Calculations In Chemistry

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Module 30: Weak Acids and Bases
Module 31: Brønsted-Lowry Definitions

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Module 30 — Weak Acids and Bases

Timing: Begin this module when you are assigned calculations involving K_a.

Prerequisites: Do Lessons 28C and 28D on equilibrium and Module 29 on acid-base fundamentals before starting this module.

Pretests: In this module, if you think you are familiar with a lesson topic, try the last problem in each problem *set* of the lesson. If you get those right, move to the next lesson.

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Lesson 30A: K_a Math and Approximation Equations

Pretest: This lesson has two parts. The first part is a quick review of the math of powers and roots covered in Lessons 19A and 28B. The second part is new material. Even if you can do the Practice A problems quickly, devote extra care to the section after Practice A.

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Squares and Square Roots

The calculations in this module require solving the square and square root of numbers in exponential notation. Rules for these calculations were covered in Lesson 19A. The following is a brief reminder of those rules (which you need to be able to apply from memory).

Estimating exponential calculations is one way to catch mistakes in calculator use. For this reason, we will review squares and square roots both with and without the calculator.

Rules for Squares and Square Roots in Exponential Notation

1. To take an exponential term to a power, multiply the exponentials.
2. "Taking the square root" has the same meaning as taking a quantity to the **1/2** power.

   When taking the square root of exponential notation, *write* $\sqrt{x}$ as $x^{1/2}$.
3. When taking exponential notation to a power, handle numbers by number rules and exponents by exponential rules.
4. A square root of a number in exponential notation can be calculated with*out* entering the exponent on the calculator. The steps are:
   a. Write the square root as exponential notation taken to the 1/2 power.
   b. Make the *exponent even*. If the exponent is odd, make the *significand* 10 times *larger*, and the *exponent* ten times (one number) *smaller*. Then,
   c. Take the square root of the *significand* on the calculator. Take the square root of the exponential term by multiplying the exponent by 1/2.

   Example: $\sqrt{2.5 \times 10^{-7}} = (2.5 \times 10^{-7})^{1/2} = (25 \times 10^{-8})^{1/2} = 5.0 \times 10^{-4}$
5. A square root can be estimated by making the exponent even, estimating the square root of the significand, and attaching the exact root of the exponential.

Practice A: Do the *last part* of each numbered problem, then more if you need more practice. Convert final answers to scientific notation. Check answers at the end of this lesson. If you cannot solve these problems easily, review Lesson 19A.

1. a. $(10^3)^2 =$ b. $(10^{-4})^{1/2} =$ c. $\sqrt{10^{-16}} =$

For problems 2-4, convert final answers to scientific notation.

2. Without a calculator:

   a. $(7.0 \times 10^{-5})^2 =$

   b. $(36 \times 10^{-6})^{1/2} =$

   c. $\sqrt{0.0064} =$

3. Solve the Problem 2 questions using the square and square root function on your calculator.

   a. $(7.0 \times 10^{-5})^2 =$

   b. $(36 \times 10^{-6})^{1/2} =$

   c. $\sqrt{0.0064} =$

Compare Problems 2 and 3. Which was easier: with or without a calculator?

4. Use a calculator for the significand (the number in front), but do the exponential part by inspection.

   a. $(2.5 \times 10^{-5})^2 =$

   b. $(2.56 \times 10^{-4})^{1/2} =$

   c. $\sqrt{1.44 \times 10^{-6}} =$

5. *Estimate* the square root of a. 45 b. 18 c. 95 d. 7

6. Use a calculator to take a square root and compare to above a. 45 b. 18 c. 95 d. 7

7. Estimate the square root. Need help? See Rule 5 above.

   a. $(4.2 \times 10^{+5})^{1/2} =$

   b. $(8.1 \times 10^{-7})^{1/2} =$

   c. $\sqrt{7.2 \times 10^{-3}} =$

8. *Calculate* the square root. Need help? See Rule 4. Compare answers to Problem 7.

   a. $(4.2 \times 10^{+5})^{1/2} =$

   b. $(8.1 \times 10^{-7})^{1/2} =$

c. $\sqrt{7.2 \times 10^{-3}}$ =

Bottom Line On Calculator Use

With practice, you can quickly do squares and square roots of exponential notation on the calculator, but first write a quick estimate of the answer without the calculator. Check that the estimate and the calculator answer are *close*.

Approximation Equations

If mathematical expressions involve both large and small numbers, they can often be simplified to approximations that are easier to solve. The rules are:

> **For *K* approximations**,
>
> - You can*not* ignore small numbers that are *by themselves* as terms in equations, but
> - You *can ignore small numbers* that are *added or subtracted* from much larger numbers.

In the following questions, ≈ means approximately equals, A is any large number, B is any different large number, and x is any number much smaller than A and B. Write the approximation equation for the following term by applying the rule above.

Q. $\dfrac{(\mathrm{A} + x)(x)}{(\mathrm{B} - x)} \approx$ **?**

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A. $\dfrac{(\mathrm{A} + x)(x)}{(\mathrm{B} - x)} \approx \boldsymbol{\dfrac{(\mathrm{A})(x)}{\mathrm{B}}}$

Let's test this rule using numbers. Calculate a numeric answer (to three decimal places) for

$\dfrac{(18.0 + 0.10)(0.10)}{(9.0 - 0.10)} =$

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A. Exact: $\dfrac{(18.1)(0.10)}{(8.9)} =$ **0.204**

Now simplify the equation by applying the approximation rules. In the term below, cross out the small terms added or subtracted from larger terms, calculate a numeric answer, then compare to the answer above.

$\dfrac{(18.0 + 0.10)(0.10)}{(9.0 - 0.10)} \approx$

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A. Approximation: $\dfrac{(18.0 + \cancel{0.10})(0.10)}{(9.0 - \cancel{0.10})} \approx \dfrac{(18.0)(0.10)}{(9.0)} = \mathbf{0.200}$

Compare the answers to Q1 and Q2 above. Are they close?

If the small numbers that are added or subtracted from the large numbers are removed, the difference between the two answers is 2%. In some science experiments and procedures, that would be more error than we would like to see. However, because K values often involve significant inherent uncertainty, a change in an answer of up to 5% due to the use of an approximation is is generally considered as acceptable.

To solve K calculations involving weak acids quickly, our rule will be: use approximation equations.

Practice B. Using the notation and rules above, simplify these equations using approximations. Save a few for your next practice session.

1. $\dfrac{(A + x)(x)}{(A - x)} \approx$

2. $\dfrac{(x)(x)}{(B - x)} \approx$

3. $\dfrac{(B + x)(x)}{(A - x)} \approx$

4. $\dfrac{(A + x)}{(A - x)(x)} \approx$

5. Assuming x is much smaller than the other numbers in these equations, simplify these terms.

   a. $\dfrac{(0.050 + x)\,(x)}{0.020 - x} \approx$

   b. $\dfrac{(2x)\,(x)}{0.10 - x} \approx$

   c. $\dfrac{(x)\,(x)}{0.020 - x} \approx$

   d. $\dfrac{(x + x)}{[WB] + x} \approx$

6. Assuming x is very small compared to the other numbers, apply the approximation rules and then solve for x. Simplify the terms here, then finish in your notebook. See if you can solve these without a calculator.

   a. $\dfrac{(x)\,(x)}{2.0 - x} = 8.0 \times 10^{-12}$

   b. $\dfrac{(2x + x)}{0.50 + x} = 1.8 \times 10^{-5}$

   c. $\dfrac{(0.60 + x)\,(x)}{0.20 - x} = 3.6 \times 10^{-9}$

   d. $\dfrac{(2x)\,(x)}{4.0 - x} = 1.25 \times 10^{-11}$

ANSWERS

Practice A

1a. $\mathbf{10^{6}}$ 1b. $\mathbf{10^{-2}}$ 1c. $\mathbf{10^{-8}}$

2,3: a. $\mathbf{4.9 \times 10^{-9}}$ b. $\mathbf{6.0 \times 10^{-3}}$ c. $(64 \times 10^{-4})^{1/2} = \mathbf{8.0 \times 10^{-2}}$

4. a. $\mathbf{6.2 \times 10^{-10}}$ b. $\mathbf{1.60 \times 10^{-2}}$ c. $\mathbf{1.20 \times 10^{-3}}$

5. a. 45 $6^2 = 36$ and $7^2 = 49$; estimate $\approx$ **6.7** b. 95 $9^2 = 81$ and $10^2 = 100$; estimate $\approx$ **9.7**

   c. 7 $2^2 = 4$ and $3^2 = 9$; estimate $\approx$ **2.7**

6. a. **6.71** b. **9.74** c. **2.65** When estimating to *check* answers, close is a good enough.

7. To estimate the square root, first convert so that the power is divisible by 2.

7, 8. .a. $\mathbf{6.5 \times 10^{2}}$ b. $\mathbf{9.0 \times 10^{-4}}$ c. $\mathbf{8.5 \times 10^{-2}}$

Practice B

1. $\dfrac{(A + x)(x)}{(A - x)} \approx \dfrac{(A)(x)}{(A)} \approx \mathbf{x}$

2. $\dfrac{(x)(x)}{(B - x)} \approx \mathbf{\dfrac{x^2}{B}}$

3. $\dfrac{(B + x)(x)}{(A - x)} \approx \mathbf{\dfrac{(B)(x)}{A}}$

4. $\dfrac{(A + x)}{(A - x)(x)} \approx \mathbf{(x)^{-1}}$

5. a. $\dfrac{(0.050 + x)(x)}{0.020 - x} \approx \dfrac{(0.050)(x)}{0.020} = \mathbf{2.5x}$

   5b. $\dfrac{(2x)(x)}{0.10 - x} \approx \dfrac{2x^2}{0.10} = \mathbf{20x^2}$

   c. $\dfrac{(x)(x)}{0.020 - x} \approx \mathbf{\dfrac{x^2}{0.20}}$

   d. $\dfrac{(x + x)}{[WB] + x} \approx \mathbf{\dfrac{2x}{[WB]}}$

6. On these, you may do the steps differently, but you must get the same answers.

   a. $\dfrac{(x)\cancel{(x)}}{2.0 \cancel{-x}} = 8.0 \times 10^{-12}$

   $\dfrac{x^2}{2.0} = 8.0 \times 10^{-12}$

   $x^2 = 16 \times 10^{-12}$

   $\mathbf{x = 4.0 \times 10^{-6}}$

   b. $\dfrac{(2x \cancel{+x})}{0.50 + \cancel{x}} = 1.8 \times 10^{-5}$

   $\dfrac{3x}{0.50} = 1.8 \times 10^{-5}$

   $3x = 9.0 \times 10^{-6}$

   $\mathbf{x = 3.0 \times 10^{-6}}$

   c. $\dfrac{(0.60 \cancel{+x})(x)}{0.20 \cancel{-x}} = 3.6 \times 10^{-9}$

   $\dfrac{(0.60)(x)}{0.20} = 3.6 \times 10^{-9}$

   $3x = 3.6 \times 10^{-9}$

   $\mathbf{x = 1.2 \times 10^{-9}}$

   d. $\dfrac{(2x)(x)}{4.0 \cancel{-x}} = 1.25 \times 10^{-11}$

   $\dfrac{2x^2}{4.0} = 1.25 \times 10^{-11}$

   $x^2 = 25.0 \times 10^{-12}$

   $\mathbf{x = 5.0 \times 10^{-6}}$

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Lesson 30B: Weak Acids and K_a Expressions

So far, our acid-base calculations have all involved either strong monoprotic acids (such as HCl and HNO_3) or strong bases (such as NaOH and KOH). Those compounds are widely used in laboratories and industrial processes when strong acids and bases are needed.

However, far more compounds are *weak* acids and bases than strong. An understanding of weak acids and bases is important in fields as interesting and diverse as the biological sciences and the culinary arts.

Weak Acid Solutions

Strong acids dissociate (ionize) 100% to form H^+ ions when dissolved in water. Weak acids are defined as substances that dissociate to form H^+ ions when dissolved in water, but do so only slightly.

The general equation describing the behavior of a weak acid dissolved in water is:

1 weak acid ⇆ 1 proton + 1 conjugate base (left side favored)

A specific example is the behavior of ammonium ion (a weak acid) in water:

$$NH_4^+(aq) \leftrightarrows H^+(aq) + NH_3(aq) \qquad \text{(goes slightly)}$$

The loss of a proton by an acid is reversible: the proton can return to re-form the acid. In a weak acid solution at equilibrium, the weakly acidic proton leaves and returns continuously, but because both reactions proceed at the same rate, no *net* change occurs.

Because acid ionization is a reaction that in practice is nearly always reversible, we will represent the reaction *arrow* as ⇆ rather than →. For strong acid ionization, equilibrium favors the right side products, but for weak acids, equilibrium favors the reactants.

A familiar weak acid solution is vinegar, which can be formed by the action of bacteria and oxygen on fruit juice. The oxidation of the sugar in fruit juice produces a mixture that is composed primarily of water and *acetic acid,* a weak acid that is soluble in water. Most vinegar solutions are about one volume of acetic acid per 10 to 20 volumes of water.

When dissolved in water, acetic acid ionizes slightly to produce H^+ ions. As the products form, the reverse reaction of the proton returning to the acetate ion also occurs, and the solution will quickly reach an *equilibrium* state where no further net change takes place.

The behavior of acetic acid in water can be represented as either a separation into ions (which can be termed an **ionization** or a **dissociation):**

$$1\ CH_3COOH(aq) \leftarrow\leftarrow\rightarrow 1\ H^+(aq) + 1\ CH_3COO^-(aq) \qquad \text{(goes ~ 1\%)}$$

In water: ~99% un-ionized ~ 1% ionized (~ means approximately)

or as a **hydrolysis** (a reaction with water):

$$1\ CH_3COOH(l) + 1\ H_2O(l) \leftarrow\leftarrow\rightarrow 1\ H_3O^+(aq) + 1\ CH_3COO^-(aq) \qquad \text{(goes ~ 1\%)}$$

Compare the two equations. Both represent a weak acid that is dissolved in water but ionizes only slightly. Recall that H^+ and H_3O^+ are equivalent ways of representing the proton released by acids. These two equations are *equivalent* ways of representing the same reaction.

In equations involving acid ionization, if no state is shown after a particle formula, assume the state is *(aq)*.

Arrow Conventions

In theory, all chemical reactions are reversible. In practice, many reactions strongly favor one side or the other of a reaction's reactants and products. The arrows that we use to represent a reaction may differ depending on the aspect of a reaction that is being studied.

In these lessons, we will use the following reaction arrows for different types of reactions.

- When considering the behavior of a reaction as it goes to the right: $\rightarrow$
- For a reaction that is reversible and goes to equilibrium: $\leftrightarrows$
- For a reversible reaction that goes only slightly (favors the left): $\leftarrow\leftarrow\rightarrow$
- For a reaction that strongly favors the products: $\rightarrow\rightarrow$

$[H^+]$ In Weak versus Strong Acids

In water, strong acids dissociate completely, but when *weak* acids dissolve in water, equilibrium favors the *un*-dissociated (*un*-ionized) species. A weak acid solution therefore has fewer H^+ ions, and a *higher* pH (is less acidic) than a strong acid solution with the same concentration.

For example:

In **0.10 M** HCl as mixed, a solution of a *strong* acid, the approximate concentrations and pH include

$$[HCl] = \mathbf{0\ M}, \quad [\mathbf{H^+}] = \mathbf{0.10}\ M = 10^{-1}\ M; \quad pH = \mathbf{1}\ .$$

In a **0.10 M** acetic acid solution, roughly one acetic acid particles per 100 is ionized. This means that in this solution,

$$[CH_3COOH] \approx 0.099\ M \approx \mathbf{0.10\ M}, \ [\mathbf{H^+}] \approx \mathbf{0.001}\ M \approx 10^{-3}\ M, \quad pH \approx \mathbf{3}.$$

Compare the $[H^+]$, and pH in the two solutions. At the same mixed concentrations of the acids, the hydrochloric acid solution has about 100 times more protons than the acetic acid.

Vinegar can be used in cooking because acetic acid solutions do not contain high concentrations of the reactive, corrosive particles in acids: $\mathbf{H^+}$. However, even at low concentrations, the $[\mathbf{H^+}]$ in aqueous solutions can have a major impact on reactions in chemistry and biology.

Conjugate Bases

An acid can be defined as any particle that can *lose a proton*. This means that acids can be positive or negative *ions* as well as electrically neutral particles.

Examples: **H**Cl, $N\mathbf{H}_4^+$, and $\mathbf{H}PO_4^{2-}$ can all act as an acid by losing a proton.

The ionization of an acid produces a proton and a particle termed the acid's **conjugate base.** The chemical formula for the conjugate base is simply the acid formula with *one less H* atom and *one less positive charge*.

Example:

For the weak acid HF ionizing in water, the reaction can be represented in three ways.

As the general reaction: **1 weak acid $\leftarrow\!\leftarrow\!\rightarrow$ 1 proton + 1 conjugate base**

In the *ionization* format: $HF(aq) \leftarrow\!\leftarrow\!\rightarrow \mathbf{H^+}(aq) + F^-(aq)$

In the *hydrolysis* format: $HF(aq) + H_2O(l) \leftarrow\!\leftarrow\!\rightarrow \mathbf{H_3O^+}(aq) + F^-(aq)$

Use the definition of a conjugate base to answer these two questions.

Q. Assume the first particle in each reaction is acting as an *acid*. Complete the reaction by writing chemical formulas for the products. Circle the conjugate base of the acid. (For particles in a solution, if no state is shown, assume *(aq)*.)

1. $HCN(aq) \rightarrow$

2. $NH_4^+ + H_2O(l) \rightarrow$

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1. $HCN(aq) \rightarrow H^+(aq) + CN^-(aq)$

An acid ionizes to produce a proton (H^+). The other particle is the conjugate base: the acid particle with one less H atom and one less positive charge.

2. $NH_4^+ + H_2O(l) \rightarrow H_3O^+ + NH_3$

When a weak acid ionization is written in the hydrolysis format (losing a proton by donating the proton to water), one of the product particles is the always the hydronium ion (H_3O^+); the other is the conjugate base.

All reaction equations must be balanced for atoms and charge. Check the balancing in each of the answers above.

Practice A: In the reactions below, assume that the first particle is acting as a weak acid in an aqueous solution. Write the formulas for the products. Circle the conjugate base.

1. $HI \rightarrow$

2. $HCO_3^- \rightarrow$

3. $HS^- + H_2O \rightarrow$

4. $HPO_4^{2-} + H_2O \rightarrow$

The K_a Expression

For the reaction of an acid losing one proton, the equilibrium constant K is given a special name, the **acid-dissociation constant**, and a special symbol, $\mathbf{K_a}$. For any reaction in which one acid particle ionizes to form one H^+ or reacts with water to form one H_3O^+, the symbol for the equilibrium constant is K_a.

By convention, an acid ionization or hydrolysis reaction is always written with *one un*-ionized acid particle on the *left* and one H^+ (or H_3O^+) on the *right*.

Example: The loss of a proton by acetic acid can be represented by either:

$$CH_3COOH(aq) \leftrightarrows \mathbf{H^+}(aq) + CH_3COO^-(aq)$$

or $$CH_3COOH(aq) + H_2O(l) \leftrightarrows \mathbf{H_3O^+}(aq) + CH_3COO^-(aq)$$

Q. Write the K expression for the two reactions in the example above.

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Because each reaction consists of a weak acid releasing one proton, the K is a K_a .

A K_a expression always has $[H^+]^{\mathbf{1}}$ *or* $[H_3O^+]^{\mathbf{1}}$ on *top* and [weak acid]$^{\mathbf{1}}$ on the bottom.

For the above two reactions,

$$K_a = \frac{[\mathbf{H^+}]_{eq.}\,[CH_3COO^-]_{eq.}}{[CH_3COOH]_{at\ eq.}} \quad or \quad K_a = \frac{[\mathbf{H_3O^+}]\,[CH_3COO^-]}{[CH_3COOH]}$$

For all K_a expressions,

- as in standard K expressions: product concentrations are on top and reactant concentrations on the bottom.
- Because H^+ and H_3O^+ are considered to be equivalent ways to represent a proton in acid solutions, the two reaction formats and the two resulting K_a expressions are equivalent. One format may be substituted for the other.
- If the state of a particle is left out, it is assumed to be aqueous.
- In K expressions, concentrations are assumed to be measured *at equilibrium*, and if a label after a concentration term is omitted, the label $[\ ]_{\textbf{at equilibrium}}$ is understood.
- The powers of all of the concentrations are **1** and are omitted as understood.
- $[H_2O]$ is *not* included in the K_a expression for the hydrolysis reaction.

$[H_2O]$ is represented by a 1 in K_a hydrolysis expressions for the same reason that it is represented by a 1 in the K_w expression. During acid hydrolysis, the concentration of liquid water remains high and close to constant, at about 55 M, except in solutions that have a very high concentration of the acid. By convention, if a particle concentration in a reaction equation cannot be significantly changed, its constant concentration is represented by a 1 in the K expression, and the 1 is omitted if it is in the expression denominator.

Pure acetic acid (CH_3COOH) is a *liquid* at room temperature. Because acetic acid is a polar molecule, it is soluble in water: when these two liquids are mixed, the result is one layer rather than the two layers of immiscible "oil and water." In the dilute acetic acid solutions used in most experiments, its concentration is low compared to the [water], and the *state* of the acetic acid is better described as aqueous (dissolved in a comparably large amount of water) rather than liquid. Depending on how much acetic acid is mixed into the water, the [CH_3COOH*(aq)*] can *vary* substantially, so the [CH_3COOH] term is *included* in the *K* expression.

In general,

A [dissolved liquid] term is included in a *K* expression but the [solvent] is not.

A polyprotic acid can ionize to lose more than one proton, but in all polyprotic acid solutions, each successive hydrogen ionizes less than the one before. In *K* calculations, these successive ionizations are written separately, with the conjugate base of the first ionization becoming the weak acid in the second, etc. A K_a value always refers to the ionization of a weak acid to produce *one* H^+ or *one* H_3O^+.

Practice B: In the reactions below, assume that the first particle is acting as a weak acid in an aqueous solution. Complete the reaction by writing the formulas for the products. Then write the K_a *expression* for each reaction.

1. $H_2CO_3 \leftrightarrows$

2. $HCO_3^- \leftrightarrows$

3. $H_2S + H_2O(l) \leftrightarrows$

4. $NH_4^+ + H_2O(l) \leftrightarrows$

K_a Values

Acids have *characteristic K_a values* at a given temperature.

Sample K_a Values at 25ºC:

Hydrochloric acid (strong)	$HCl \leftrightarrows H^+ + Cl^-$	K_a = very large
Hydrofluoric acid (weak)	$HF \leftrightarrows H^+ + F^-$	$K_a = 6.8 \times 10^{-4}$
Acetic acid (weak)	$CH_3COOH \leftrightarrows H^+ + CH_3COO^-$	$K_a = 1.8 \times 10^{-5}$
Hydrocyanic acid (weak)	$HCN \leftrightarrows H^+ + CN^-$	$K_a = 6.2 \times 10^{-10}$

For *strong* acids, ionization strongly favors the products. The K_a values for strong acids are very large**:** a number much greater than one**.** Since strong acid ionization is considered to go to completion rather than equilibrium, the *K* value is not needed for calculations.

Weak acids have K_a values between 1.0 and 10^{-16}, usually written in scientific notation with a negative power of 10. The weaker is the acid, the less it will ionize and the smaller will be its K_a. In the table above, the weakest acid is ? ? ?

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HCN

As the temperature of a weak acid solution rises, more bonds to H break, more protons form, and K_a values increase. However, unless otherwise noted, you should assume that K_a calculations are based on reactions at 25ºC (77ºF).

For each H atom in a compound, a K_a value can be measured that represents the tendency of the H to ionize. However, if a K_a value is smaller than 10^{-16}, the H will not react as an acid except with bases that are *very* strong: stronger than hydroxides. Under most circumstances, an H with a K_a smaller than 10^{-16} is considered to be a non-reactive (non-acidic) rather than an *acidic* hydrogen (see Lesson 14A).

Because *K* values can be difficult to measure precisely, reported *K* values can vary slightly among textbooks. When doing textbook calculations, use *K* values in that text.

Practice C:

1. For the weak acid NH_4^+, the K_a value is 5.6×10^{-10}.
   a. Write the *reaction* for which this is the *K* value.
   b. Write the K_a expression for this reaction.
   c. What term (or terms) does a K_a expression always have in its numerator?
2. The weak acid HSO_3^- has a K_a value of 6.2×10^{-8}.
   a. Write the *reaction* for which this is the *K* value.
   b. Write the K_a expression for this reaction.
3. Which particle above is the weaker acid: NH_4^+ or HSO_3^- ?

ANSWERS

Practice A

1. $HI \leftrightarrows H^+ + I^-$
2. $HCO_3^- \leftrightarrows H^+ + CO_3^{2-}$
3. $HS^- + H_2O \leftrightarrows H_3O^+ + S^{2-}$
4. $HPO_4^{2-} + H_2O \leftrightarrows H_3O^+ + PO_4^{3-}$

Practice B: In the *K* expressions below, all concentrations are measured at equilibrium.

1. $H_2CO_3 \leftrightarrows H^+ + HCO_3^-$

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

2. $HCO_3^- \leftrightarrows H^+ + CO_3^{2-}$

$$K_a = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

3. $H_2S + H_2O(l) \leftrightarrows H_3O^+ + HS^-$

$$K_a = \frac{[H_3O^+][HS^-]}{[H_2S]}$$

4. $NH_4^+ + H_2O\ (l) \leftrightarrows H_3O^+ + NH_3$

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$$

For 3 and 4, in aqueous solutions $[H_2O]$ is essentially constant and is given a value of 1 in K expressions.

Practice C:

1a. $NH_4^+ \leftrightarrows H^+ + NH_3$

A K_a is always a K for the reaction where a weak acid loses an H^+ ion. In the equation for a K_a reaction, an H^+ or H_3O^+ ion will always be on the right side.

1b. $$K_a = \frac{[H^+][NH_3]}{[NH_4^+]}$$

1c. A K_a expression always has $[H^+]$ or $[H_3O^+]$ in the numerator.

2a. $HSO_3^- \leftrightarrows H^+ + SO_3^{2-}$

2b. $$K_a = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$$

3. The weaker acid is the one with the lower K_a value: NH_4^+

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Lesson 30C: K_a Calculations

K_a Equations

The K_a *expression* and the K_a *value* together form the **K_a equation**.

For the ionization of acetic acid: $1\ CH_3COOH \leftleftarrows\!\rightarrow 1\ H^+ + 1\ CH_3COO^-$

the K_a equation is: $$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \mathbf{1.8 \times 10^{-5}} \quad \text{at } 25^oC$$

Calculations using K_a follow the same rules as other K calculations:

- *Units* are *not* attached to K values,
- Units may be omitted when substituting into the K expression, and
- When a concentration is WANTED, the *unit* moles/liter (M) must be added to the answer.

When To Use K_a

In solutions of *strong* acids, a K_a value is not needed to calculate particle concentrations at equilibrium. Since HCl and HNO_3 ionize completely in a 1 to 1 to 1 ratio, the original [HCl and $HNO_3]_{mixed}$ *equals* the $[H^+]$ and $[Cl^-$ *or* $NO_3^-]$ that form in the solution. Because of these simple ratios, the ion concentrations in strong acid solutions can be solved by inspection.

Weak acids ionize to form one proton, but the reaction goes slightly: to establish an equilibrium instead of to completion. The mixed original [weak acid] does not directly convey how much of the weak acid ionizes, nor how much of the products form. For reactions that go to equilibrium, a *K* equation is needed to calculate the particle concentrations at equilibrium.

This we will call weak acid-base Rule

> **1.** In calculations involving acids and [particles],
>
> - For *100%* ionization (as in HCl or HNO_3 solutions), use the ***REC*** steps.
> - For *slight* ionization (as in weak acid solutions), use ***WRECK*** steps.

The *WRECK* Steps For Weak Acid Ionization

For *all* weak acid ionizations, the general ***R*** and ***E*** (Reaction and Extent) can be written

$$\textbf{1 WA} \quad \leftarrow\leftarrow\rightarrow \quad \textbf{1 H}^{+} + \textbf{1 conjugate base (CB)} \qquad \text{(goes slightly)}$$

Since the reaction does not go to completion, the *WRECK* steps are needed to solve calculations. Write the ***K*** expression for this general reaction above.

* * * * *

$$K_a \equiv \frac{[H^+]_{\text{at eq.}} \bullet [CB]_{\text{at eq.}}}{[WA]_{\text{at equilibrium}}} \qquad \textbf{(Definition)}$$

Because this ionization forms $\mathbf{H^+}$, the ***K*** is a $K_\mathbf{a}$. The $[\ ]_{\text{at equilibrium}}$ subscript is often omitted as understood in *K* expression terms, but in this case it will be helpful to emphasize in the discussion that follows.

In Lesson 28F, to solve *K* calculations, we used a *RICE* table. However, compared to general *K* calculations, K_a *RICE* tables are simplified because

- There is only one reactant and it is always a weak acid.
- One product is always $[H^+]$ or $[H_3O^+]$ and the other is the conjugate base.
- The initial quantities of the products are zero.
- The coefficients are always **1** weak acid particle used up *equals* **1** H^+ ion formed *and* **1** conjugate base formed

This means:

> For *all* weak acid ionization or hydrolysis, the general *RICE* table in moles or mol/L is the same

We use *RICE* tables in *K* calculations to find particle moles or moles/liter at equilibrium: the numbers in the *RICE* table bottom row. However, because all weak acid ionization calculations are so similar, instead of writing a *RICE* table for each problem, it is quicker to instead write the key first and last *RICE rows* by inspection as part of the *WRECK* steps.

Let's walk through the logic of abbreviating the *RICE* table with the ***WRECK*** steps.

1. **<u>Use x to represent small concentrations.</u>**

   Since the coefficients in a weak acid ionization are all *one*,

   $$\underline{1}\ \text{WA} \quad \leftarrow\!\leftarrow\!\rightarrow \quad \underline{1}\,\text{H}^+ + \underline{1}\ \text{conjugate base} \qquad \text{(goes slightly)}$$

   the *ratio* of moles of weak acid *used up* to *moles* $\mathbf{H^+}$ *formed* to moles of conjugate base (**CB**) *formed* is always **1** to **1** to **1**.

   Since all of the particles in an ionization reaction are dissolved in the same volume of solution, the moles *per liter* ratios are also **1** to **1** to **1**. This means that *all three* of the following concentrations can be represented by an x representing a relatively small concentration.

   $$x = small = [\mathbf{WA}]_{\text{that } ionizes} = [\mathbf{H^+}]_{\text{formed}} = [\mathbf{CB}]_{\text{formed}}$$

2. <u>The ***REC*** steps</u>. In a solution, the [WA] at equilibrium, *after* ionization, is usually difficult to measure directly. However, the mol/L of weak acid that we *originally added* to *mix* the solution is usually a quantity that we know.

   Substituting x from the equality above simplifies the math. By definition:

   $$[\mathbf{WA}]_{\textbf{at eq.}} \equiv [\mathbf{WA}]_{\textbf{mixed}} - \text{small } [\mathbf{WA}]_{\text{that } ionizes} \equiv [\mathbf{WA}]_{\textbf{mixed}} - x$$

   If we can solve for x, we solve for *four* quantities:

   $$x = [\mathbf{H^+}]_{\text{formed}} = [\mathbf{CB}]_{\text{formed}} = [\mathbf{WA}]_{\text{that } ionizes} \text{ plus } [\mathbf{WA}]_{\textbf{at eq.}} \ (\equiv [\mathbf{WA}]_{\textbf{mixed}} - x)$$

   Substitute into the blanks in the ***C*** step below a symbol for each concentration. Write a term that *includes* x and uses the symbols for measurable concentrations in the equalities above.

   Reaction and ***E***xtent: 1 **WA** ←←→ **1 H⁺** + **1** CB (goes slightly)
   ^ ^ ^

   Conc. At Equilib.: ________________ ___ ___

   * * * * *

   Reaction and ***E***xtent: 1 **WA** ←←→ **1 H⁺** + **1** CB (goes slightly)
   ^ ^ ^

   Conc. At Equilib.: $[\mathbf{WA}]_{\textbf{mixed}} - x$ x x

   The ***C*** row will be the same for *all* weak acid ionization reactions.

3. **<u>The *K* step</u>.** Substitute into the ***K*** definition, for each of the three *concentration* terms below, the symbol for that term that includes x from the ***C*** row above.

   $$K_a \equiv \frac{[\text{H}^+]_{\text{at eq.}} \bullet [\text{CB}]_{\text{at eq.}}}{[\text{WA}]_{\text{at eq.}}} \equiv \underline{\qquad\qquad\qquad\qquad}$$

   * * * * *

$$K_a \equiv \frac{[H^+]_{\text{at eq.}}[CB]_{\text{at eq.}}}{[WA]_{\text{at eq.}}} \equiv \frac{x^2}{[WA]_{\textbf{mixed}} - x} \equiv K_a$$

^ *Definition* based on ***R*** row ^ *Exact* based on ***C*** row

Both of the K_a equations above are true at equilibrium, but the exact form of the equation has an advantage. Our goal is usually to solve for x, and the exact equation can be solved for x if the K_a value and the [WA *as mixed*] are known, as they usually are.

However, because the exact equation has both x^2 and x terms, it is a quadratic equation (see Lesson 28J). To solve exactly, you can solve for **a**, **b**, and **c**, and then use the quadratic formula.

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

The steps needed to solve a quadratic are not difficult, but they are time-consuming. For most weak acid calculations, the following approximation may be used which solves for x more *quickly*.

4. **<u>The *K* approximation</u>**. In a weak acid solution, the value of x is small compared to the value of the [WA] as mixed. Using the approximation rule from the previous lesson, write the simplified, approximate term in the blank below.

$$[WA]_{\text{at equilibrium}} \equiv [WA]_{\text{mixed}} - x \approx \underline{\qquad\qquad}$$

* * * * *

$$[WA]_{\text{at equilibrium}} \equiv [WA]_{\text{mixed}} - x \approx \mathbf{[WA]_{mixed}}$$

When a small quantity is added to or subtracted from a larger quantity, the larger quantity remains approximately the same. In a weak acid solution, the weak acid concentration at equilibrium is not very different from the concentration as mixed.

Now fill in the box below: write an approximation based on the exact equation.

$$K_a \equiv \frac{[H^+]_{\text{eq.}}[CB]_{\text{eq.}}}{[WA]_{\text{at eq.}}} \equiv \frac{x \bullet x}{[WA]_{\text{mixed}} - x} \approx \boxed{\qquad\qquad\qquad}$$

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The K_a expression can be simplified to this *approximation*:

$$K_a \equiv \frac{[H^+]_{\text{eq.}}[CB]_{\text{eq.}}}{[WA]_{\text{at eq.}}} \equiv \frac{x^2}{[WA]_{\text{mixed}} - x} \approx \boxed{\frac{x^2}{[WA]_{\text{mixed}}} \approx K_a}$$

^ Definition ^Exact ^ Approximation

The small ($-x$) difference between the *exact* and the *approximation* equation means that solving the exact equation for x requires solving a quadratic, while solving the approximation requires only a square root. The approximation can therefore be solved more *quickly*. For K_a calculations, we will first solve the *approximation* equation, and in most cases the approximation will be an acceptable answer.

Summary

For weak acid dissociation (ionization) reactions, these are always the *same*:

- The general reaction: WA ←←→ H^+ + CB
- The *RICE* table.
- The ***WRECK*** steps.
- The ***C*** step (which is the same as the bottom row of the *RICE* table).
- The ***K*** step: the definition, exact, and approximate expressions.

In weak acid ionization (K_a) calculations, all that will vary are the specific formulas for WA and CB, and the values for $[WA]_{\text{as mixed}}$, $\boldsymbol{x}$, and K_a. By representing each weak acid ionization with the *general* reaction equation, we can simplify problem-solving.

Practice A: Check your answers as you go.

1. For the ionization of the weak acid WA to form a proton and its conjugate base (CB),
   a. Write the ***REC*** steps. In the ***C*** row, each term should include $\boldsymbol{x}$.
   b. Write the K_a definition based on the **R** row reaction..
   c. Write the K_a exact equation using ***C*** row terms that include $\boldsymbol{x}$.
   d. Write the K_a approximation equation.
2. For the ionization of the weak acid NH_4^+ :
   a. Write the ***R***eaction and its ***E***xten***t***, using the particle formulas in the reaction.
   b. Below the ***R***eaction and ***E***xten***t***, write the ***C***oncentrations at equilibrium, defined so that each term includes $\boldsymbol{x}$.
   c. Write the K_a definition equation, using the particle formulas.
   d. Write the K_a exact equation based on the terms in the ***C*** step.
   e. Write the K_a approximation equation, based on the answer in part d.

K_a Calculations

We will solve K_a calculations in the same way we solved K calculations: by writing the *WRECK* steps. To simplify K_a calculations, we will add a step: we will write *both* the reaction showing the particles for the specific weak acid and then the general reaction equation for *all* weak acids. These two ***R*** steps will define the terms in the equations.

We will then solve all weak acid calculations using the same general equations. Our rule will be weak acid rule

> **2. <u>The K_a Prompt:</u>** If a problem involves a ***weak acid*** or K_a and [ions], write the ***WRRECK*** steps.
>
> - **W**ANTED: Write the general and specific symbol WANTED.
> - Write the *specific* **R**eaction using the symbol for the particles in the problem, then write these *general* ***R, E, C,*** and ***K*** steps***:***
>
>   ***R***xn. and ***E***xtent: **WA** $\leftarrow\leftarrow\rightarrow$ **H$^+$** + **conjugate base** (goes slightly)
>
> - ***C***onc. at Eq: $[WA]_{mixed} - x$ x x
> - $$K_a \equiv \frac{[H^+]_{eq.}[CB]_{eq.}}{[WA]_{at\ eq.}} \equiv \frac{x^2}{[WA]_{mixed} - x} \approx \boxed{\frac{x^2}{[WA]_{mixed}} \approx K_a}$$
>
>   ^Definition   ^ Exact   ^Approximation
>
> c. SOLVE the K_a *approximation* equation for the WANTED symbol.

<u>In short:</u> See weak acid or K_a and [ions]? Write ***WRRECK,*** solve the approximation.

Use the rules above on this example..

Q. In a 2.0 M acetic acid (CH_3COOH) solution, calculate the [H$^+$] (K_a = 1.8 x 10^{-5})

* * * * *

<u>Answer</u>

<u>*W*</u>ANT: **[H$^+$]** = x

For calculations involving K_a, apply the WRRECK steps

*Specific **R***: 1 CH_3COOH $\leftarrow\leftarrow\rightarrow$ 1 H^+ + 1 CH_3COO^-

<u>***R***</u> & <u>***E***</u>: 1 WA $\leftarrow\leftarrow\rightarrow$ 1 H^+ + 1 CB (goes slightly)

<u>***C***</u>onc. **at Eq:** $[WA]_{mixed} - x$ x x

$$K_a \equiv \frac{[H^+]_{eq.}[CB]_{eq.}}{[WA]_{at\ eq.}} \equiv \frac{x^2}{[WA]_{mixed} - x} \approx \boxed{\frac{x^2}{[WA]_{mixed}} \approx K_a}$$

^Definition   ^ Exact   ^Approximation

Solve the boxed *approximation*. Start with a DATA TABLE using the equation *symbols.*

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DATA: x = **[H$^+$] = ?**

$[WA]_{mixed} = [CH_3COOH]_{mixed}$ = 2.0 M

K_a = 1.8 x 10^{-5}

Use those values to solve the approximation for the WANTED symbol.

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Since $\boxed{K_a \approx \frac{x^2}{[\text{WA}]_{\text{mixed}}}}$ Substituting: $1.8 \times 10^{-5} = \frac{x^2}{2.0}$

Solve for x^2, then x.

* * * * *

$$x^2 = (K_a)\,([\text{WA}]_{\text{mixed}}) = (1.8 \times 10^{-5})\,(2.0) = 3.6 \times 10^{-5} = 36 \times 10^{-6}$$

$x = ? = \boxed{6.0 \times 10^{-3}\ \text{M} = [\text{H}^+]}$ (Solving a K for [ ], add M as the unit.)

Practice B. Do both problems. If in doubt, check your answers after each part.

1. Hydrogen cyanide (HCN) is both a weak acid and a notorious poison.
   a. Calculate the $[H^+]$ in a 0.50 M HCN solution. Use $K_a = 6.2 \times 10^{-10}$ for HCN .
   b. Calculate the pH of the HCN solution.
2. The weak acid hydrogen fluoride (HF) is used to etch glass. The $[F^-]$ in a 0.25 Molar HF solution is measured to be 0.012 Molar.
   a. Find the K_a value for HF at the temperature of this experiment.
   b. What is the pH of the solution?
   c. What is the $[OH^-]$ in this HF solution?

ANSWERS

Practice A

1a. ***R&E***: $1\ \text{WA} \leftleftarrows\!\rightarrow 1\ \text{H}^+ + 1\ \text{CB}$ (goes slightly)

Cat eq.: $[\text{WA}]_{\text{mixed}} - x$ $\quad x \quad x$

$$K_a \equiv \frac{[\text{H}^+]_{\text{eq}}[\text{CB}]_{\text{eq}}}{[\text{WA}]_{\text{eq.}}} \equiv \frac{x^2}{[\text{WA}]_{\text{mixed}} - x} \approx \frac{x^2}{[\text{WA}]_{\text{mixed}}}$$

1b,c,d. ^ Definition ^Exact ^Approximation

2a. ***R&E***: $1\ \text{NH}_4^+ \leftleftarrows\!\rightarrow 1\ \text{H}^+ + 1\ \text{NH}_3$ (goes slightly)

2c. $K_a \equiv \frac{[\text{H}^+]_{\text{eq}}[\text{NH}_3]_{\text{eq}}}{[\text{NH}_4^+]_{\text{at eq}}}$

2b. ***C***at eq.: $\mathbf{[NH_4^+]_{mixed}} - x$ $\quad x \quad x$

2d. $K_a \equiv \frac{x \cdot x}{[\text{NH}_4^+]_{\text{mixed}} - x}$

1e. $K_a \approx \frac{x^2}{[\text{NH}_4^+]_{\text{as mixed}}}$

Practice B

1a. If K_a *and [ions]* are mentioned, write the *WRRECK's,* solve the approximation.

WANTED: $[H^+]$ = **?**

Specific **R**eaction: 1 HCN ←← → 1 H^+ + 1 CN^- (goes slightly)

R&**E**: 1 WA ←← → 1 H^+ + 1 CB (goes slightly)

Conc. at Eq: $[WA]_{mixed} - x$ $\quad x \quad x$

$$K_a \equiv \frac{[H^+]_{eq}[CB]_{eq}}{[WA]_{at\ eq.}} \equiv \frac{x^2}{[WA]_{mxd} - x} \approx \boxed{\frac{x^2}{[WA]_{mixed}} \approx K_a}$$

^ Definition ^Exact ^Approximation

Solve the K_a approximation for the WANTED symbol.

$$x^2 \approx (K_a)([WA]_{mixed}) = (6.2 \times 10^{-10})(0.50) = 3.1 \times 10^{-10}$$

$$x = [H^+] = ? \approx (\text{estimate: } 1\text{-}2 \times 10^{-5}) \approx \boxed{1.8 \times 10^{-5}\ M = [H^+]}$$

1b. See pH? Write $\boxed{\mathbf{pH} \equiv -\log [H^+] \quad \text{and} \quad [H^+] \equiv 10^{-pH}}$

WANT **pH** = $-\log(1.8 \times 10^{-5})$ = estimate **4.?** = $\boxed{4.74}$ (4.74 rounded up = 5: Check.)

2a. If K_a *and [ions]* are mentioned, write the *WRRECK's,* solve the approximation.

WANTED: K_a = **?**

Specific **R**eaction: 1 HF ←← → 1 H^+ + 1 F^- (goes slightly)

R&**E**: 1 WA ←← → 1 H^+ + 1 CB (goes slightly)

Conc. at Eq: $[WA]_{mixed} - x$ $\quad x \quad x$

$$K_a \equiv \frac{[H^+]_{eq}[CB]_{eq}}{[WA]_{at\ eq.}} \equiv \frac{x^2}{[WA]_{mxd} - x} \approx \boxed{\frac{x^2}{[WA]_{mixed}} \approx K_a}$$

^ Definition ^Exact ^Approximation

Solve the K_a approximation for the WANTED symbol.

$$? = K_a \approx \frac{x^2}{[WA]_{mixed}} \approx \frac{(1.2 \times 10^{-2})^2}{0.25} \approx \frac{1.44 \times 10^{-4}}{0.25} = \boxed{5.8 \times 10^{-4}}$$

Or, since this problem supplies x, you can easily solve the exact equation:

$$? = K_a = \frac{x^2}{[WA]_{mixed} - x} = \frac{(1.2 \times 10^{-2})^2}{0.25 - 0.012} \approx \frac{1.44 \times 10^{-4}}{0.238} = \boxed{6.1 \times 10^{-4}}$$

A K value is not assigned units.

Note that the two answers are close. Since K values have high uncertainty, if the approximation is within 5% of the exact answer, solving with the approximation is considered "close enough."

b. pH? $\boxed{\mathbf{pH} \equiv -\log [H^+] \quad \text{and} \quad [H^+] \equiv 10^{-\mathbf{pH}}}$

WANT: $\mathbf{pH} = -\log \mathbf{[H^+]} = -\log (1.2 \times 10^{-2}) = \mathbf{1.?} = \mathbf{1.92}$ (estimate, then calculate.)

c. In an acid solution, find $[H^+]$ using acid rules, then $[OH^-]$ using K_w.

DATA: $\mathbf{[H^+]} = \boldsymbol{x} = \mathbf{0.012\ M} = \mathbf{1.2 \times 10^{-2}\ M}$ (from Part a)

SOLVE: $\boldsymbol{K_w} = \boxed{[H^+][OH^-] = 1.0 \times 10^{-14}}$

$$\mathbf{[OH^-]} = \frac{1.0 \times 10^{-14}}{\mathbf{[H^+]}} = \frac{1.0 \times 10^{-14}}{\mathbf{1.2 \times 10^{-2}}} = 0.83 \times 10^{-12} = \mathbf{8.3 \times 10^{-13}\ M}$$

(K_w check: $[H^+] \times [OH^-]$ (circled) must estimate to $\mathbf{10.0} \times 10^{-\mathbf{15}}$ or $\mathbf{1.0} \times 10^{-\mathbf{14}}$).

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Lesson 30D: Percent Dissociation – and Shortcuts

Moving Numbers Instead of Symbols

For past calculations that use equations, we have solved in symbols before plugging in numbers. We did so because when using algebra, symbols can be written more quickly than numbers with their units. In K calculations, however, you may choose to plug numbers into the K equation and *then* do the algebra. Why? The numbers without units used in K calculations often move more quickly than symbols.

The downside is that in K_a as in other K calculations, you lose unit cancellation as a check on your algebra. This means that in ***K*** calculations, you must *double* check your math.

Solving the Approximation Directly

It is important to be able to solve K_a calculations by writing out the methodical ***WRRECK*** steps. For upcoming problems that are more complex, we will need those methodical steps. However, once you master the ***WRRECK*** steps, you may solve K_a calculations by writing these WA *quick* steps (***WASS***): ***W***ANTED, ***A***pproximation, ***S***ubstitute, ***S***olve.

- Write the WANTED symbol.
- Write the K_a approximation equation: $\boxed{K_a \approx \dfrac{x^2}{[\text{WA}]_{\text{mixed}}}}$
- Substitute the DATA and solve the approximation for the WANTED symbol.

Try those steps on this problem.

Q. Hypochlorous acid ionizes by this reaction.

$HOCl \leftrightarrows H^+ + OCl^-$ $\qquad K_a = 3.5 \times 10^{-8}$

Calculate the $[H^+]$ in a 0.40 M HOCl solution.

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Answer

***W**ANTED:* $[H^+] = x$

Since hypochlorous acid has a small K_a , it is a *weak acid*.

Using the WA *quick* steps, write the K_a approximation, substitute, solve.

$$\boxed{K_a \approx \frac{x^2}{[WA]_{mixed}}} \qquad \text{Substituting:} \quad 3.5 \times 10^{-8} = \frac{x^2}{0.40}$$

SOLVE: To find x WANTED, first solve for x^2.

$x^2 = (3.5 \times 10^{-8}) \times (0.40) = 1.4 \times 10^{-8}$

$x = \boxed{\mathbf{1.2 \times 10^{-4}\ M = [H^+]}}$ (When solving a K for [ ], add M as the unit.)

Practice A

1. Using the quick steps, calculate the pH of a 0.50 M formic acid (HCOOH) solution ($K_a = 1.8 \times 10^{-4}$).

Percent Dissociation

P**ercent dissociation**, **Percent ionization, percent dissociation,** and **percent hydrolysis** are all terms that have the same meaning. The percent dissociation is simply the percentage of the original weak acid concentration that ionizes. Since [WA that ionizes] = x , for equation consistency we will write as weak acid Rule

3. $$\boxed{\textbf{\% Dissociation} \equiv \frac{x}{[WA]_{mixed}} \bullet \mathbf{100\%}} \equiv \frac{[WA]_{ionized}}{[WA]_{mixed}} \bullet 100\%$$

The dissociation terminology and the definition equations must be committed to memory.

When calculations involve fractions that must be found using conversions, our rule is: work in fractions rather than percentages. However, since problems with this equation generally involve straightforward substitution for symbols, we will use the equation as it is defined above.

Apply the definition to the following problem..

Q. Benzoic acid ionizes to form the benzoate ion.

$$C_6H_5COOH \leftrightarrows H^+ + C_6H_5COO^- \qquad K_a = 6.3 \times 10^{-5}$$

a. Calculate the $[H^+]$ in a 0.040 M benzoic acid solution.
(Use the quick steps: solve the approximation equation directly.)

b. Calculate the percent dissociation in the solution.

* * * * *

Answer

a. WANTED: $[H^+] = x = ?$

To solve using the WA quick steps,

$$\boxed{K_a \approx \frac{x^2}{[WA]_{mixed}}}$$

Substituting: $6.3 \times 10^{-5} \approx \dfrac{x^2}{0.040 \text{ M}}$

SOLVE: To find the x WANTED, first solve for x^2.

$x^2 \approx (6.3 \times 10^{-5})(0.040) = 2.5 \times 10^{-6}$

$? = x \approx$ (estimate $1\text{-}2 \times 10^{-3}$) $\approx \boxed{\mathbf{1.6 \times 10^{-3}\ M = [H^+]}}$

If needed, adjust your work and then try part b.

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b. Watch for the answer from one part to be used as DATA for later parts.

Since the dissociation equation is simple, you may solve without listing the symbols and values in a DATA table.

SOLVE: $\boxed{\textbf{\% Dissoc.} = \frac{x}{[WA]_{mixed}} \bullet 100\%} = \dfrac{\mathbf{1.6 \times 10^{-3}\ M}}{4.0 \times 10^{-2}\text{ M}} \bullet 10^2\ \% = \boxed{\mathbf{4.0\ \%}}$

In 0.040 M C_6H_5COOH at 25°C, **4.0%** of the weak acid is ionized.

Practice B

1. For a weak acid solution, $[H^+]$ is 2.0×10^{-3} M at [WA] = 0.40 M. Find the percent of ionization of the weak acid.
2. A 2.0 Molar solution of a monoprotic weak acid has a pH of 4.49 .
   a. Calculate the $[H^+]$ in the solution.
   b. Calculate the percentage of ionization in this solution.
3. If the weak acid in a 0.50 M solution is 0.30% dissociated, what is its K_a ?

ANSWERS

Practice A

1. WANTED: **pH** pH Prompt: $\boxed{\mathbf{pH} \equiv -\log [H^+] \quad \text{and} \quad [H^+] \equiv 10^{-\mathbf{pH}}}$

First find $[H^+]$.

The quick steps: Write the **w**anted unit, K approximation equation, **s**ubstitute, and **s**olve.

$$K_a \approx \frac{x^2}{[WA]_{mixed}} = \frac{x^2}{0.50} = 1.8 \times 10^{-4}$$

$x^2 = (1.8 \times 10^{-4})(0.50) = 0.90 \times 10^{-4} = 90 \times 10^{-6}$

$x = [H^+] = \mathbf{?} = 9.5 \times 10^{-3}$ M

WANT: **pH** = — log [**H⁺**] = — log (9.5 x 10⁻³) = **2.?** = **2.02** (estimate, then calculate.)

Practice B

1. WANT: Percent ionization = Percent dissociation Write the equation using the WANTED term.

$$\%\ \text{Dissociation} = \frac{x}{[WA]_{mixed}} \bullet 100\%$$

Make a DATA table using the equation terms.

DATA: $\mathbf{[WA]}_{mixed} = 0.40$ M

$x = [H^+] = 2.0 \times 10^{-3}$ M.

SOLVE:

$$\%\ \text{Dissociation.} = \frac{x}{[WA]_{mixed}} \bullet 100\% = \frac{2.0 \times 10^{-3}\ \text{M}}{0.40\ \text{M}} \bullet 10^2\ \% = 5.0 \times 10^{-1}\ \% = \mathbf{0.50\ \%}$$

2a. pH Prompt: $\boxed{\mathbf{pH} \equiv -\log [H^+] \quad \text{and} \quad [H^+] \equiv 10^{-\mathbf{pH}}}$

WANT: $\mathbf{[H^+]} = ? = x$

For K_a and [ions], write the *WRRECK's*, *but* K_a is *not* mentioned in this problem.

Want $[H^+]$ and know pH. The relationship between the two that solves for $[H^+]$ is:

$$\boxed{[H^+] = 10^{-\mathbf{pH}}} = 10^{-\mathbf{4.49}} = \boxed{\mathbf{3.2 \times 10^{-5}\ M = [H^+]}}$$ (check: 4.49 up = 5)

b. For weak acids, $x = \mathbf{[H^+]}$ from part a.

$$\%\ \text{Ionization} = \boxed{\mathbf{\%\ Dissoc.} = \frac{x}{\mathbf{[WA]}_{mixed}} \bullet \mathbf{100\%}} = \frac{\mathbf{3.2 \times 10^{-5}}\ \text{M}}{2.0\ \text{M}} \times 10^2\ \mathbf{\%} = 1.6 \times 10^{-3}\ \% = \boxed{0.0016\ \%}$$

3. WANT: K_a Write needed equations based on the terms used in the problem.

$$\%\ \text{Dissociation} = \frac{x}{[WA]_{mixed}} \bullet 100\%$$

$$K_a \approx \frac{x^2}{[WA]_{mixed}} \qquad \text{(Approximation)}$$

DATA: $[WA]_{mixed} = 0.50$ M

% Dissociation = 0.30 %

In this problem, the % dissociation equation above has one unknown value, and the *K* approximation has two. Begin by substituting into the top equation to find *x*.

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$$0.30\ \% = \frac{x}{0.50\text{ M}} \bullet 100\% \quad ; \quad x = (0.30\ \%/100\%) \bullet 0.50\text{ M} = \mathbf{0.0015\ M = 1.5 \times 10^{-3}\ M}$$

SOLVE for the WANTED symbol:

$$K_a \approx \frac{x^2}{[\text{WA}]_{\text{mixed}}} \approx \frac{(1.5 \times 10^{-3})^2}{0.50} \approx \mathbf{4.5 \times 10^{-6}}$$

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Lesson 30E: Solving K_a Using the Quadratic Formula

Timing: Do this lesson *if* you are asked to solve K_a calculations using the *5% test* and/or the quadratic formula.

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The 5% Test

So far, we have solved K_a calculations using the K_a *approximation*. For weak acid ionization, the only difference between the K_a *exact* equation and the K_a *approximation* equation is the $-x$ term in the denominator.

$$K_a \equiv \frac{[\text{H}^+][\text{conjugate}]}{[\text{WA}]_{\text{mixed}} - x} \qquad \boxed{\approx \frac{x^2}{[\text{WA}]_{\text{mixed}}}}$$

^Exact ^Approximation

If x is small, the $-x$ term does not substantially change the answer, and the above approximation may be used. However, if a weak acid solution is very dilute, and/or the weak acid is close to being a strong acid and ionizes to a significant extent, x may not be relatively small, and the approximation can introduce significant error in K_a calculations.

When can you safely use the K_a approximation and solve using squares and square roots? When must you use exact Equation 2 and solve the quadratic formula?

The generally accepted rule is that if the percent dissociation (ionization) is *less than 5%*, using the approximation is permitted. In most experiments involving K_a, a *5%* variation is within the range of experimental error.

When solving a K_a equation, the *approximation* equation is solved *first*. The **5% test** is then applied to the answer by calculating the *% dissociation*. If the % dissociation is 5% or less, the approximation result is accepted. If the percent dissociation is more than 5%, the calculation is done again, with the original problem data substituted into the *exact* equation. The exact equation is then converted to the general quadratic *format*. The quadratic *formula* is then solved to find x.

We will add this rule to our steps for solving K_a calculations:

> In K_a calculations,
> - SOLVE first for the WANTED symbol using the *approximation* equation.
> - Calculate % dissociation. IF greater than 5%, solve the exact K_a quadratic.

Solving K_a with the Quadratic Formula

Weak acid calculations in which the dissociation is more than 5% error generally involve weak acids that either are not very weak (those with a K_a of 10^{-6} or larger) *or* are very dilute solutions.

Try this example in your notebook, then check the answer below.

Q. In a 0.010 M HF solution at 25°C (K_a HF = 6.8×10^{-4}),

a. find $[H^+]$ using the approximation equation.

b. Does the HF in this solution ionize more than 5%?

* * * * *

Answer

Part a: WANT: $[H^+] = x$

$$K_a \approx \frac{x^2}{[WA]_{mixed}}$$

$$x^2 \approx (6.8 \times 10^{-4})(0.010) = 6.8 \times 10^{-6}$$

$$x = ? \approx (\text{estimate } 2\text{-}3 \times 10^{-3}) \approx \boxed{2.6 \times 10^{-3}\ M \approx [H^+]}$$ Now try *Part b*.

* * * * *

Part b:

WANT: $\boxed{\%\ \text{Dissociation} = \frac{x}{[WA]_{mixed}} \bullet 100\%} = \frac{2.6 \times 10^{-3}}{1.0 \times 10^{-2}} \bullet 10^2\ \% = \mathbf{26\ \%}$

Applying the 5% test, because the % dissociation is 26%, the x value is too high to use the approximation equation. In such cases, the *exact* K_a equation should be solved. Write the *exact* form of the K_a equation, then substitute the values for K_a and [WA].

* * * * *

$$K_a \equiv \frac{x^2}{[WA]_{mixed} - x} \qquad \text{Substituting:} \quad 6.8 \times 10^{-4} = \frac{x^2}{0.010 - x}$$

The substituted equation is a quadratic because it has x^2 and x terms. Solve the substituted equation above for x by applying the quadratic formula. Use an online or handheld calculator if permitted for solving quadratics in your course. Refer to Lesson 28J if needed.

* * * * *

Begin by converting the numeric equation into the quadratic *format*: $ax^2 + bx + c = 0$,

$$6.8 \times 10^{-4} = \frac{x^2}{0.010 - x}$$

$$6.8 \times 10^{-4}\,(0.010 - x) = x^2$$

$$6.8 \times 10^{-6} - (6.8 \times 10^{-4})\,x = x^2$$

$$\mathbf{x^2 + (6.8 \times 10^{-4})(x) - 6.8 \times 10^{-6} = 0}$$

To solve for x, substitute values for **a**, **b,** and **c** into the quadratic formula.

* * * * *

a = 1 , **b** = 6.8×10^{-4} , **c** = -6.8×10^{-6} . For substituting into an online quadratic calculator, you may need to convert to **a** = 1, **b** = 0.000 68, **c** = −0.000 006 8 .

Solving without the online calculator by substituting into the quadratic formula:

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-(6.8 \times 10^{-4}) \pm \{(-6.8 \times 10^{-4})^2 - 4(1)(-6.8 \times 10^{-6})\}^{1/2}}{2(1)} =$$

$$x = \frac{(-6.8 \times 10^{-4}) \pm \{(+\ 46.2 \times 10^{-8}) + (27.2 \times 10^{-6})\}^{1/2}}{2} =$$

$$x = \frac{(-6.8 \times 10^{-4}) \pm \{(+\ 0.462 \times 10^{-6}) + (27.2 \times 10^{-6})\}^{1/2}}{2} =$$

$$x = \frac{(-6.8 \times 10^{-4}) \pm (+\ 27.7 \times 10^{-6})^{1/2}}{2} = \frac{(-6.8 \times 10^{-4}) \pm (+\ 5.26 \times 10^{-3})}{2} =$$

$$x = \frac{(-0.68 \times 10^{-3}) + (5.26 \times 10^{-3})}{2} \quad \text{OR} \quad x = \frac{(-0.68 \times 10^{-3}) - (+\ 5.26 \times 10^{-3})}{2}$$

$$x = \frac{(+\ 4.58 \times 10^{-3})}{2} \quad \text{OR} \quad x = \frac{-\ 5.94 \times 10^{-3}}{2}\ ;\ x = \mathbf{+\ 2.29 \times 10^{-3}} \quad \text{OR} \quad x = \mathbf{-\ 2.97 \times 10^{-3}}$$

Since x is a concentration, and concentrations cannot be negative, $\boxed{x = \mathbf{2.3 \times 10^{-3}\ M}}$

Using the approximation equation in Part a**,** x was **0.0026 M**. Using the exact equation, x = **0.0023 M.** The difference between those answers is roughly 12%. For a weak acid that is not very weak, the exact formula provides significantly more accurate answers.

Practice

Use the exact K_a equation to solve. Use an online quadratic formula calculator or handheld calculator for assistance if it is allowed in your course.

1. In a 0.010 M CH_3COOH solution, find the $[H^+]$. ($K_a = 1.8 \times 10^{-5}$)

ANSWERS

1. WANTED = $[H^+]$ = $\boldsymbol{x}$. The exact K_a equation based on the original [WA] as mixed, is

$$K_a \equiv \frac{x^2}{[WA]_{mixed} - x} \qquad \text{Substituting:} \qquad 1.8 \times 10^{-5} = \frac{x^2}{0.010\text{ M} - x}$$

Since the equation includes x^2 and x terms, it is a quadratic.

To solve, convert to the quadratic format, then solve the quadratic formula.

$$x^2 = (1.8 \times 10^{-5})(0.010\text{ M} - x)$$

$$x^2 = (1.8 \times 10^{-7}) - (1.8 \times 10^{-5})x$$

$$x^2 + (1.8 \times 10^{-5})x - (1.8 \times 10^{-7}) = 0$$

a = 1 , b = 1.8×10^{-5} , c = -1.8×10^{-7} For a quadratic calculator, you may need to input

a = 1 , **b** = 0.000 018 , **c** = — 0.000 000 18

Substituting these values into a quadratic equation calculator to solve:

$x = +4.15 \times 10^{-4}$ ***or*** $x = -4.33 \times 10^{-4}$

Since x is a concentration and must be positive, $\boxed{x = 4.2 \times 10^{-4}\text{ M} = [H^+]}$

* * * * *

Lesson 30F: Weak Bases and K_b Calculations

Timing: Do this lesson *if* you are assigned calculations involving K_b.

* * * * *

Weak Bases

A **base** reacts with water to produce $\mathbf{OH^-}$ ions and the **conjugate acid** of the base.

The strong bases NaOH and KOH will dissociate (ionize) ~100% when dissolved in water. For a weak base (**WB**), only a small percentage of particles will react with water.

An example of the reaction of a weak base and water occurs in the mixture of ammonia (NH_3) and water, a solution used in many glass-cleaning products. When ammonia gas is dissolved in water, a small percentage of the NH_3 molecules react by removing a proton from a water molecule. This *hydrolysis* (reaction with water) of a base can be represented as

Specific: $NH_3(aq) + H_2O(l) \leftarrow\leftarrow\rightarrow \mathbf{OH^-}(aq) + NH_4^+(aq)$ (goes slightly)

General: $WB + H_2O \leftarrow\leftarrow\rightarrow \mathbf{OH^-}$ + conjugate acid (goes slightly)

The formation of OH^- ions in the reaction with water makes ammonia a *base*. The small percentage of ammonia molecules that react means that ammonia is a *weak* base.

The reaction of a weak base with water is reversible, and in the closed system of an aqueous solution the reaction will go to equilibrium. The equilibrium constant expression for the hydrolysis of a weak base is given the symbol $\boldsymbol{K_b}$.

Write the *K* expressions for the general and specific reactions above.

* * * * *

General: $K_\mathbf{b} = \dfrac{\mathbf{[OH^-]}\,[\text{conjugate acid}]}{[\text{WB}]}$ Specific: $K_\mathbf{b} = \dfrac{\mathbf{[OH^-]}\,[NH_4^+]}{[NH_3]}$

with all concentrations measured at equilibrium.

A $K_\mathbf{b}$ expression always has **$[OH^-]$** on *top* and [WB] on the bottom.

As in the case of K_a and K_w expressions, the concentration of liquid water is not included in the K_b expression. In most weak base solutions, the concentration of water remains very high and essentially constant during hydrolysis reactions.

One difference between weak acids and weak bases is that a weak acid nearly always *contains* an H atom and *loses* an H^+ ion when it ionizes or hydrolyzes ("Lewis acids" are an exception). In contrast, as in the case of NH_3 above, most *weak* bases do *not* contain OH^- ions, so that they do not dissociate (ionize) to lose them. Instead, most weak bases *create* an OH^- by hydrolysis: by reacting with water to *remove* an H^+ from H—OH.

For example, the weak acid behavior of acetic acid can be represented as either

ionization: $CH_3COOH(aq) \leftleftarrows\rightarrow \mathbf{H^+}(aq) + CH_3COO^-(aq)$

or *hydrolysis*: $CH_3COOH(l) + \mathbf{H_2O(l)} \leftleftarrows\rightarrow \mathbf{H_3O^+}(aq) + CH_3COO^-(aq)$

but the weak base behavior of ammonia (NH_3) can only be represented by hydrolysis:

$$NH_3(aq) + H\text{—}OH(l) \leftleftarrows\rightarrow NH_4^+(aq) + \mathbf{OH^-}(aq)$$

As with weak acids, the values of K_b for the hydrolysis of weak bases will be between 1.0 and 10^{-16}. The equilibrium constant *equation* for the hydrolysis of ammonia is

$$K_\mathbf{b} = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} \text{ at } 25^\circ C.$$

K_b Calculation Rules

The rules for calculations involving weak bases and K_b are similar to those for weak acids and K_a. Compare:

1. Acids hydrolyze (react with water) to form H_3O^+ ions.

   Bases hydrolyze (react with water) to form **OH^-** ions.

2. Weak acids react with water (ionize slightly in water) to form H_3O^+ (or H^+) ions.

   Weak bases *react with water* slightly to form **OH^-** ions.

3. In acid-base reactions, acid particles lose an H^+ to form the conjugate base particle.

   In acid-base reactions, *base* particles *gain* an H^+ to form the *conjugate acid* particle.

Using those definitions, cover the answer below and then try this problem.

Q. Fluoride ion (**F^-**) is a weak base. When F^- is mixed with water, which particles will form in the hydrolysis reaction?

$$\mathbf{F^-} + H_2O \rightleftarrows$$

* * * * *

Answer

$$\underset{\text{Weak base}}{\downarrow}\mathbf{F^-} + H_2O \rightleftarrows \underset{\text{Conjugate acid}}{\downarrow}\mathbf{HF} + \mathbf{OH^-}$$

↑ ~99% un-reacted ~1% of the **F^-** reacts to form these at equilibrium

The base particle **F^-** gains an H^+ when it reacts, and becomes the conjugate acid of HF. When a base reacts with water, one of the products is always **OH^-** ion.

Check that this equation is balanced for atoms and charge.

Practice A: Check your answers at the end of the lesson.

1. Assuming the *first* particle is acting as a *base*, complete the reaction.
   a. $HS^- + H_2O \leftrightarrows$
   b. $CH_3COO^- + H_2O \leftrightarrows$
   c. $H_2PO_4^- + H_2O \leftrightarrows$
2. Write the *expression* for K_b for each reaction above.
3. If each particle below is acting as a base, write the formula for its conjugate acid.
   a. CO_3^{2-} b. HSO_4^- c. HPO_4^{2-}

More K_a and K_b Comparisons

4. The general reaction for the hydrolysis of a weak *acid* is

$$W\mathbf{A} + H_2O \rightleftarrows \mathbf{H_3O^+} + \textbf{conjugate base} \qquad \text{(goes slightly)}$$

The general reaction for the hydrolysis of a weak *base* is

$$\mathbf{WB} + H_2O \rightleftarrows \mathbf{OH^-} + \textbf{conjugate acid} \qquad \text{(goes slightly)}$$

The conjugate acid will have one more H *and* one more **+** charge than the base.

5. When a weak acid is mixed with water,

$$[\text{WA}]_{\text{that ionizes}} = \boldsymbol{x} = [\text{H}_3\text{O}^+ \textit{ or } \text{H}^+]_{\text{formed}} = [\text{conjugate base}]_{\text{formed}}$$

When a weak *base* is mixed with water, $\boldsymbol{x}$ is the small mol/L of weak base that reacts.

$$[\text{WB}]_{\text{that hydrolyzes}} = \boldsymbol{x} = [\mathbf{OH^-}]_{\text{formed}} = [\textbf{conjugate acid}]_{\text{formed}}$$

6. The K for the ionization of an acid is termed the acid-dissociation constant: K_a.

   The K for the hydrolysis of a **base** is termed the **base-hydrolysis** constant: $\boldsymbol{K_b}$.

   Since most bases do not *dissociate* by losing an OH^- ion, **base-hydrolysis** is the preferred term.

7. K_a is between 1 and 10^{-16} for a weak acid. $\boldsymbol{K_b}$ is between 1 and 10^{-16} for a *weak base.*

   The higher the K_a, the stronger the acid. The higher the $\boldsymbol{K_b}$, the stronger the base.

8. $$K_a \equiv \frac{[\text{H}^+]_{\text{eq.}}\,[\text{conjugate base}]_{\text{eq.}}}{[\text{WA}]_{\text{at eq.}}} \equiv \frac{x^2}{[\text{WA}]_{\text{mixed}} - x} \quad \boxed{\approx \frac{x^2}{[\text{WA}]_{\text{mixed}}}}$$

   $$\boldsymbol{K_b} \equiv \frac{[\mathbf{OH^-}]_{\text{eq.}}\,[\text{conjugate acid}]_{\text{eq.}}}{[\text{W}\mathbf{B}]_{\text{at eq.}}} \equiv \frac{x^2}{[\text{W}\mathbf{B}]_{\text{mixed}} - x} \quad \boxed{\approx \frac{x^2}{[\text{W}\mathbf{B}]_{\text{mixed}}}}$$

   ^ Definition ^Exact ^ Approximation

9. K_a expressions have $[H^+]$ *or* $[H_3O^+]$ on top. $\boldsymbol{K_b}$ expressions have $\mathbf{[OH^-]}$ on *top*.

* * * * *

Percent Hydrolysis for Bases

In K_b expressions, $\boldsymbol{x}$ measures the small [WB] used up in the hydrolysis reaction. The **percent hydrolysis** is the percentage of the original base that reacts.

The percent hydrolysis of a weak base can be calculated in the same way as the percent dissociation of a weak acid. We will therefore modify Rule 3 to read

3: % Dissociation/Ionization/Hydrolysis/5% Test:

$$\boxed{\textbf{\% Dissociation} = \frac{x}{[\,\textbf{WA} \textit{ or } \textbf{WB}\,]_{\textbf{mixed}}} \bullet \textbf{100\%}} = \frac{[\,\text{WA } \textit{or} \text{ WB}\,]_{\text{hydrolyzed}}}{[\,\text{WA } \textit{or} \text{ WB}\,]_{\text{mixed}}} \bullet 100\%$$

The 5% Test For Weak Bases

If you are asked to use the 5% dissociation test for weak bases, use the same steps as for weak acids. First solve with approximation equation, then do the 5% test. If the percent hydrolysis of the weak base is greater than 5%, solve for $\boldsymbol{x}$ using exact equation (with the $-\boldsymbol{x}$ term) and a procedure for solving quadratic equations.

Summary: Weak Base Calculations.

4. **K_b Prompt**. If a problem involves a weak base and/or K_b and its [ions], write the ***WRRECK*** steps.
   - ***W***ANTED: Write the general and specific symbol.
   - Write the *specific* reaction using the symbol for the particles in the problem, then write this *general* reaction for weak base *hydrolysis* and its extent:

     R & ***E***: $\quad WB + H_2O \leftarrow\leftarrow\rightarrow \mathbf{OH^-} +$ conjugate acid (goes slightly)
   - ***C***onc. $\quad [WB]_{mixed} - x \qquad x \qquad x$
   - $$K_b \equiv \frac{[OH^-]_{eq.}[conjugate]_{eq.}}{[WB]_{at\ eq.}} \equiv \frac{x^2}{[WB]_{mixed} - x} \approx \boxed{\frac{x^2}{[WB]_{mixed}}}$$

     where: $x = [OH^-]$ = [conjugate acid] = $[WB]_{hydrolyzed}$

5. In K_a and K_b calculations, first solve the *approximation* for the WANTED unit or symbol, then calculate the percent dissociation. IF >5%, solve the exact equation using the quadratic formula.

6. K_a expressions have $[H^+]$ *or* $[H_3O^+]$ on top. K_b expressions have $[OH^-]$ on *top*. K_a solves for $x = [H^+]$, K_b solves for $x = [OH^-]$.

In short: For K_a and K_b calculations, write the ***WRRECK***'s, solve the approximation, then calculate % dissociation. If greater than 5%, solve the exact quadratic.

After mastering the ***WRRECK*** steps, you may solve K_a and K_b calculations using the ***WASS*** quick steps: Write the ***W***ANTED symbol, the ***A***pproximation equation, ***S***ubstitute, ***S***olve, and then apply the 5% test.

Quick 5% Test

Here's a quick way to apply the 5% test to see if a K_a or K_b approximation may be used.

- Using *scientific* notation, compare [WA] to the calculated $[H^+]$ or [WB] to $[OH^-]$.
- If the *exponents differ* by *3 or more*, the ionization must be *less* than 5% and the approximation is acceptable to use.
- If the exponents differ by *2 or less*, solve the % dissociation equation for the 5% test.

Let's test this rule.

Q. For a weak acid solution, $[H^+]$ is calculated using the K_a approximation to be 9.9×10^{-4} M at [WA] = 0.10 M. Does this calculation pass the 5% test?

* * * * *

[WA] = 0.10 M = 1.0×10^{-1} M , $[H^+] = x = 9.9 \times 10^{-4}$ M.

Since the difference between −1 and −4 is **3** or greater, this ionization must be less than 5%, so the approximation gives acceptable results, but let's calculate to be sure.

$$\textbf{\% Dissoc.} = \frac{x}{\textbf{[WA or WB]}_{\textbf{mixed}}} \bullet \textbf{100\%} = \frac{9.9 \times 10^{-4}\text{ M}}{1.0 \times 10^{-1}\text{ M}} \bullet 10^2\ \% = \textbf{0.99 \%}$$

This example is contrived to show the highest percent dissociation possible when the exponents differ by 3 or more, and it passes the 5% test, so the *quick* rule works.

Practice B: Try both.

1. Codeine ($C_{18}H_{21}NO_3$) is a physically addictive opiate which is an ingredient in some prescription cough suppressants. Codeine is a weak base with a $K_b = 9.2 \times 10^{-7}$. Use the full *WRRECK* steps to calculate the $[OH^-]$ in a 0.010 M codeine solution.
2. $[OH^-]$ is 3.6×10^{-5} M in a 0.12 M solution of the weak base hydroxylamine ($HONH_2$).
   a. Using the quick steps, calculate the K_b value for $HONH_2$.
   b. Apply the 5% test to the K_b approximation calculation.

Calculating K_b from K_a

In general,

- The *conjugate* of a *strong* acid or base (K = very large) is pH *neutral*.
- The conjugate of a *weak* acid or base is a *weak* opposite.
- The conjugate of a *very weak* acid or base ($K < 10^{-16}$) is a *strong* opposite.

The term **weak** acid or base generally refers to particles with a K between 1 and $\sim 10^{-16}$. For these particles, at a given temperature,

- a weak acid has a characteristic K_a, and its *conjugate base* has a characteristic K_b.
- A weak base has a characteristic K_b, and its *conjugate acid* has a characteristic K_a.

Because weak base solutions are systems at equilibrium, the weak base reacts slightly to form an conjugate acid, and the conjugate acid can react in the reverse reaction to re-form the weak base. ***K*** values take into account both the forward and reverse reactions.

Since reactions for weak acids and bases are reversible, they can be written backwards, from the perspective of the conjugate. One consequence of this reversibility is that for a weak acid *or* a weak base and its conjugate, the K_b and K_a of the particles in the **conjugate pair** are related mathematically. K_a and K_b, when multiplied, must equal K_w.

For conjugate acid-base pairs: $K_w = \boxed{\mathbf{K_a \times K_b = 1.0 \times 10^{-14}}}$ at 25ºC.

Note that for any conjugate pair, K_b and K_a are inversely proportional: the larger is one, the smaller must be the other.

We will summarize these points as rules

7. An acid particle *loses* an H^+ to become the *conjugate base* of the acid.
   A base particle *gains* an H^+ to become the *conjugate acid* of the base.
8. For conjugate acid-base *pairs*: $K_w = \boxed{\mathbf{K_a \times K_b = 1.0 \times 10^{-14}}}$ at 25ºC.

K_a values are often listed in tables. K_b values are less often listed in tables. However, if *either* a K_a or K_b value is known, the K value of the *conjugate* can be calculated by

- writing the *chemical formula* for the conjugate, and
- applying the relationship between the K values of conjugate acid-base pairs:

$$K_w = \boxed{K_a \bullet K_b = 1.0 \times 10^{-14}}.$$

Using that rule, try this problem.

Q. The K_a for HF is 6.8×10^{-4}.

a. What is the chemical formula for its conjugate base?

b. What is the K_b of its conjugate base?

* * * * *

Answer

a. The formula for the conjugate base of HF is $\mathbf{F^-}$. The conjugate base of an acid has one fewer H atoms and one fewer positive charges.

b. WANT: K_b of F^-

DATA: K_a for HF $= 6.8 \times 10^{-4}$.

To find the K_b of F^-, write the chemical formula for its conjugate acid: **HF.** Then apply the K_a value of HF and the rule for conjugate acid-base pairs:

$$K_w = \boxed{K_a \bullet K_b = 1.0 \times 10^{-14}}$$

SOLVE: $\mathbf{? = K_b} = \dfrac{1.0 \times 10^{-14}}{K_a} = \dfrac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = \mathbf{1.5 \times 10^{-11}} = K_b$ of F^-

Check: just as $[H^+] \bullet [OH^-]$ must estimate to $= \mathbf{K_w} = \mathbf{10.0} \times 10^{-15}$ or $\mathbf{1.0} \times 10^{-14}$,

$K_b \bullet K_a$ (circled) must estimate to $= \mathbf{K_w} = \mathbf{10.0} \times 10^{-15}$ or $\mathbf{1.0} \times 10^{-14}$.

Practice C

Complete the odd-numbered problems, and more if you need more practice.

1. Write Rules 1-8 for weak acids and bases until you can write them from memory.
2. If the K_b of the weak base methylamine (CH_3NH_2) is 4.4×10^{-5}, what is the K_a value for $CH_3NH_3^+$?
3. Phosphoric acid is triprotic: it has three hydrogens that can ionize. Each acid particle that can lose a proton has a different K_a value, as shown in this chart.

   Based on this data, what would be the K_b of HPO_4^{2-}?

Acid	K_a at 25°C
H_3PO_4	7.5×10^{-3}
$H_2PO_4^-$	6.2×10^{-8}
HPO_4^{2-}	4.2×10^{-13}

4. In acetic acid, $CH_3COO\mathbf{H}$, the last H in the formula is weakly acidic. The K_a for acetic acid is 1.8×10^{-5}. Write the
   a. Chemical formula for the conjugate base of acetic acid.
   b. K_b value for the conjugate base.
   c. Balanced equation for the reaction that this K_b is the equilibrium constant *for*.
   d. K_b expression for the hydrolysis of the conjugate base of acetic acid.
5. Aniline ($C_6H_5NH_2$) is a weak base used in synthesizing textile dyes ($K_b = 3.8 \times 10^{-10}$).
   a. Find the K_a of $C_6H_5NH_3^+$.
   b. Write a balanced equation for aniline reacting as a weak base with water.
   c. Find the $[OH^-]$ in a 0.020 M aniline solution. Use the full *WRRECK* steps.
   d. What will be the pH of the *Part c* solution?

ANSWERS

Practice A

1. a. $HS^- + H_2O \rightarrow \mathbf{H_2S + OH^-}$ b. $CH_3COO^- + H_2O \rightarrow \mathbf{CH_3COOH + OH^-}$

   c. $H_2PO_4^- + H_2O \rightarrow \mathbf{H_3PO_4 + OH^-}$ Bases reacting with water *form* OH^-.

2. a. $K_b = \dfrac{[H_2S]\mathbf{[OH^-]}}{[HS^-]}$ b. $K_b = \dfrac{[CH_3COOH]\mathbf{[OH^-]}}{[CH_3COO^-]}$ c. $K_b = \dfrac{[H_3PO_4]\mathbf{[OH^-]}}{[H_2PO_4^-]}$

   K_b expressions always have $[\mathbf{OH^-}]$ on top.

3. Conjugate acids: a. CO_3^{2-} $\mathbf{HCO_3^-}$ b. HSO_4^- $\mathbf{H_2SO_4}$ c. HPO_4^{2-} $\mathbf{H_2PO_4^-}$

Practice B

2a. If K_b *and [ions]* are mentioned, write the *WRRECK's,* solve the approximation, do the 5% test.

W**ANT:* **[OH⁻] = *x

Specific ***R**eaction:* 1 $C_{18}H_{21}NO_3$ + H_2O ←← → 1 $\mathbf{OH^-}$ + 1 $\mathbf{H}C_{18}H_{21}NO_3^+$ (goes slightly)

(In this problem, those specific formulas are not needed to solve.)

General ***R**+**E***: WB + H_2O ←← → $\mathbf{OH^-}$ + conjugate acid (goes slightly)

***C**onc. at Eq:* $[WB]_{mixed} - x$ $\quad x \quad x$

$\underline{\mathbf{K_b}}$: $K_b = \dfrac{[OH^-][\text{conjugate acid}]}{[WB]_{mixed} - x} \approx \boxed{\dfrac{x^2}{[WB]_{mixed}} \approx K_b}$

Solve the K_b approximation for x:

$$\boldsymbol{x^2} \approx (9.2 \times 10^{-7})(0.010) = 9.2 \times 10^{-9} = 92 \times 10^{-10}$$

$$x \approx (\text{estimate } 9\text{-}10 \times 10^{-5}) \approx \boxed{\mathbf{9.6 \times 10^{-5}\ M = [OH^-]}}$$

Since the approximation was used, apply the 5% test:

$$\% \text{ Hydrolysis} = \frac{x}{[\text{WA or WB}]_{mixed}} \bullet 100\% = \frac{9.6 \times 10^{-5}}{1.0 \times 10^{-2}} \bullet 10^2\ \%$$

$= 9.6 \times 10^{-1}\ \%$ $\mathbf{= 0.96\ \%}$, which is less than 5%, so approximation is OK.

2a. ***W**ANT:* $\mathbf{K_b}$ starting from the approximation equation.

$$\boxed{K_b \approx \frac{x^2}{[WB]_{mixed}}}$$

Remember that in K_b, x solves for $[OH^-]$.

SOLVE: $\mathbf{? = K_b} \approx \dfrac{x^2}{[WB]_{mixed}} = \dfrac{(3.6 \times 10^{-5})^2}{0.12} = \dfrac{13.0. \times 10^{-10}}{0.12} = \boxed{\mathbf{1.1 \times 10^{-8} = K_b}}$

b. **% Hydrolysis** $= \dfrac{x}{[\text{WA or WB}]_{mixed}} \bullet 100\% = \dfrac{3.6 \times 10^{-5}}{0.12} \bullet 10^2\ \% = 3.0 \times 10^{-2}\ \%$

$= \mathbf{0.03\%} < 5\%$

Practice C

2. WANT: K_a of conjugate acid (the conjugate acid has one more H and one more **+** charge)

DATA: K_b of base = 4.4×10^{-5}

For conjugate acid-base pairs: $K_w = \boxed{K_a \times K_b = 1.0 \times 10^{-14}}$

SOLVE: $\mathbf{K_a} = \dfrac{K_w}{K_b} = \dfrac{1.0 \times 10^{-14}}{K_b} = \dfrac{1.0 \times 10^{-14}}{\mathbf{4.4 \times 10^{-5}}} = 0.227 \times 10^{-9} = \boxed{\mathbf{2.3 \times 10^{-10} = K_a}}$

Quick check: $K_b \times K_a$ must estimate to $\mathbf{K_w} = \mathbf{10.0} \times 10^{-15}$ or $\mathbf{1.0} \times 10^{-14}$. Try it.

3. WANT: K_b of HPO_4^{2-}

DATA: K_b can be found from the K_a values in the table using K_w, but which K_a is used?

That of the *conjugate acid* of HPO_4^{2-}, which is $\mathbf{H_2PO_4^-}$ with a $K_a = 6.2 \times 10^{-8}$

$K_w = \boxed{\mathbf{K_a \times K_b = 1.0 \times 10^{-14}}}$

SOLVE: $\mathbf{K_b} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{\mathbf{6.2 \times 10^{-8}}} = 0.16 \times 10^{-6} = \boxed{\mathbf{1.6 \times 10^{-7} = K_b}}$

Quick check: $K_b \times K_a$ must estimate to = $\mathbf{K_w}$ = **10.0** x $10^{\mathbf{-15}}$ or **1.0** x $10^{\mathbf{-14}}$.

4. a. $\mathbf{CH_3COO^-}$. The conjugate base is the acid particle minus an H^+.

b. WANT: K_b of conjugate base

DATA: K_a of acid = 1.8×10^{-5}

For conjugate acid-base pairs: $K_w = \boxed{\mathbf{K_a \times K_b = 1.0 \times 10^{-14}}}$

SOLVE: $\mathbf{K_b} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{\mathbf{1.8 \times 10^{-5}}} = 0.56 \times 10^{-9} = \boxed{\mathbf{5.6 \times 10^{-10} = K_b}}$

Quick check: $K_b \times K_a$ must estimate to = K_w = **10.0** x $10^{\mathbf{-15}}$ or **1.0** x $10^{\mathbf{-14}}$

c. $\mathbf{K_b}$ is always the K for this reaction: **base + $\mathbf{H_2O}$** ←←→ conjugate acid + $\mathbf{OH^-}$

Here the conjugate acid-base pair are CH_3COOH and CH_3COO^-.

So the base is the acetate ion: $\mathbf{CH_3COO^- + H_2O \leftarrow\leftarrow\rightarrow CH_3COOH + OH^-}$

d. K_b is always the K expression for the reaction of a base with water: the reaction in Part c above:

$$\mathbf{K_b = \frac{[OH^-]\,[CH_3COOH]}{[CH_3COO^-]}}$$

with all concentrations are measured at equilibrium.

A $\mathbf{K_b}$ expression always has $\mathbf{[OH^-]}$ on top.

5. a. WANT: K_a of $C_6H_5NH_3^+$ (the conjugate acid of aniline - one more H and one more **+** charge)

DATA: K_b of base = 3.8×10^{-10}

For conjugate acid-base pairs: $K_w = \boxed{K_a \times K_b = 1.0 \times 10^{-14}}$

SOLVE: $\mathbf{K_a} = \frac{1.0 \times 10^{\mathbf{-14}}}{K_b} = \frac{1.0 \times 10^{-14}}{\mathbf{3.8 \times 10^{-10}}} = 0.26 \times 10^{-4} = \boxed{\mathbf{2.6 \times 10^{-5} = K_a}}$

Quick check: $K_b \times K_a$ must estimate to = $\mathbf{K_w}$ = **10.0** x $10^{\mathbf{-15}}$ or **1.0** x $10^{\mathbf{-14}}$.

b. Aniline is a weak base. Weak bases take a proton from water:

Specific ***R***eaction: $\mathbf{C_6H_5NH_2 + H_2O \leftarrow\leftarrow\rightarrow C_6H_5NH_3^+ + OH^-}$ (goes slightly)

c. ***W**ANT:* **[OH⁻]** = **x = ?** For K_a or K_b and [ions] calculations, write the *WRRECK's.*

General ***R+E***: $\text{WB} + H_2O \leftleftarrows\rightarrow \textbf{OH}^- + \text{conjugate acid}$ (goes slightly)

Conc. at Eq: $[\text{WB}]_{\text{mixed}} - x \quad x \quad x$

$\mathbf{K_b}$: $K_b = \dfrac{[OH^-][\text{conjugate}]}{[\text{WB}]_{\text{mixed}} - x} \approx \boxed{\dfrac{x^2}{[\text{WB}]_{\text{mixed}}} \approx K_b}$

Since **[OH⁻] = ? = *x***, solve the K_b approximation for ***x***:

$x^2 \approx (K_b)([\text{WB}]_{\text{mixed}}) = (3.8 \times 10^{-10})(0.020) = 7.6 \times 10^{-12}$

$x \approx$ (estimate: 2-3 x 10^{-6}) = $\boxed{\mathbf{2.8 \times 10^{-6}\ M = [OH^-]}}$

Since the K_b approximation was used, ask: is the weak base more than 5% dissociated?

By the quick 5% test, since for 2.8×10^{-6} M = [OH⁻] and $\mathbf{K_b} = 3.8 \times 10^{-10}$, the exponents differ by more than 3, we can assume the dissociation is less than 5%. To be sure:

$$\textbf{\% Hydrolysis} = \frac{x}{[\text{WA or WB}]_{\text{orig.}}} \bullet \textbf{100\%} = \frac{2.8 \times 10^{-6}}{2.0 \times 10^{-2}} \bullet \mathbf{10^2\ \%} =$$

$\mathbf{= 1.4 \times 10^{-2}\ \%}$ = 0.014%, which is less than 5%, so the approximation is OK.

d. WANT: **pH** Write $\boxed{\textbf{pH} \equiv -\log[H^+] \quad \text{and} \quad [H^+] \equiv 10^{-\textbf{pH}}}$

We don't know [H⁺]. We know **2.8 x 10⁻⁶ M = [OH⁻]** One way to solve is to find **pOH,** then pH:

$\boxed{\text{p}\textbf{OH} \equiv -\log[\textbf{OH}^-],\ [\textbf{OH}^-] = 10^{-\text{p}\textbf{OH}}}$ and $\boxed{\text{pH} + \text{pOH} = 14.00}$

p**OH** ≡ — log[**OH⁻**] = — log(**2.8 x 10⁻⁶**) = 5.? = **5.55** = p**OH**

then $\boxed{\textbf{pH} + \text{pOH} = 14.00}$; **pH** = 14.00 – pOH = 14.00 – 5.55 = $\boxed{\textbf{8.45 = pH}}$

Note that this is a slightly basic pH as would be expected in a weak base solution.

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Lesson 30G: Polyprotic Acids

Timing: Do this lesson if you are assigned problems that involve calculating the ion concentrations or pH in polyprotic acid solutions.

* * * * *

K_a Values For Polyprotic Acids

Acids that have more than one acidic hydrogen are *polyprotic* acids. Examples of polyprotic acids include H_2SO_4 (sulfuric acid), H_2CO_3 (carbonic acid), H_3PO_4 (phosphoric acid), and $H_3C_6H_5O_7$ (citric acid).

Polyprotic acids, by definition, lose their first proton to form *another* acid.

For example, the weak polyprotic acid H_2CO_3 can lose one proton to form HCO_3^-. The HCO_3^- can also act as an acid, losing its proton to form CO_3^{-2}. These two reactions can be written as

$$H_2CO_3 \rightarrow H^+ + \mathbf{HCO_3^-} \qquad K_a = 4.3 \times 10^{-7}$$
$$\mathbf{HCO_3^-} \rightarrow H^+ + CO_3^{2-} \qquad K_a = 5.6 \times 10^{-11}$$

For all polyprotic acids,

- the conjugate base formed by the first acid dissociation is the acid in the second;
- the second hydrogen ionizes less readily than the first, and, if there are more acidic protons, the each ionizes less readily than the prior hydrogen;
- K_a values are smaller for each successive ionization.

When the successive ionizations of a polyprotic acid are written in a series, if there are middle particles in the series (between the first and last particles), all will be amphoteric: they can react as an acid when mixed with bases, and a base when mixed with acids.

The K_a values for the successive ionizations are often numbered.

For example, for H_2CO_3 above, $K_{a1} = 4.3 \times 10^{-7}$ and $K_{a2} = 5.6 \times 10^{-11}$.

K_{a1} is the K_a value for the reaction where H_2CO_3 loses its first proton. K_{a2} is the K_a for the reaction in which the second proton of the original polyprotic acid is lost: the proton is lost from $\mathbf{HCO_3^-}$.

Try this problem.

Q. For citric acid $(H_3C_6H_5O_7)$,

$K_{a1} = 7.1 \times 10^{-4}$, $K_{a2} = 1.7 \times 10^{-5}$, and $K_{a3} = 4.0 \times 10^{-7}$.

a. Write the K_a value for $HC_6H_5O_7^{2-} \rightarrow H^+ + C_6H_5O_7^{3-}$

b. For $K_{a2} = 1.7 \times 10^{-5}$, write the reaction that this is a K_a value for.

* * * * *

Answer

a. It helps to write the equations for the successive ionizations.

K_{a1} is the K value for this reaction: $\mathbf{H_3}C_6H_5O_7 \rightarrow H^+ + \mathbf{H_2}C_6H_5O_7^-$

K_{a2} is the K value for: $\mathbf{H_2}C_6H_5O_7^- \rightarrow H^+ + \mathbf{H}C_6H_5O_7^{\mathbf{2-}}$

K_{a3} is the K value for: $\mathbf{H}C_6H_5O_7^{\mathbf{2-}} \rightarrow H^+ + C_6H_5O_7^{\mathbf{3-}}$

For *part a*: $\mathbf{H}C_6H_5O_7^{2-} \rightarrow H^+ + C_6H_5O_7^{3-}$ $\quad K_a = K_{a3} = \mathbf{4.0 \times 10^{-7}}$.

b. K_{a2} is the K value for: $\mathbf{H_2C_6H_5O_7^-} \rightarrow H^+ + HC_6H_5O_7^{2-}$, the reaction in which $H_3C_6H_5O_7$, after losing one acidic hydrogen, loses a second.

Practice A

1. For phosphoric acid (H_3PO_4),

   $Ka_1 = 7.5 \times 10^{-3}$, $Ka_2 = 6.7 \times 10^{-8}$, and $Ka_3 = 4.2 \times 10^{-13}$.

   a. Write the K_a value for: $H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$

   b. For Ka_3, write the reaction that this is a K_a value for.

The $[H^+]$ in Polyprotic Acid Solutions

To calculate the $[H^+]$ in polyprotic acid solutions, there are three cases to consider.

- Acids in which a numeric Ka_1 is 100 or more times larger than K_{a2};
- Acids in which Ka_1 is *not* 100 or more times larger than K_{a2}, and
- The special case of sulfuric acid, which is both a strong and a weak acid.

For the first case, in which the first two K_a values are *widely separated*, the $[H^+]$ and pH of a weak polyprotic acid solution is calculated using only Ka_1. The $[H^+]$ contributed by the second ionization will be small: so small that it can be ignored when calculating the and pH due to the larger first ionization. This will be the case for *most* polyprotic weak acids.

However, in citric acid, as shown in the example above, Ka_1 and Ka_2 are relatively close. In the case of sulfuric acid (H_2SO_4), the first ionization is essentially 100%, and the dissociation of the second proton is high ($Ka_2 = 1.0 \times 10^{-2}$). In both of these cases, the $[H^+]$ from both the first and second ionizations are calculated and added. There are no polyprotic acids in which Ka_3 has a substantial effect on the pH of the weak acid solution. We will call this Rule

9. <u>For solutions of polyprotic acids</u>, to find $[H^+]$ and pH:

- ***If*** Ka_1 is 100 or more times larger than Ka_2, use Ka_1 to find $[H^+]$ and ignore Ka_2 ;
- ***If*** Ka_1 is *not* 100 or more times larger than Ka_2, add $[H^+]$ from Ka_1 and Ka_2 .

Practice B

1. For phosphoric acid (H_3PO_4), calculate the $[H^+]$ in a 3.5 M H_3PO_4 solution. Use the approximation equation and the *K* values in Practice A above.

2. For sulfuric acid (H_2SO_4), Ka_1 = very large, and $Ka_2 = 1.0 \times 10^{-2}$. Calculate the $[H^+]$ in a 0.50 M H_2SO_4 solution.

ANSWERS

Practice A

1a. Phosphoric acid has 3 acidic hydrogens. For clarity, write the three ionization equations.

K_{a_1} is the K value for: $H_3PO_4 \rightarrow H^+ + H_2PO_4^-$

K_{a_2} is the K value for: $H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$

K_{a_3} is the K value for: $HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$

For the *part a* reaction, the K_a is K_{a_2} = 6.7×10^{-8}

1b. As shown above, K_{a_3} is the K value for $HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$, the reaction where the original phosphoric acid, after losing two acidic hydrogens, loses its third.

Practice B

1. For phosphoric acid, K_{a_1} is > 100 (10^2) times larger than K_{a_2}; so the second ionization is small compared to the first and can be ignored. Calculate $[H^+]$ based only on the first ionization, using K_{a_1}.

K_{a_1} is the K value for: $H_3PO_4 \rightarrow H^+ + H_2PO_4^-$ $K_{a_1} = 7.5 \times 10^{-3}$

Solve the approximation equation, then apply the 5% test.

WANT: $[H^+]$ = ***x***

$\boxed{K_a \approx \dfrac{x^2}{[\text{WA}]_{\text{mixed}}}}$ Substituting: $7.5 \times 10^{-3} = \dfrac{x^2}{3.5}$

$x^2 \approx (7.5 \times 10^{-3})(3.5) = 2.6 \times 10^{-2}$

$x = [H^+] = ? \approx$ (estimate: 1-2 x 10^{-1}) $\approx$ $\boxed{\mathbf{0.16\ M = [H^+]}}$

Since the approximation was used, apply the 5% test:

$$\text{5\% test} = \text{\% Hydrolysis} = \frac{x}{[\text{WA or WB}]_{\text{mixed}}} \bullet 100\% = \frac{0.16\text{ M}}{3.5\text{ M}} \bullet 10^2\ \%$$

= 4.6 **%**, which is *close* but less than 5%, so the approximation may be used.

2. Because sulfuric acid is both a strong and a weak acid, the $[H^+]$ must be calculated in two parts. Since the first K_a is very large, the first H^+ from H_2SO_4 is formed essentially 100%, as in strong acids.

For strong acids losing one proton: $H_2SO_4 \rightarrow \mathbf{H^+} + HSO_4^-$ (goes ~100%)

^ ^ ^

0.50 M used up **0.50 M** formed of both

The HSO_4^- formed *also* ionizes substantially, since it has a relatively high K_{a_2} = 1.0×10^{-2}

which is the K_a for this reaction: $HSO_4^- \rightarrow \mathbf{H^+} + SO_4^{2-}$ (goes slightly)

Calculate the $[H^+]$ in the solution due to the ionization of the moderately weak acid HSO_4^-.

* * * * *

If K_a and [ions] are mentioned, write the *WRRECK*'s, solve the approximation, apply the 5% test.

WANTED: $[H^+]$ = **?** = ***x***

R& ***E***:	$\mathbf{HSO_4^-}$	→ $\mathbf{H^+}$	+	SO_4^{2-}	(goes slightly, use *K*)
	^	^		^	
Conc. at Eq:	$[WA]_{mixed} - \boldsymbol{x}$	***0.50 + x***		***x***	(*rice* bottom row)

Note the $[H^+]$ in the ***C*** step above. The $[H^+]$ must include the H^+ present from the first ionization. Use the ***C*** step results to write the *K* expression.

K step:

$$K_a \equiv \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]_{mixed} - x} \equiv \frac{(0.50 + x)(x)}{0.50 - x} \approx \frac{(0.50)(x)}{0.50} = x \approx K_a$$

^ Definition ^ Exact ^ Approximate

where $\boldsymbol{x} = [\mathbf{H^+}] = [SO_4^{2-}] = [HSO_4^-]_{\text{that ionized}}$ in the second ionization

Based on the approximation, the result is $\boldsymbol{x} \approx K_a = \mathbf{1.0 \times 10^{-2}} =$ **0.010 M**

Since an approximation was used, apply the 5% test:

$$\%\ \text{Hydrolysis} = \frac{x}{[\text{WA or WB}]_{mixed}} \bullet 100\% = \frac{0.010\ \text{M}}{0.50\ \text{M}} \bullet 100\ \%$$

= 2.0 **%**, which is less than 5%, so using the approximation is OK.

The TOTAL $[H^+]$ = the sum from the two ionizations = 0.50 + 0.010 M = $\boxed{\mathbf{0.51\ M\ H^+}}$

When adding *sf*, round to the highest *place* with doubt. In this solution, the second ionization occurs, but does not have a *major* impact on the $[H^+]$ due to the first ionization. In less concentrated sulfuric acid solutions, the effect of the second ionization is larger.

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SUMMARY -- Weak Acids and Bases

You may want to organize this summary into charts and flashcards.

1. In acid and base solutions, to calculate [particles],
   - in *strong* acids such as HCl or HNO_3, or strong bases such as NaOH and KOH, either write the *REC* steps for 100% ionization, or use the quick steps to find [ions].
   - in *weak* acid and base solutions, write the ***WRECK*** steps. Use ***x*** to represent the small mol/L of weak acid or base that reacts (ionizes or hydrolyzes).
2. **K_a Prompt:** If a problem has a K_a and [*ions*], write the ***WRRECK*** steps.
   - ***W***ANTED: Write the general and specific symbol.
   - Write the *specific* reaction using the symbol for the particles in the problem, then write these *general R, E, C*, and K steps:
   - ***R***xn. and ***E***xtent: **WA** ←← → $\mathbf{H^+}$ + **conjugate base** (goes slightly)
     ^ ^ ^
   - ***C***onc. $[WA]_{mixed} - \boldsymbol{x}$ $\boldsymbol{x}$ $\boldsymbol{x}$

- $K_a \equiv \dfrac{[H^+]_{eq.}[CB]_{eq.}}{[WA]_{at\ eq.}} \equiv \dfrac{x^2}{[WA]_{mixed} - x} \approx \boxed{\dfrac{x^2}{[WA]_{mixed}} \approx K_a}$

  ^Definition ^ Exact ^Approximate

3: **<u>% Dissociation and 5% Test</u> :** $\boxed{\textbf{\% Dissociation} = \dfrac{x}{[WA\text{ or }WB]_{mixed}} \bullet \textbf{100\%}}$

4: **<u>K_b Prompt</u>**. If a problem is about a K_b and its [ions], write the *WRRECK's:*

- ***W***ANTED: Write the general and specific symbol.
- Write the *specific* reaction using the symbol for the particles in the problem, then write this *general* reaction for weak base *hydrolysis* and its extent:

  <u>***R***</u> & <u>***E***</u>: WB + H_2O ←←→ **OH^-** + conjugate acid (goes slightly)

- <u>***C***</u>onc. $[WB]_{mixed} - x$ x x

- $K_b \equiv \dfrac{[OH^-]_{eq.}[\text{conjugate acid}]_{eq.}}{[W\mathbf{B}]_{at\ eq.}} \equiv \dfrac{x^2}{[W\mathbf{B}]_{mixed} - x}$ $\boxed{\approx \dfrac{x^2}{[W\mathbf{B}]_{mixed}}}$

  ^Definition ^ Exact ^Approximate

  where: x = **$[OH^-]$** = [conjugate] = $[WB]_{\text{used up/reacting/hydrolyzing}}$

5. In K_a and K_b calculations, first solve the *approximation* for the WANTED unit or symbol, then calculate the percent dissociation. IF >5%, solve the exact equation using the quadratic formula.

6. **<u>The Quick 5% Test</u>** to see if an approximation equation provides acceptable results.
   - Using *scientific* notation, compare [WA] to $[H^+] = x$ or [WB] to $[OH^-] = x$ **.**
   - If the *exponents differ* by *3 or more*, the ionization is less than 5%.
   - If the exponents differ by *2 or less*, use the % dissociation *equation* for the 5% test.

7. K_a expressions have $[H^+]$ *or* $[H_3O^+]$ on top. K_b expressions have **$[OH^-]$** on *top*.
   K_a solves for $x = [H^+]$, K_b solves for $x = [OH^-]$.

8. An acid particle *loses* an H^+ to become the **conjugate base** of the acid.
   A base particle *gains* an H^+ to become the **conjugate acid** of the base.

9. For **conjugate acid-base pairs**: $K_w = \boxed{K_a \times K_b = 1.0 \times 10^{-14}}$

10. **For polyprotic acid solutions**, to find $[H^+]$ and pH:
    - *If* K_{a1} is 100 or more times larger than K_{a2}, use K_{a1} to find $[H^+]$ and ignore K_{a2} ;
    - *If* K_{a1} is *not* 100 or more times larger than K_{a2}, add $[H^+]$ from K_{a1} and K_{a2} .

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Module 31 — Brønsted-Lowry Definitions

Timing: Do this module when you are assigned problems that involve the Brønsted-Lowry definitions or you are asked to predict whether acid and base particles will react.

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Lesson 31A: Brønsted-Lowry Acids and Bases

Proton-Transfer

So far, we have defined acids and bases in terms of their reaction with water. Those definitions are useful in calculations involving particle concentrations.

An important qualitative question is: when acids and bases are *combined*, which combinations react, and which do not? To answer these questions, it is helpful to use a broader definition of acids and bases, termed the **Brønsted-Lowry definitions**. These expanded definitions will help to predict and explain a wide variety of important acid-base interactions in chemistry and biology.

By the Brønsted-Lowry definitions:

1. An acid-base reaction is a **proton transfer**: a proton moves from one particle to another.
2. An *acid* is a particle that can *release* an H^+. A *base* is a particle that can *accept* an H^+.
3. Proton-transfer reactions are reversible: in a closed system, reactions go to equilibrium.
4. *Each side* of an acid-base reaction equation has a *one acid* (the **proton donor**) and *one base* (the **proton acceptor**). In an acid-base reaction equation, the difference between the particle formulas on one side and the other is the particle to which the mobile proton is attached.
5. A particle that is an *acid* on one side of a reaction *loses* its proton and becomes a *base* on the other. A *base* particle on one side *gains* a proton to become the *acid* on the other.
6. Particles in acid-base reaction behave as *two* conjugate acid-base *pairs*. In a conjugate pair, the particles are identical, except that the acid on one side has an H^+ that its conjugate base on the other does not.

It will help in learning the rules to do a few examples. Apply the rules above to the questions below. If unsure about an answer, check it before doing the next question.

Q1. Circle the two acids in this reaction: $HCO_3^- + F^- \leftrightarrows CO_3^{2-} + HF$

Q2. Is F^- in the above reaction an acid or a base? Explain your answer.

Q3. Complete this reaction with the first reactant behaving as an acid.

$$H_2PO_4^- + CO_3^{2-} \leftrightarrows$$

Q4. Complete this reaction with the first reactant acting as a base.

$$HSO_3^- + H_2O \leftrightarrows$$

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Answers

Q1. HCO_3^- + F^- ⇆ $\mathbf{CO_3^{2-}}$ + **HF**

Each side must have *one* acid. The HCO_3^- gives up a proton in going to the right: it is therefore acting as the *acid* on the left side. The HF gives away its proton when the reaction goes to the left, making HF the acid on the right side.

Q2. $\mathbf{F^-}$ is a base because (a) the other particle on that side is an acid, and each side must have an acid *and* a base, and/or (b) F^- gains a proton in going to the right, and gaining a proton is what a base does when it reacts.

Q3. $H_2PO_4^-$ + CO_3^{2-} ⇆ $\mathbf{HPO_4^{2-}}$ + $\mathbf{HCO_3^-}$ Acids donate an H^+ in reactions.

Q4. HSO_3^- + H_2O ⇆ $\mathbf{H_2SO_3}$ + $\mathbf{OH^-}$ Base particles gain a proton in reactions.

Check: are each of the above reactions balanced for atoms and charge?

Practice A: Identifying Acids and Bases in Proton-Transfer Reactions

1. For these reactions, assume that the charges on the left side are correct. If no charge is shown on the left, assume the particle is neutral. On the *right* side, *add* correct charges to the particles. If the particle is neutral, leave the charge blank.

   a. SO_4^{2-} + HCl ⇆ $\mathbf{HSO_4}$ + **Cl**

   b. HPO_4^{2-} + HS^- ⇆ $\mathbf{PO_4}$ + $\mathbf{H_2S}$

   c. NH_4^+ + HSe^- ⇆ $\mathbf{NH_3}$ + $\mathbf{H_2Se}$

2. In 1c above, which particle is in the *conjugate* acid-base *pair* with HS^-?

3. Assuming that the first reactant below is acting as an acid, complete these reactions.

   a. HNO_3 + NH_3 ⇆

   b. HS^- + SO_4^{2-} ⇆

   c. OH^- + OH^- ⇆

4. Assuming that the first reactant below is acting as a base, complete these reactions.

   a. HCO_3^- + OH^- ⇆

   b. H_2O + H_2O ⇆

   c. PO_4^{3-} + $H_2PO_4^-$ ⇆

Stronger and Weaker Acids and Bases

7. A simple proton-transfer equilibrium consists of 4 particles: two pairs of conjugate acids and bases. Each of the four particles can be labeled as one of the following.

- **Stronger acid (sA)**: the molecule or ion that releases a proton in the reaction. In the stronger acid, the proton is more "loosely bound" than in the weaker acid.
- **Weaker acid (wA)**: the particle in an equilibrium that has the stronger bond to its acidic hydrogen.
- **Stronger base (sB)**: the particle that more strongly attracts a proton. It will form the stronger bond to the proton if it is acquired.
- **Weaker base (wB)**: the particle that can accept a proton, but does not tend to do so. If it does acquire a proton, it will bind it weakly.

In these lessons, we will use the upper case **S**A and **S**B when referring to strong acids and bases in absolute terms (K_a or K_b = very large), and **W**A and **W**B when referring to particles that are weak acids and bases (K_a or K_b < 1). When *comparing* two particles, we will use the lower case **s** and **w**.

For example, both HCN and HF are weak acids (WA) because both have a $K_a < 1$, but in *comparing* the two, based on their K_a values, HF ($K_a = 6.8 \times 10^{-4}$) is the strong***er*** acid (**s**A) and HCN ($K_a = 6.2 \times 10^{-10}$) is the weak***er*** acid (**w**A).

8. In a reaction, the particle that is the stronger acid (sA), upon losing H^+ becomes the weaker base (wB). The stronger base, upon gaining a proton, becomes the weaker acid.

9. In a proton-transfer reaction equation, the stronger base (sB) and stronger acid (sA) are always on the same side and the wA and wB are always on the same side.

10. Equilibrium favors the side with the weaker acid (wA) and weaker base (wB).

An A and B react to form another A and B, which can then react to re-form the original A and B. Which particles win the battle to *react* more often? The A and B that are *stronger*. This means that the wA and wB are *formed* more often.

When more than one proton-transfer reaction is possible, the proton from the strongest acid will migrate to the strongest base to form the weakest acid.

11. Acid-base behavior is explained by chemical structure.

a. A particle that bonds a proton strongly is a strong base without the proton and a weak acid with it.

b. A particle that can accept a proton, but does not bond it tightly, is a strong acid when it has the proton, and a weak base when it does not.

Practice B: Learn the 11 rules above, *then* test your knowledge with these.

TRUE or FALSE. In proton-transfer equilibria,

_____ a. An acid and a base react to form another acid and another base.

_____ b. The stronger acid winds up at equilibrium with the proton.

_____ c. A strong base will bond weakly to the proton it acquires.

_____ d. The weaker acid has a stronger bond to H^+ than the stronger acid.

_____ e. The stronger acid is on the same side of the equation as the weaker base.

_____ f. Equilibrium favors the weaker base.

_____ g. The weaker base attracts a proton more than the stronger base.

_____ h. The stronger acid reacts to become the weaker base.

_____ i. The weaker acid becomes the stronger base when it reacts.

ANSWERS

Practice A

1. a. $SO_4^{2-} + HCl \leftrightarrows HSO_4^- + Cl^-$

   b. $HPO_4^{2-} + HS^- \leftrightarrows PO_4^{3-} + H_2S$

   c. $NH_4^+ + HSe^- \leftrightarrows NH_3 + H_2Se$

   The acid particle loses an H^+ in the reaction. The base particle gains an H^+. Reactions must be balanced for atoms and charge.

2. **H_2S.** The particles in a conjugate acid-base pair differ only by one H^+.

3. a. $HNO_3 + NH_3 \leftrightarrows$ **$NO_3^- + NH_4^+$**

   b. $HS^- + SO_4^{2-} \leftrightarrows$ **$S^{2-} + HSO_4^-$**

   c. $OH^- + OH^- \leftrightarrows$ **$O^{2-} + H_2O$**

4. a. $HCO_3^- + OH^- \leftrightarrows$ **$H_2CO_3 + O^{2-}$**

   b. $H_2O + H_2O \leftrightarrows$ **$H_3O^+ + OH^-$**

   c. $PO_4^{3-} + H_2PO_4^- \leftrightarrows$ **$2\ HPO_4^{2-}$**

Practice B

True a. An acid and a base react to form another acid and another base.

False b. The stronger acid winds up at equilibrium with the proton.

False c. A strong base will bond weakly to the proton it acquires.

True d. The weaker acid has a stronger bond to H^+ than the stronger acid.

False e. The stronger acid is on the same side of the equation as the weaker base.

True f. Equilibrium favors the weaker base.

False g. The weaker base attracts a proton more than the stronger base.

True h. The stronger acid reacts to become the weaker base.

True i. The weaker acid becomes the stronger base when it reacts.

* * * * *

Lesson 31B: Which Acids and Bases React?

Prerequisites: Lesson 31A.

* * * * *

Most chemistry textbooks contain a table of acid strengths. An abbreviated version of such a table is given below.

Table of Acid Strengths

Acid			Base	K_a Values at 25°C
HCl	→	H^+ +	Cl^-	Very Large
HNO_3	→	H^+ +	NO_3^-	Very Large
H_2SO_4	→	H^+ +	HSO_4^-	Very Large
H_3O^+	→	H^+ +	H_2O	1.0
HSO_4^-	→	H^+ +	SO_4^{2-}	1.0×10^{-2}
H_3PO_4	→	H^+ +	$H_2PO_4^-$	7.2×10^{-3}
HF	→	H^+ +	F^-	$6.8 \times 10^{-4*}$
C_6H_5COOH	→	H^+ +	$C_6H_5COO^-$	6.3×10^{-5}
CH_3COOH	→	H^+ +	CH_3COO^-	1.8×10^{-5}
H_2CO_3	→	H^+ +	HCO_3^-	4.3×10^{-7}
$H_2PO_4^-$	→	H^+ +	HPO_4^{2-}	6.3×10^{-8}
HCN	→	H^+ +	CN^-	$6.2 \times 10^{-10*}$
NH_4^+	→	H^+ +	NH_3	5.6×10^{-10}
HCO_3^-	→	H^+ +	CO_3^{2-}	5.6×10^{-11}
HPO_4^{2-}	→	H^+ +	PO_4^{3-}	4.2×10^{-13}
H_2O	→	H^+ +	OH^-	$1.8 \times 10^{-16**}$

* K_a values vary among textbooks. When doing textbook homework, use the textbook's values for K_a.

** For consistency when comparing water's K_a to other acids, $K_a = K_w$ /55 M is used.

In acid-strength tables:

- The strongest acid has the largest K_a ; the weakest acid has the smallest K_a.
- The *strongest acids* are listed at the *top left* in the table. The acid strength and K_a values for the acids go down as you go down the left (acid) column.
- If conjugate bases are listed on the right, the *strongest base* is at the *bottom right* of the table. Why? The weakest acid is at the bottom left. When it loses its proton, it becomes the strongest base.

The arrangement of the acid strength table in most textbooks is

Strongest Acid ↓	→	H^+ + Weakest Base ↑	K_a = very large
Weakest Acid	→	H^+ + **Strongest Base**	K_a = very small

Cover the answer below and, using the above table, try this question.

Q1. Label below the particles in this proton-transfer reaction: the strong**er** acid (sA), the strong**er** base (sB), the weak**er** acid (wA), or the weak**er** base (wB).

$$Cl^- + CH_3COOH \leftrightarrows HCl + CH_3COO^-$$

* * * * *

<u>**Answer**</u>

First, label each particle as acting as an acid or a base (some particles can act as both). Recall that acids release protons, each side will have one acid and one base, and if a particle is acting on one side as an acid, on the other side is its conjugate base.

* * * * *

$$\underset{\mathbf{B}}{Cl^-} + \underset{\mathbf{A}}{CH_3COOH} \leftrightarrows \underset{\mathbf{A}}{HCl} + \underset{\mathbf{B}}{CH_3COO^-}$$

Next, using the table, identify one particle as the strong*er* of the two *acids*.

* * * * *

$$\underset{B}{Cl^-} + \underset{A}{CH_3COOH} \leftrightarrows \underset{\mathbf{sA}}{HCl} + \underset{B}{CH_3COO^-}$$

If you do the first label correctly, labeling the rest is automatic: the stronger acid must be on the same side as the stronger base, and the weaker acid and base must also be on the same side.

$$\underset{\mathbf{wB}}{Cl^-} + \underset{\mathbf{wA}}{CH_3COOH} \leftrightarrows \underset{sA}{HCl} + \underset{\mathbf{sB}}{CH_3COO^-}$$

To check, find the two bases on the *right* of the arrows in the table. The stronger base (**sB)** should be nearer the *bottom* of the table than the weaker base.

Answer these.

Q2. Which *side* of a reversible acid-base reaction is *favored* at equilibrium?

Q3. When will an acid and a base *react* if they are combined?

Q4. When will an acid and base *not* react?

* * * * *

A2. The side with the *weaker* acid and base.

A3. When the reaction can form a *weaker* acid and base as products.

A4. They will *not* react *if* the only possible products are a *stronger* acid and base.

Based on your answers to **Q1-Q4** above, for the reaction in **Q1**,

Q5. Which side of the reaction will be favored at equilibrium: left or right?

Q6. Will the acid and base on the *left* react when mixed? If so, what will they form?

Q7. Will the acid and base on the *right* react when mixed? If so, what will they form?

* * * * *

Answer

A5. The *left* side is favored. The favored side at equilibrium is the side with the *weaker* acid and base.

A6. The acid and base on the *left* will tend *not* to react. At equilibrium, all reactants and products must be present, so a very small amount of the stronger acid and base in the products will exist, but since the proton is attached to the weaker acid on the left, the *favored* side at equilibrium already exists, and very little reaction going to the right will take place.

A7. The acid and base on the right are the *stronger* of the two possibilities, so they *will* react. At equilibrium, nearly all of the limiting reactant in the stronger pair is used up, an equal number of moles of the reactant on its side is also used up, and both of the *weaker* acid and base in their conjugate pairs in the table have formed.

Practice A: Do each numbered problem. Do every other letter on the problems with parts, and more if you need more practice. Check answers as you go.

1. Write a letter below each particle to label it as an acid (A) or base (B) in these reactions.

   a. $HCl + F^- \leftrightarrows Cl^- + HF$

   b. $CH_3COO^- + HCN \leftrightarrows CH_3COOH + CN^-$

   c. $SO_4^{2-} + C_6H_5COOH \leftrightarrows HSO_4^- + C_6H_5COO^-$

2. In the above reactions, label each particle as the stronger acid (sA), the stronger base (sB), the weaker acid (wA), or the weaker base (wB).
3. In the above reactions, circle the side of the reaction that is favored at equilibrium.
4. Label each of the above reactions as *will go* to make the products, or *won't go*.
5. Complete these reactions, and then label the reaction as *will go* or *won't go*.

   a. $HF + CN^- \leftrightarrows$

   b. $H_2PO_4^- + SO_4^{2-} \leftrightarrows$

   c. $CN^- + H_2PO_4^- \leftrightarrows$

d. F^{-} + Cl^{-} ⇆

e. HNO_3 + HCl ⇆

Quick Predictions For Acid-Base Reactions

In the previous lesson, to predict whether an acid and base react, we used the

> **Labeling Rule**: Using the acid-strength table, label each particle in the reactants and products as strong**er** acid (sA), sB, wA, or wB. Equilibrium favors the side with the wA and wB: sA and wB react, wA and wB form, and wA and wB will not react.

A quicker way to predict whether an acid and base mixed together will *react* can be added to our Brønsted-Lowry rules as number

12. If the strongest acid or bases in an acid-strength table are listed at the *top left* and if particle concentrations are similar, any particle to the *left* of the arrows will tend to react with any particle on the *right* of the arrows *BELOW* it in the table. The products will be the conjugates of each particle: the weaker acid and the weaker base.

Cover the answer below, then use Brønsted-Lowry Rule 12 on these examples.

Q. Assuming the particle concentrations are similar, use the acid-strength table to label each combination as *will react* or *won't react* as acids and bases when mixed.

a. CN^{-} + HCl ⇆

b. CH_3COOH + SO_4^{2-} ⇆

c. PO_4^{3-} + NO_3^{-} ⇆

d. $H_2PO_4^{-}$ + PO_4^{3-} ⇆

* * * * *

Answers

a. CN^{-} + HCl ⇆ **Will react.** The table lists the strongest acid at the top left. HCl is an acid at the top left, and CN^{-} is on the base side *and* below it.

b. CH_3COOH + SO_4^{2-} ⇆ **Won't react.** CH_3COOH is an acid at the middle left of the table; SO_4^{2-} is on the base side but above the acid.

c. PO_4^{3-} + NO_3^{-} ⇆ **Won't react.** Both are in the table as bases. To have an acid-base reaction, you need an acid and a base.

d. $H_2PO_4^{-}$ + PO_4^{3-} ⇆ **Will react.** The $H_2PO_4^{-}$ appears on **both** sides of the table: it can be an acid *or* a base. But PO_4^{3-}, since it does not have a proton, must be the base, and on the acid (left) side $H_2PO_4^{-}$ appears above it. Particles on the left *react* with particles on the right and lower.

Practice B: Complete the odd numbers. Save the even for later practice. Use the acid-strength table to label these as *will react* or *won't react*.

1. HSO_4^{-} + F^{-} $\leftrightarrows$

2. HPO_4^{2-} + HCN $\leftrightarrows$

3. C_6H_5COOH + CH_3COOH $\leftrightarrows$

A short version of Rule 12 is the

Diagonal Rule: Particles \ diagonal react to form / diagonals; particles / do not react.

Use the diagonal rule and the acid-strength table to answer the following.

Q. Assuming the particle concentrations are similar, label these as *will react* or *won't react*.

1. HNO_3 + $H_2PO_4^{-}$ $\leftrightarrows$

2. $H_2PO_4^{-}$ + HF $\leftrightarrows$

* * * * *

Answers

A1. HNO_3 + $H_2PO_4^{-}$ $\leftrightarrows$ **Will react.** HNO_3 is \ above $H_2PO_4^{-}$ on the right.

A2. $H_2PO_4^{-}$ + HF $\leftrightarrows$ **Won't react.** HF is / to the $H_2PO_4^{-}$ on the base side.

Practice C: Complete the odds; save the even for later. Use the acid-strength table and diagonal rule to label these as *will react* or *won't react*.

1. HCO_3^{-} + HCN $\leftrightarrows$

2. NH_4^{+} + PO_4^{3-} $\leftrightarrows$

3. HPO_4^{2-} + HF $\leftrightarrows$

Constructing An Acid-Strengths Table

In some problems, a complete acid-base strengths table will not be supplied. Instead, you will be given a list of acids only, with the strongest at the top. If this is the case, you can make your own acid-base table by writing the conjugate bases on the right. You can then use your table to solve problems.

Cover the answer below and try the following example.

Q. The following is a list of acids, ordered with the strongest at the top.

HCl

CH_3COOH

H_2CO_3

NH_4^+

HCO_3^-

H_2O

a. Add the conjugate bases in a column on the right. (Do this part, check your answer, and then try the parts b - d below.)

b. What is the formula for the strongest base in your completed table?

c. What is the formula for the weakest base in your table?

d. Will these react: $\mathbf{CH_3COOH + OH^- \rightarrow}$ If so, what products will form?

* * * * *

Answer

a. See table at right.

b. Strongest base? $\mathbf{OH^-}$ The weakest acid is H_2O. Its conjugate is the strongest base.

c. Weakest base? $\mathbf{Cl^-}$. The weakest base is formed when a proton leaves the strongest acid.

d. They **will** react. This reaction will *go*. The acid CH_3COOH on the left will react with the base OH^- below it in the acid-strength table. The two reactants form conjugates that are listed opposite them in the table.

Acid	Conjugate base
HCl	Cl^-
$\mathbf{CH_3COOH}$	CH_3COO^-
H_2CO_3	HCO_3^-
NH_4^+	NH_3
HCO_3^-	CO_3^{2-}
H_2O	$\mathbf{OH^-}$

Practice D

1. Use the acid-strength table that you constructed above to answer these questions.

   a. Complete this reaction, and then label below each particle: sA, sB, wA, or wB.

   $NH_4^+ + OH^- \leftrightarrows$

   b. Will the reactants in *part 1a* form the products? Will the acid-base reaction go?

   c. In the *part 1a* reaction, NH_4^+ is part of an *ionic* compound. Ionic compounds do not boil or evaporate to form gases except at very high temperatures. At room temperature they have no odor because they do not form gas particles that can travel through the air. Ammonia (NH_3) is a covalent compound and a gas at room temperature that dissolves readily but reversibly in water. A mixture of ammonia and water is often used in commercial blue-dyed glass cleaning solutions that have a characteristic, unpleasant "ammonia odor."

In the 1a reaction above, NH_4^+ and OH^-, before they are mixed, are ionic; they will have no odor. After those two ions are mixed in the above reaction, will the mixture have an odor? Why or why not?

2. You spill an aqueous 1.0 M solution of ammonia (NH_3) on the floor. The odor is unpleasant. Using the acid-strength table that you constructed above, state whether 1.0 M solutions of each of these will deodorize the ammonia by changing it to NH_4^+.

   a. H_2O b. CH_3COOH c. NaOH d. $NaHCO_3$ e. HCl

3. To the right is a table of acids in order of strength, with the strongest acid at the top.

HCl
CH_3COOH
H_2CO_3
C_6H_5OH
C_2H_5OH

   a. If bicarbonate ion (HCO_3^-) is added to a mixture of CH_3COOH, C_2H_5OH, and C_6H_5OH, which of those three will react with the bicarbonate?

   b. If the bicarbonate does react, which products will be formed?

ANSWERS

Practice A

1, 2, 3, 4. a. $HCl + F^- \leftrightarrows Cl^- + HF$
sA **sB** **wB** **wA** **Will go** **-** equilibrium favors weaker acid and base.

b. $CH_3COO^- + HCN \leftrightarrow CH_3COOH + CN^-$
wB **wA** **sA** **sB** **Won't go** **-** favors wA and wB.

c. $SO_4^{2-} + C_6H_5COOH \leftrightarrows HSO_4^- + C_6H_5COO^-$
wB **wA** **sA** **sB** **Won't go** to right.

5. a. $HF + CN^- \leftrightarrows$ **F^- + HCN**
sA **sB** **wB** **wA** **Will go.** Equilibrium favors weaker A and B.

b. $H_2PO_4^- + SO_4^{2-} \leftrightarrows$ **HPO_4^{2-} + HSO_4^-**
wA **wB** **sB** **sA** **Won't go** **-** favors wA and wB.

c. $CN^- + H_2PO_4^- \leftrightarrows$ **HCN + HPO_4^{2-}**
sB **sA** **wA** **wB** **Will go.** Equilibrium favors weaker A and B.

d. $F^- + Cl^- \leftrightarrows$
B **B** **Can't go.** Need an acid and a base.

e. HNO_3 + HCl ⇆

A **A** **Can't go.** Need an acid and a base.

Practice B

1. HSO_4^- + F^- ⇆ **Will react.** HSO_4^- on acid side is above F^- on base side.
2. HPO_4^{2-} + HCN ⇆ **Won't react.** HCN is acid; HPO_4^{2-} on the base side is above HCN.
3. C_6H_5COOH + CH_3COOH ⇆ **Won't react.** Both are in the table as acids.

Practice C

1. HCO_3^- + HCN ⇆ **Won't react.** HCN is an acid, HCO_3^- on the base side is / .
2. NH_4^+ + PO_4^{3-} ⇆ **Will react.** NH_4^+ is an acid, PO_4^{3-} is a base and they are \ .
3. HPO_4^{2-} + HF ⇆ **Will react.** HF is acid, HPO_4^{2-} can be a base and they are \ .

Practice D

1. a. NH_4^+ + OH^- ⇆ **NH_3 + H_2O**

   sA **sB** **wB** **wA**

   b. The reaction **will** go to form the products, because **a)** equilibrium favors the weaker acid and base; and/or **b)** the acid is in the table above the base.

   c. **Yes.** The mixture will smell like ammonia, because **NH_3** is a product of the reaction, and the reaction goes to form ammonia.

2. a. H_2O **No.** To change the NH_3 to NH_4^+ ions, you need an acid, because the ammonia must act as a base. H_2O can act as an acid, but NH_3 as a base is above water as an acid in the table, so the acid-base reaction will not take place. The odor continues.

   b. CH_3COOH **Yes.** This is an acid above the base NH_3 in the table, so the reaction **will** take place. NH_3 gas which can leave the water becomes NH_4^+ ions which cannot. The ammonia odor dissipates.

   c. NaOH **No.** Solid NaOH mixed in a water solution is soluble. It will dissolve and form OH^- ions. In the table, OH^- ions are a base. NaOH is a strong base. We need an acid to change NH_3 to NH_4^+, so there will be **no** acid-base reaction. The odor continues.

   d. $NaHCO_3$ **No.** When Na, an alkali metal, is part of a compound, the compound will be soluble in water and separate into ions 100%. The HCO_3^- (bicarbonate) ion that forms upon ionization is in the table twice, as both an acid and a base. As a base, it can't convert NH_3 to NH_4^+. As an acid, bicarbonate is below the base NH_3. There will be no reaction. The odor continues.

   e. HCl **Yes.** HCl is a very strong acid, and the NH_3 is below it as a base. Reaction **occurs** when HCl is added, and NH_3 is converted to NH_4^+. The ammonia odor dissipates.

3. In the stated mixture, only the **CH_3COOH** is an acid above the HCO_3^- base in the table. When CH_3COOH is added, the bicarbonate ion will change to **H_2CO_3** which will quickly decompose into H_2O and bubbles of CO_2 (see Lesson 14E). Acetate ion also forms.

Acid	**Conjugate base**
HCl	
CH_3COOH	
H_2CO_3	**HCO_3^-**
C_6H_5OH	
C_2H_5OH	

   The reaction is:

   $CH_3COOH + HCO_3^- \rightarrow [H_2CO_3] + CH_3COO^- \rightarrow \mathbf{H_2O + CO_2\uparrow + CH_3COO^-}$

* * * * *

SUMMARY -- Brønsted-Lowry Definitions

1. Using the **Brønsted-Lowry definitions** of acids and bases:
   a. An acid-base reaction is a **proton transfer**: H^+ moves from one particle to another.
   b. An acid and a base react to form another acid and another base.
   c. The acid is the proton donor and the base is the proton acceptor.
   d. The particles in the equilibrium are two conjugate acid-base pairs. A particle on one side has its conjugate on the other side.
   e. The stronger acid reacts to become the weaker base. The stronger base reacts to become the weaker acid.
   f. The stronger acid and base are on the same side of the equilibrium equation.
   g. Equilibrium favors the weakest acid and the weakest base.

2. If the strongest acid *or* bases in an acid-strength table are listed at the *top left*, if particle concentrations are similar, a particle on the *left* will tend to react with a particle on the *right BELOW* it in the table. The products will be the conjugates of each particle: the weaker acid and the weaker base.

This can be summarized as the

<u>Diagonal Rule</u>: Particles \ diagonal react to form / diagonals; particles / do not react.

# # # # #