ( $K_a$ ). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant ( $K_b$ ). For any conjugate acid–base pair,  $K_a K_b = K_w$ . Smaller values of  $pK_a$  correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of  $pK_b$  correspond to larger base ionization constants and hence stronger bases. At 25°C,  $pK_a + pK_b = 14.00$ . Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than  $H_3O^+$  and no base stronger than  $OH^-$  can exist in aqueous solution, leading to the phenomenon known as the leveling effect. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base.

## Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- Relationship between  $K_a$  and  $K_b$  of a conjugate acid–base pair:

$$K_a K_b = K_w$$

- Definition of  $pK_a$ :

$$pK_a = -\log_{10} K_a$$
$$K_a = 10^{-pK_a}$$

- Definition of  $pK_b$ :

$$pK_b = -\log_{10} K_b$$
$$K_b = 10^{-pK_b}$$

- Relationship between  $pK_a$  and  $pK_b$  of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w$$
$$pK_a + pK_b = 14.00 \text{ at } 25^\circ\text{C}$$

## Contributors and Attributions

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