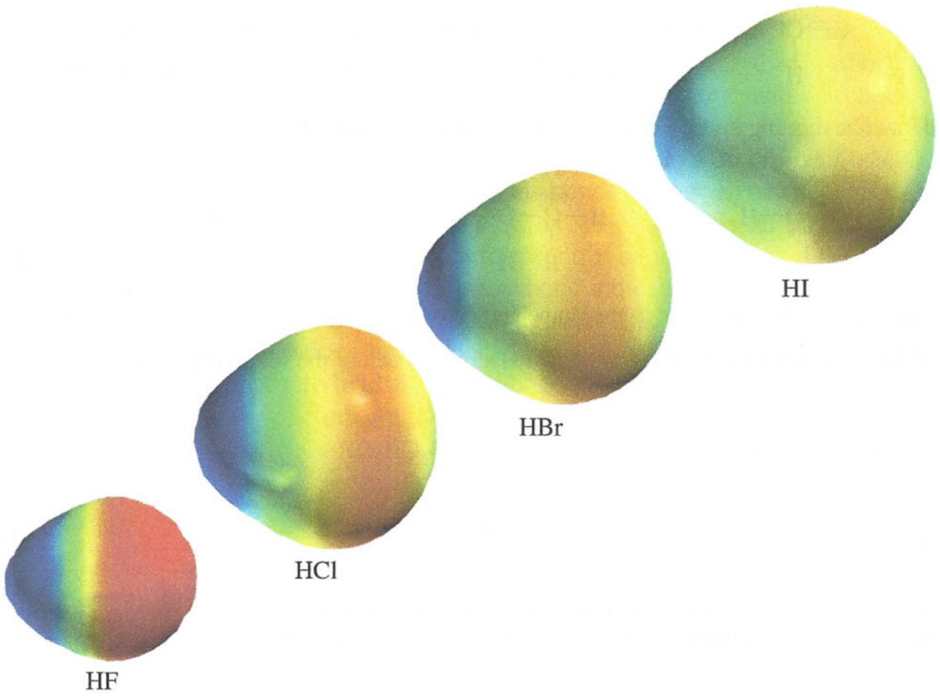
CHAPTER 2

Acids and Bases



Early chemists called any compound that tasted sour an acid (from *acidus*, Latin for "sour"). Some familiar acids are citric acid (found in lemons and other citrus fruits), acetic acid (found in vinegar), and hydrochloric acid (found in stomach acid—the sour taste associated with vomiting). Compounds that neutralize acids were called bases, or alkaline compounds. Glass cleaners and solutions designed to unclog drains are familiar alkaline solutions.

2.1 AN INTRODUCTION TO ACIDS AND BASES

Brønsted and Lowry defined an **acid** as a species that donates a proton, and a **base** as a species that accepts a proton. (Remember that positively charged hydrogen ions are called protons.) In the reaction shown below, hydrogen chloride (HCl) is an acid because it donates a proton to water, and water is a base because it accepts a proton from HCl. Water can accept a proton because it has two lone pairs, either of which can form a covalent bond with a proton. In the reverse reaction, H_3O^+ is an acid because it donates a proton to Cl^-, and Cl^- is a base because it accepts a proton from H_3O^+. The reaction of an acid with a base is called an **acid–base reaction**. Both an acid and a base must be present in an acid–base reaction, because an acid cannot donate a proton unless a base is present to accept it.

$$\underset{\text{an acid}}{H\ddot{\underset{\cdot\cdot}{Cl}}:} + \underset{\text{a base}}{H_2\ddot{O}:} \rightleftharpoons \underset{\text{a base}}{:\ddot{\underset{\cdot\cdot}{Cl}}:^-} + \underset{\text{an acid}}{H_3\ddot{O}^+}$$

Notice that according to the Brønsted–Lowry definitions, *any species that has a hydrogen can potentially act as an acid, and any compound that has a lone pair can potentially act as a base.*

When a compound loses a proton, the resulting species is called its **conjugate base.** Thus, Cl^- is the conjugate base of HCl, and H_2O is the conjugate base of H_3O^+. When a compound accepts a proton, the resulting species is called its **conjugate acid**. Thus, HCl is the conjugate acid of Cl^-, and H_3O^+ is the conjugate acid of H_2O.

In a reaction between ammonia and water, ammonia (NH_3) is a base because it accepts a proton, and water is an acid because it donates a proton. Thus, HO^- is the conjugate base of H_2O, and ${}^+NH_4$ is the conjugate acid of NH_3. In the reverse reaction, ammonium ion (${}^+NH_4$) is an acid because it donates a proton, and hydroxide ion (HO^-) is a base because it accepts a proton.

$$\underset{\text{a base}}{\ddot{N}H_3} + \underset{\text{an acid}}{H_2\ddot{O}:} \rightleftharpoons \underset{\text{an acid}}{{}^{+}NH_4} + \underset{\text{a base}}{H\ddot{\underset{..}{O}}:^-}$$

Notice that water can behave as either an acid or a base. It can behave as an acid because it has a proton that it can donate, but it can also behave as a base because it has a lone pair that can accept a proton. In Section 2.2, we will see how we can predict that water acts as a base in the first reaction and as an acid in the second reaction.

Acidity is a measure of the tendency of a compound to give up a proton. **Basicity** is a measure of a compound's affinity for a proton. A strong acid is one that has a strong tendency to give up its proton. This means that its conjugate base must be weak because it has little affinity for the proton. A weak acid has little tendency to give up its proton, indicating that its conjugate base is strong because it has a high affinity for the proton. Thus, the following important relationship exists between an acid and its conjugate base: *the stronger the acid, the weaker is its conjugate base*. For example, since HBr is a stronger acid than HCl, we know that Br^- is a weaker base than Cl^-.

PROBLEM 1 ◆

a. Draw the conjugate acid of each of the following:
   1. NH_3 2. Cl^- 3. HO^- 4. H_2O

b. Draw the conjugate base of each of the following:
   1. NH_3 2. HBr 3. HNO_3 4. H_2O

PROBLEM 2

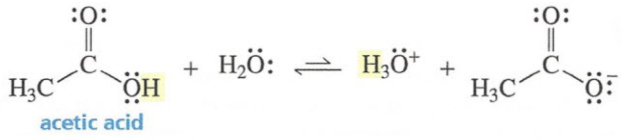
a. Write an equation showing CH_3OH reacting as an acid with NH_3 and an equation showing CH_3OH reacting as a base with HCl.

b. Write an equation showing NH_3 reacting as an acid with HO^- and an equation showing NH_3 reacting as a base with HBr.

2.2 pK_a AND pH

When a strong acid such as hydrogen chloride is dissolved in water, almost all the molecules dissociate (break into ions), which means that the *products* are favored at equilibrium—the equilibrium lies to the right. When a much weaker acid, such as acetic acid, is dissolved in water, very few molecules dissociate, so the *reactants* are favored at equilibrium—the equilibrium lies to the left. Two half-headed arrows are used to designate equilibrium reactions. A longer arrow is drawn toward the species favored at equilibrium.

$$\underset{\text{hydrogen chloride}}{H\ddot{\underset{..}{Cl}}:} + H_2\ddot{O}: \rightleftharpoons H_3\ddot{O}^+ + :\ddot{\underset{..}{Cl}}:^-$$


acetic acid

BIOGRAPHY

Born in Denmark, **Johannes Nicolaus Brønsted (1879–1947)** *studied engineering before he switched to chemistry. He was a professor of chemistry at the University of Copenhagen. During World War II, he became known for his anti-Nazi position, and as a consequence was elected to the Danish parliament in 1947. He died before he could take his seat.*

The stronger the acid, the more readily it gives up a proton.

The stronger the acid, the weaker is its conjugate base.

BIOGRAPHY

Thomas M. Lowry (1874–1936) *was born in England, the son of an army chaplain. He earned a Ph.D. at Central Technical College, London (now Imperial College). He was head of chemistry at Westminster Training College and, later, at Guy's Hospital in London. In 1920, he became a professor of chemistry at Cambridge University.*

The degree to which an acid (HA) dissociates in an aqueous solution is indicated by the **acid dissociation constant, K_a**. Brackets are used to indicate the concentration in moles/liter, that is, the molarity (M).

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

The larger the acid dissociation constant, the stronger is the acid—that is, the greater is its tendency to give up a proton. Hydrogen chloride, with an acid dissociation constant of 10^7, is a stronger acid than acetic acid, with an acid dissociation constant of only 1.74×10^{-5}. For convenience, the strength of an acid is generally indicated by its **pK_a** value rather than by its K_a value, where

$$pK_a = -\log K_a$$

The stronger the acid, the smaller is its pK_a value.

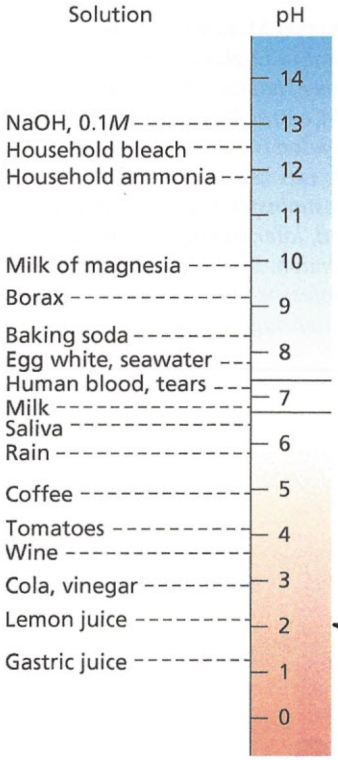
The pK_a of hydrogen chloride is −7, and the pK_a of acetic acid, a much weaker acid, is 4.76. Notice that the stronger the acid, the smaller is its pK_a value.

very strong acids	$pK_a < 1$
moderately strong acids	$pK_a = 1{-}3$
weak acids	$pK_a = 3{-}5$
very weak acids	$pK_a = 5{-}15$
extremely weak acids	$pK_a > 15$

The concentration of positively charged hydrogen ions in the solution is indicated by **pH**. The concentration can be written as $[H^+]$ or, because a hydrogen ion in water is solvated, as $[H_3O^+]$.

$$pH = -\log[H_3O^+]$$

The lower the pH, the more acidic is the solution. Acidic solutions have pH values less than 7; basic solutions have pH values greater than 7. The pH values of some commonly encountered solutions are shown in the margin. The pH of a solution can be changed simply by adding acid or base to the solution. Do not confuse pH and pK_a: the pH scale is used to describe the acidity of a *solution*; the pK_a is characteristic of a particular *compound*, much like a melting point or a boiling point—it indicates the tendency of the compound to give up its proton.



PROBLEM 3 ◆

a. Which is a stronger acid, one with a pK_a of 5.2 or one with a pK_a of 5.8?

b. Which is a stronger acid, one with an acid dissociation constant of 3.4×10^{-3} or one with an acid dissociation constant of 2.1×10^{-4}?

PROBLEM-SOLVING STRATEGY

Vitamin C has a pK_a value of 4.17. What is its K_a value?

You will need a calculator to answer this question. Remembering that $pK_a = -\log K_a$:

1. Enter the pK_a value on your calculator.
2. Multiply it by −1.
3. Determine the inverse log by pressing the key labeled 10^x.

You should find that vitamin C has a K_a value of 6.76×10^{-5}.

Now continue on to Problem 4.

PROBLEM 4 ◆

Butyric acid, the compound responsible for the unpleasant odor and taste of sour milk, has a pK_a value of 4.82. What is its K_a value? Is it a stronger or a weaker acid than vitamin C?

ACID RAIN

Rain is mildly acidic (pH = 5.5) because when the CO_2 in the air reacts with water, a weak acid—carbonic acid (pK_a = 6.4)—is formed.

$$CO_2 + H_2O \rightleftharpoons \underset{\text{carbonic acid}}{H_2CO_3}$$

In some parts of the world, rain has been found to be much more acidic—with pH values as low as 4.3. Acid rain is formed when sulfur dioxide and nitrogen oxides are produced, because when these gases react with water, strong acids—sulfuric acid (pK_a = −5.0) and nitric acid (pK_a = −1.3)—are formed. Burning fossil fuels for the generation of electric power is the factor most responsible for forming these acid-producing gases.

Acid rain has many deleterious effects. It can destroy aquatic life in lakes and streams; it can make soil so acidic that crops cannot grow; and it can cause the deterioration of paint and building materials, including monuments and statues that are part of our cultural heritage. Marble—a form of calcium carbonate—decays because acid reacts with CO_3^{2-} to form carbonic acid, which decomposes to CO_2 and H_2O, the reverse of the reaction shown to the left.

$$CO_3^{2-} \xrightleftharpoons{H^+} HCO_3^- \xrightleftharpoons{H^+} H_2CO_3 \rightleftharpoons CO_2 + H_2O$$

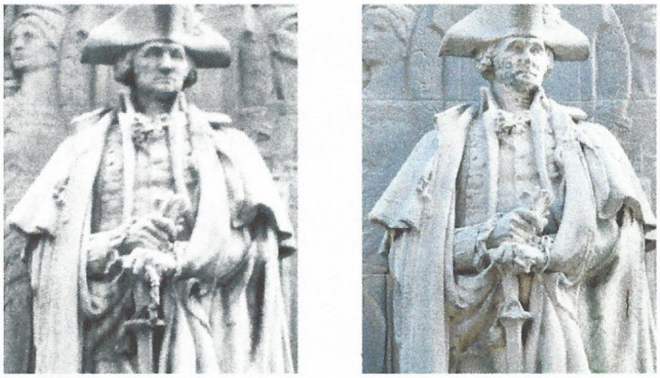


photo taken in 1935

photo taken in 1994

Statue of George Washington in Washington Square Park in Greenwich Village, New York.

PROBLEM 5

Antacids are compounds that neutralize stomach acid. Write the equations that show how Milk of Magnesia, Alka-Seltzer, and Tums remove excess acid.

a. Milk of Magnesia: $Mg(OH)_2$

b. Alka-Seltzer: $KHCO_3$ and $NaHCO_3$

c. Tums: $CaCO_3$

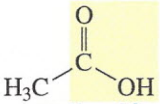
PROBLEM 6 ♦

Are the following body fluids acidic or basic?

a. bile (pH = 8.4) **b.** urine (pH = 5.9) **c.** spinal fluid (pH = 7.4)

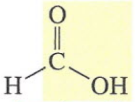
2.3 ORGANIC ACIDS AND BASES

The most common organic acids are carboxylic acids—compounds that have a COOH group. Acetic acid and formic acid are examples of carboxylic acids. Carboxylic acids have pK_a values ranging from about 3 to 5. (They are weak acids.) The pK_a values of a wide variety of organic compounds are given in Appendix II.



acetic acid

pK_a = 4.76

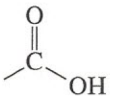


formic acid

pK_a = 3.75

3-D Molecule:
Acetic acid

The carboxyl group of a carboxylic acid can be represented in several different ways.



a carboxyl group

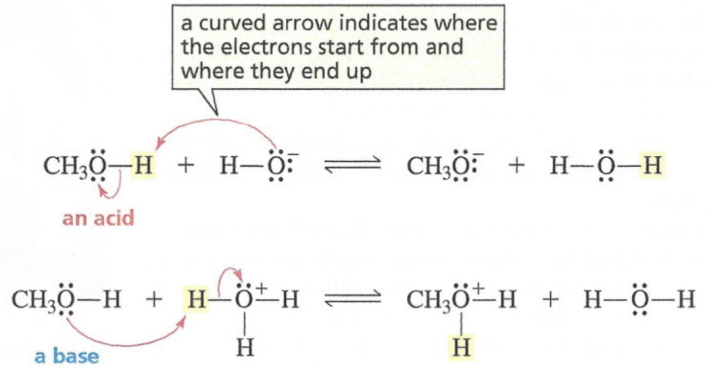
$-\mathrm{COOH}$ $\quad -\mathrm{CO_2H}$

carboxyl groups are frequently shown in abbreviated forms

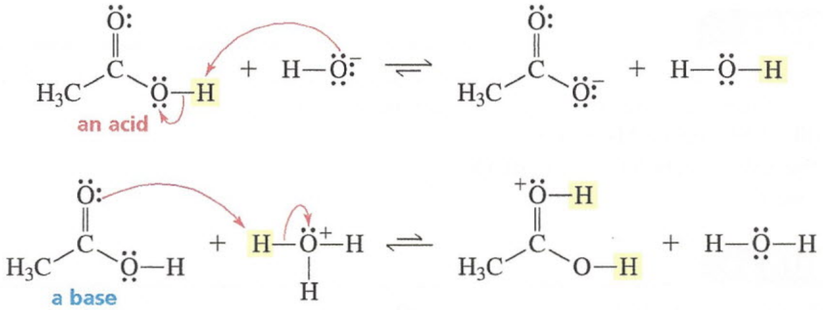
Alcohols—compounds that have an OH group—are much weaker acids than carboxylic acids, with pK_a values close to 16. Methyl alcohol and ethyl alcohol are examples of alcohols.

CH_3OH	CH_3CH_2OH
methyl alcohol	ethyl alcohol
pK_a = 15.5	pK_a = 15.9

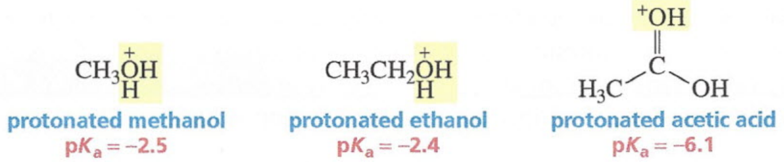
We have seen that water can behave both as an acid and as a base. An alcohol behaves similarly; it can behave as an acid and donate a proton, or as a base and accept a proton.


a curved arrow indicates where the electrons start from and where they end up

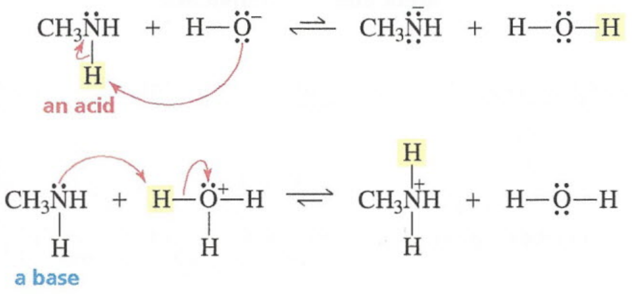
A carboxylic acid also can behave as an acid and donate a proton, or as a base and accept a proton.



A *protonated* compound is a compound that has gained an additional proton. Protonated alcohols and protonated carboxylic acids are very strong acids. For example, protonated methyl alcohol has a pK_a of −2.5, protonated ethyl alcohol has a pK_a of −2.4, and protonated acetic acid has a pK_a of −6.1. Notice that the sp^2 oxygen of the carboxylic acid is the one that is protonated. We will see why this is so in Section 11.9.



A compound with an NH_2 group is an amine. An amine can behave as an acid and donate a proton, or as a base and accept a proton.



Amines, however, have such high pK_a values that they rarely behave as acids. Ammonia also has a high pK_a value.

CH_3NH_2	NH_3
methylamine	ammonia
pK_a = 40	pK_a = 36

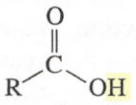
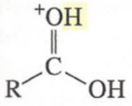
Amines are much more likely to act as bases. In fact, amines are the most common organic bases. Instead of talking about the strength of a base in terms of its pK_b value, it is easier to talk about the strength of its conjugate acid as indicated by its pK_a value, remembering that the stronger the acid, the weaker is its conjugate base. For example, protonated methylamine is a stronger acid than protonated ethylamine, which means that methylamine is a weaker base than ethylamine. Notice that the pK_a values of protonated amines are about 10 to 11.

$CH_3\overset{+}{N}H_3$	$CH_3CH_2\overset{+}{N}H_3$
protonated methylamine	protonated ethylamine
pK_a = 10.7	pK_a = 11.0

It is important to know the approximate pK_a values of the various classes of compounds we have discussed. An easy way to remember them is in units of five, as shown in Table 2.1. (R is used when the particular carboxylic acid, alcohol, or amine is not specified.) Protonated alcohols, protonated carboxylic acids, and protonated water have pK_a values less than 0, carboxylic acids have pK_a values of about 5, protonated amines have pK_a values of about 10, and alcohols and water have pK_a values of about 15. These values are also listed inside the back cover of this book for easy reference.

Be sure to learn the approximate pK_a values given in Table 2.1.

Table 2.1 Approximate pK_a Values

pK_a < 0	pK_a ~ 5	pK_a ~ 10	pK_a ~ 15
$R\overset{+}{O}H_2$ a protonated alcohol	 a carboxylic acid	$R\overset{+}{N}H_3$ a protonated amine	ROH an alcohol
 a protonated carboxylic acid			H_2O water
H_3O^+ protonated water			

PROBLEM 7 ◆

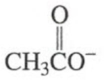
a. Which is a stronger base, CH_3COO^- or $HCOO^-$? (The pK_a of CH_3COOH is 4.8; the pK_a of HCOOH is 3.8.)

b. Which is a stronger base, HO^- or $^-NH_2$? (The pK_a of H_2O is 15.7; the pK_a of NH_3 is 36.)

c. Which is a stronger base, H_2O or CH_3OH? (The pK_a of H_3O^+ is −1.7; the pK_a of $CH_3\overset{+}{O}H_2$ is −2.5.)

PROBLEM 8 ◆

Using the pK_a values in Section 2.3, rank the following species in order of decreasing base strength (that is, list the strongest base first):

CH_3NH_2 CH_3NH^- CH_3OH CH_3O^- 

$CH_3\overset{\overset{\displaystyle O}{\|}}{C}O^-$

2.4 HOW TO PREDICT THE OUTCOME OF AN ACID–BASE REACTION

Now let's see how we can predict that water will act as a base in the first reaction in Section 2.1 and as an acid in the second reaction. To determine which of the two reactants of the first reaction will be the acid, we need to compare their pK_a values: the pK_a of hydrogen chloride is −7, and the pK_a of water is 15.7. Because hydrogen chloride is the stronger acid, it will donate a proton to water. Water, therefore, is a base in this reaction. When we compare the pK_a values of the two reactants of the second reaction, we see that the pK_a of ammonia is 36 and the pK_a of water is 15.7. In this case, water is the stronger acid, so it donates a proton to ammonia. Water, therefore, is an acid in this reaction.

PROBLEM 9 ◆

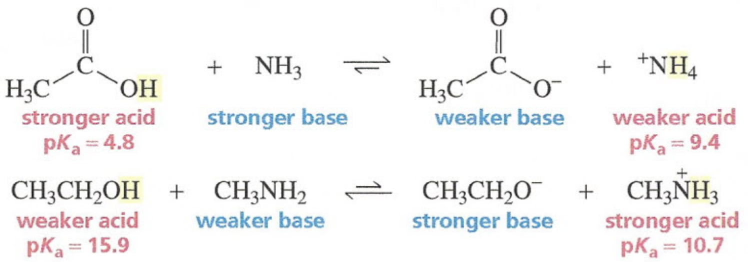
Using the pK_a values in Section 2.3, predict the products of the following reaction:

$CH_3NH_2 + CH_3OH \rightleftharpoons$

2.5 HOW TO DETERMINE THE POSITION OF EQUILIBRIUM

To determine the position of equilibrium for an acid–base reaction (that is, whether reactants or products are favored at equilibrium), we need to compare the pK_a value of the acid on the left of the arrow with the pK_a value of the acid on the right of the arrow. The equilibrium favors *reaction* of the stronger acid and *formation* of the weaker acid. Thus, the equilibrium lies away from the stronger acid and toward the weaker acid. Products, therefore, are favored in the first reaction, and reactants are favored in the second reaction. Notice that the stronger acid has the weaker (more stable) conjugate base, so the equilibrium favors formation of the more stable species.

Strong reacts to form weak.



PROBLEM 10

a. For each of the acid–base reactions in Section 2.3, compare the pK_a values of the acids on either side of the equilibrium arrows and convince yourself that the position of equilibrium is in the direction indicated. (The pK_a values you need can be found in Section 2.3 or in Problem 7.)

b. Do the same thing for the equilibria in Section 2.1. (The pK_a of $^+NH_4$ is 9.4.)

2.6 HOW THE STRUCTURE OF AN ACID AFFECTS ITS pK_a

The weaker the base, the stronger is its conjugate acid.

Stable bases are weak bases.

The more stable the base, the stronger is its conjugate acid.

The strength of an acid is determined by the stability of the conjugate base that is formed when the acid gives up its proton: the more stable the base, the stronger is its conjugate acid. A stable base is a base that readily bears the electrons it formerly shared with a proton. In other words, stable bases are weak bases—they don't share their electrons well. That is why we can say, *the weaker the base, the stronger is its conjugate acid* or, *the more stable the base, the stronger is its conjugate acid.*

Two factors that affect the stability of a base are its *size* and its *electronegativity.* The elements in the second row of the periodic table are all about the same size, but they have very different electronegativities, which increase across the row from left to right. Therefore, of the atoms shown, carbon is the least electronegative and fluorine is the most electronegative.

relative electronegativities: $C < N < O < F$

most electronegative

If we look at the acids formed by attaching hydrogens to these elements, we see that the most acidic compound is the one that has its hydrogen attached to the most electronegative atom. Thus, HF is the strongest acid and methane is the weakest acid (Table 2.2).

relative acidities: $CH_4 < NH_3 < H_2O < HF$

strongest acid

If we look at the stabilities of the conjugate bases of these acids, we find that they too increase from left to right because the more electronegative the atom, the better it can bear its negative charge. Thus, we see that the strongest acid has the most stable conjugate base.

relative stabilities: $^{-}CH_3 < {}^{-}NH_2 < HO^- < F^-$

most stable

When atoms are similar in size, the strongest acid will have its hydrogen attached to the most electronegative atom.

We therefore can conclude that *when the atoms are similar in size, the strongest acid will have its hydrogen attached to the most electronegative atom.*

The effect that the electronegativity of the atom bonded to a hydrogen has on the acidity of that hydrogen can be appreciated when the pK_a values of alcohols and amines are compared. Because oxygen is more electronegative than nitrogen, an alcohol is more acidic than an amine.

CH_3OH
methyl alcohol
pK_a = 15.5

CH_3NH_2
methylamine
pK_a = 40

Similarly, a protonated alcohol is more acidic than a protonated amine.

$CH_3\overset{+}{O}H_2$
protonated methyl alcohol
pK_a = −2.5

$CH_3\overset{+}{N}H_3$
protonated methylamine
pK_a = 10.7

Table 2.2 The pK_a Values of Some Simple Acids

CH_4 pK_a = ~60	**NH_3** pK_a = 36	**H_2O** pK_a = 15.7	**HF** pK_a = 3.2
		H_2S pK_a = 7.0	**HCl** pK_a = −7
			HBr pK_a = −9
			HI pK_a = −10

When atoms are very different in size, the strongest acid will have its hydrogen attached to the largest atom.

In comparing atoms that are very different in size, the *size* of the atom is much more important than its *electronegativity* in determining how well it bears its negative charge. For example, as we proceed down a column in the periodic table, the atoms get larger and their electronegativity decreases. However the stability of the bases increases down the column, so the strength of their conjugate acid *increases*. Thus, HI is the strongest acid of the hydrogen halides, even though iodine is the least electronegative of the halogens. Therefore, *when atoms are very different in size, the strongest acid will have its hydrogen attached to the largest atom.*

relative electronegativities: $F > Cl > Br > I$

most electronegative

largest

relative stabilities: $F^- < Cl^- < Br^- < I^-$

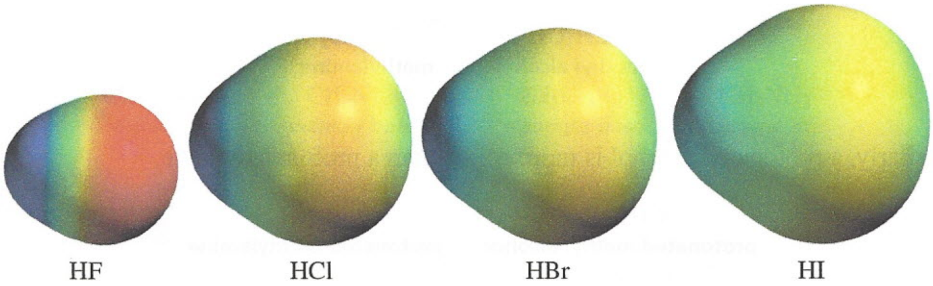
most stable

relative acidities: $HF < HCl < HBr < HI$

strongest acid

Why does the size of an atom have such a significant effect on the stability of the base that it more than overcomes the difference in electronegativity? The valence electrons of F^- are in a $2sp^3$ orbital, the valence electrons of Cl^- are in a $3sp^3$ orbital, those of Br^- are in a $4sp^3$ orbital, and those of I^- are in a $5sp^3$ orbital. The volume of space occupied by a $3sp^3$ orbital is significantly greater than the volume of space occupied by a $2sp^3$ orbital because a $3sp^3$ orbital extends out farther from the nucleus. Because its negative charge is spread over a larger volume of space, Cl^- is more stable than F^-.

Thus, as the halide ion increases in size, its stability increases because its negative charge is spread over a larger volume of space (its electron density decreases). Therefore, HI is the strongest acid of the hydrogen halides because I^- is the most stable halide ion, even though iodine is the least electronegative of the halogens (Table 2.2). The potential maps illustrate the large difference in size of the halogens:



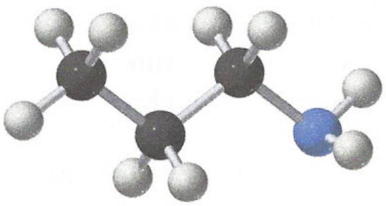
PROBLEM 11 ◆

For each of the following pairs, indicate which is the stronger acid:

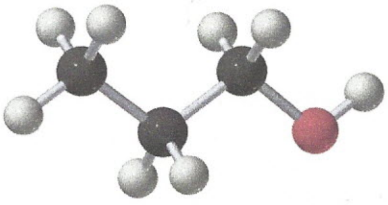
a. HCl or HBr

b. $CH_3CH_2CH_2\overset{+}{N}H_3$ or $CH_3CH_2CH_2\overset{+}{O}H_2$

c.



or

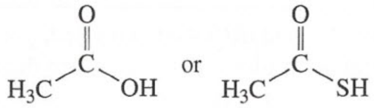


PROBLEM 12 ◆

a. Which of the halide ions (F^-, Cl^-, Br^-, I^-) is the strongest base?
b. Which is the weakest base?

PROBLEM 13 ◆

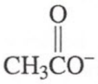
a. Which is more electronegative, oxygen or sulfur?
b. Which is a stronger acid, H_2O or H_2S?
c. Which is a stronger acid, CH_3OH or CH_3SH?
d. Which of the following is a stronger acid?



↖ watch this question

PROBLEM 14 ◆

For each of the following pairs, indicate which is the stronger base:

a. H_2O or HO^- **b.** H_2O or NH_3 **c.**  $CH_3\overset{\overset{O}{\|}}{C}O^-$ or CH_3O^- **d.** CH_3O^- or CH_3S^-

2.7 HOW pH AFFECTS THE STRUCTURE OF AN ORGANIC COMPOUND

Whether an acid will lose a proton in an aqueous solution depends on both the pK_a of the acid and the pH of the solution. *A compound will exist primarily in its acidic form (with its proton) in solutions that are more acidic than the* pK_a *value of the group that undergoes dissociation. It will exist primarily in its basic form (without its proton) in solutions that are more basic than the* pK_a *value of the group that undergoes dissociation.* When the pH of a solution equals the pK_a value of the group that undergoes dissociation, the concentration of the compound in its acidic form will equal the concentration of the compound in its basic form.

A compound will exist primarily in its acidic form if the pH of the solution is less than the compound's pK_a.

A compound will exist primarily in its basic form if the pH of the solution is greater than the compound's pK_a.

Tutorial:
Acid–base reaction
Effect of pH on structure

$$\begin{array}{ccc} \text{acidic form} & & \text{basic form} \\ RCOOH & \rightleftharpoons & RCOO^- + H^+ \\ R\overset{+}{N}H_3 & \rightleftharpoons & RNH_2 + H^+ \end{array}$$

PROBLEM-SOLVING STRATEGY

Write the form in which the following compounds will predominate in a solution with a pH = 5.5:

a. CH_3CH_2OH (pK_a = 15.9) **c.** $CH_3\overset{+}{N}H_3$ (pK_a = 11.0)

b. $CH_3CH_2\overset{+}{O}H_2$ (pK_a = −2.5)

To answer this kind of question, we need to compare the pH of the solution with the pK_a value of the compound's dissociable proton.

a. The pH of the solution is more acidic (5.5) than the pK_a value of CH_3CH_2OH (15.9). Therefore, the compound will exist primarily as CH_3CH_2OH (with its proton).

b. The pH of the solution is more basic (5.5) than the pK_a value of $CH_3CH_2\overset{+}{O}H_2$ (−2.5). Therefore, the compound will exist primarily as CH_3CH_2OH (without its proton).

c. The pH of the solution is more acidic (5.5) than the pK_a value of $CH_3\overset{+}{N}H_3$ (10.7). Therefore, the compound will exist primarily as $CH_3\overset{+}{N}H_3$ (with its proton).

Now continue on to Problem 15.

PROBLEM 15 ◆

For each of the following compounds, shown in their acidic forms, write the form that will predominate in a solution with a pH = 5.5:

a. CH_3COOH ($pK_a = 4.76$)
b. $CH_3CH_2\overset{+}{N}H_3$ ($pK_a = 11.0$)
c. H_3O^+ ($pK_a = -1.7$)
d. HBr ($pK_a = -9$)
e. $^+NH_4$ ($pK_a = 9.4$)
f. $HC{\equiv}N$ ($pK_a = 9.1$)
g. HNO_2 ($pK_a = 3.4$)
h. HNO_3 ($pK_a = -1.3$)

PROBLEM 16 ◆ *SOLVED*

a. Indicate whether a carboxylic acid (RCOOH) with a pK_a of 4.5 will have more charged molecules or more neutral molecules in a solution with the following pH value:

1. pH = 1
2. pH = 3
3. pH = 5
4. pH = 7
5. pH = 10
6. pH = 13

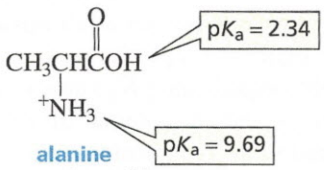
b. Answer the same question for a protonated amine ($R\overset{+}{N}H_3$) with a pK_a of 9.

c. Answer the same question for an alcohol (ROH) with a pK_a of 15.

Solution to 16 a1. First determine whether more molecules will be in the acidic form or the basic form; if the pH is less than the pK_a, more molecules will be in the acidic form; if the pH is greater than the pK_a, more molecules will be in the basic form. For 16a1, the pH = 1 and the pK_a = 4.5, so more molecules will be in the acidic form. Now determine whether the acidic form is charged or neutral. The acidic form of a carboxylic acid is neutral, so there will be more neutral molecules in the solution.

PROBLEM 17 ◆

A naturally occurring amino acid such as alanine has both a carboxylic acid group and an amine group. The pK_a values of the two groups are shown.



$$CH_3\underset{^+NH_3}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}OH$$

alanine
an amino acid

a. Write the structure of alanine in a solution at physiological pH (pH = 7.3).
b. Is there a pH at which alanine will be neutral (neither group will have a charge)?

2.8 BUFFER SOLUTIONS

A solution containing a weak acid (HA) and its conjugate base (A^-) is called a **buffer solution.** A buffer solution will maintain nearly constant pH when small amounts of acid or base are added to it, because the weak acid can donate a proton to any HO^- added to the solution, and its conjugate base can accept any H^+ that is added to the solution.

can donate an H^+ to HO^-

$$HA + HO^- \longrightarrow A^- + H_2O$$

$$A^- + H_3O^+ \longrightarrow HA + H_2O$$

can accept an H^+ from H_3O^+

BLOOD IS A BUFFERED SOLUTION

Blood is the fluid that transports oxygen to all the cells of the human body. The normal pH of human blood is 7.3 to 7.4. Death will result if this pH decreases to a value less than ~ 6.8 or increases to a value greater than ~ 8.0 for even a few seconds.

Oxygen is carried to cells by a protein in the blood called hemoglobin (HbH^+). When hemoglobin binds O_2, hemoglobin loses a proton, which would make the blood more acidic if it did not contain a buffer to maintain its pH.

$$HbH^+ + O_2 \rightleftharpoons HbO_2 + H^+$$

A carbonic acid/bicarbonate (H_2CO_3/HCO_3^-) buffer controls the pH of blood. An important feature of this buffer is that carbonic acid decomposes to CO_2 and H_2O:

$$CO_2 + H_2O \rightleftharpoons \underset{\text{carbonic acid}}{H_2CO_3} \rightleftharpoons \underset{\text{bicarbonate}}{HCO_3^-} + H^+$$

During exercise our metabolism speeds up, producing large amounts of CO_2. The increased concentration of CO_2 shifts the equilibrium between carbonic acid and bicarbonate to the right, which increases the concentration of H^+. Significant amounts of lactic acid are also produced during exercise, and this further increases the concentration of H^+. Receptors in the brain respond to the increased concentration of H^+ by triggering a reflex that increases the rate of breathing. Hemoglobin then releases more oxygen to the cells, and more CO_2 is eliminated by exhalation. Both processes decrease the concentration of H^+ in the blood by shifting both equilibria to the left.

Thus, any disorder that decreases the rate and depth of ventilation, such as emphysema, will decrease the pH of the blood—a condition called acidosis. In contrast, any excessive increase in the rate and depth of ventilation, such as hyperventilation due to anxiety, will increase the pH of blood—a condition called alkalosis.

PROBLEM 18

Write the equation that shows how a buffer made by dissolving CH_3COOH and $CH_3COO^-Na^+$ in water prevents the pH of a solution from changing when

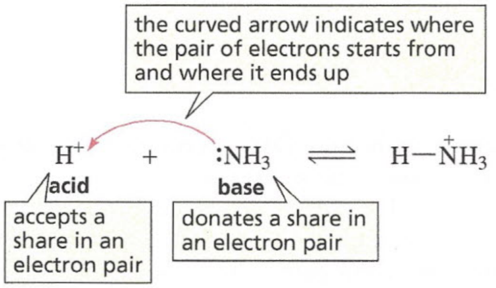
a. a small amount of H^+ is added to the solution.
b. a small amount of HO^- is added to the solution.

2.9 LEWIS ACIDS AND BASES

In 1923, G. N. Lewis (page 6) offered new definitions for the terms *acid* and *base*. He defined an acid as a species that *accepts a share in an electron pair* and a base as a species that *donates a share in an electron pair*. All proton-donating acids fit the Lewis definition because all proton-donating acids lose a proton and the proton accepts a share in an electron pair.

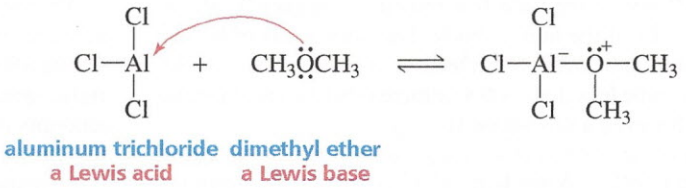
Lewis acid: need two from you.

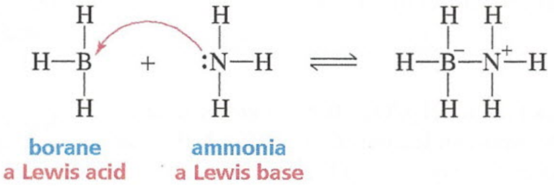
Lewis base: have pair, will share.



Lewis acids, however, are not limited to compounds that donate protons. According to the Lewis definition, compounds such as aluminum trichloride ($AlCl_3$) and borane (BH_3) are acids because they have unfilled valence orbitals and thus can accept a share in an electron pair. These compounds react with a compound that has a lone pair, just as a proton reacts with ammonia. Thus, the Lewis definition of an acid includes all proton-donating compounds and some additional compounds that do not have protons. Throughout this text, the term *acid* is used to mean a proton-donating acid, and the term **Lewis acid** is used to refer to a non-proton-donating acid such as $AlCl_3$ or BH_3.

All bases are **Lewis bases** because they all have a pair of electrons that they can share, either with an atom such as aluminum or boron or with a proton.





PROBLEM 19

Write the products of the following reactions using arrows to show where the pair of electrons starts and where it ends up:

a. $\mathrm{ZnCl_2} + \mathrm{CH_3\ddot{\underset{..}{O}}H} \rightleftharpoons$

b. $\mathrm{FeBr_3} + :\ddot{\underset{..}{\mathrm{Br}}}:^- \rightleftharpoons$

c. $\mathrm{AlCl_3} + :\ddot{\underset{..}{\mathrm{Cl}}}:^- \rightleftharpoons$

PROBLEM 20

Write the products formed from the reaction of each of the following species with HO^-:

a. CH_3OH
b. $^+NH_4$
c. $CH_3\overset{+}{N}H_3$
d. BF_3
e. $^+CH_3$
f. $FeBr_3$
g. $AlCl_3$
h. CH_3COOH

SUMMARY

An **acid** is a species that donates a proton; a **base** is a species that accepts a proton. A **Lewis acid** is a species that accepts a share in an electron pair; a **Lewis base** is a species that donates a share in an electron pair.

Acidity is a measure of the tendency of a compound to give up a proton. **Basicity** is a measure of a compound's affinity for a proton. The stronger the acid, the weaker is its conjugate base. The strength of an acid is given by the **acid dissociation constant** (**K_a**). Approximate pK_a values are as follows: protonated alcohols, protonated carboxylic acids, protonated water < 0; carboxylic acids ~ 5; protonated amines ~ 10; alcohols and water ~ 15. The **pH** of a solution indicates the concentration of positively charged hydrogen ions in the solution. In **acid–base reactions**, the equilibrium favors reaction of the stronger acid and formation of the weaker acid.

The strength of an acid is determined by the stability of its conjugate base: the more stable the base, the stronger is its conjugate acid. When atoms are similar in size, the strongest acid will have its hydrogen attached to the most electronegative atom. When atoms are very different in size, the strongest acid will have its hydrogen attached to the largest atom.

A compound exists primarily in its acidic form in solutions more acidic than its pK_a value and primarily in its basic form in solutions more basic than its pK_a value. A **buffer solution** contains both a weak acid and its conjugate base.

PROBLEMS

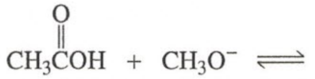
21. For each of the following compounds, draw the form in which it will predominate at pH = 3, pH = 6, pH = 10, and pH = 14:

a. CH_3COOH pK_a = 4.8

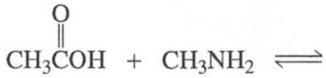
b. $CH_3CH_2\overset{+}{N}H_3$ pK_a = 11.0

c. CF_3CH_2OH pK_a = 12.4

22. Write the products of the following acid–base reactions, and indicate whether reactants or products are favored at equilibrium (use the pK_a values that are given in Section 2.3):

a. 
$CH_3\overset{\overset{O}{\|}}{C}OH + CH_3O^- \rightleftharpoons$

b. $CH_3CH_2OH + {}^-NH_2 \rightleftharpoons$

c. 
$CH_3\overset{\overset{O}{\|}}{C}OH + CH_3NH_2 \rightleftharpoons$

d. $CH_3CH_2OH + HCl \rightleftharpoons$

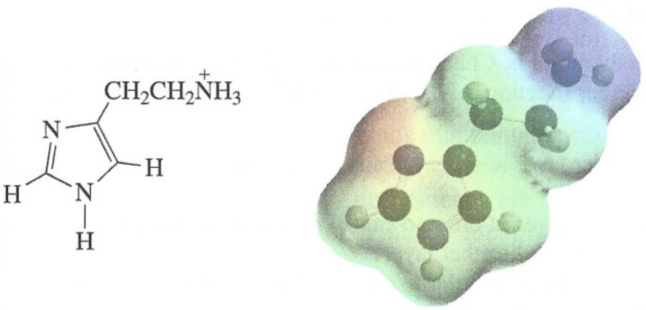
23. **a.** Which of the following is the strongest acid?
b. Which is the weakest acid?
c. Which acid has the strongest conjugate base?

1. nitrous acid (HNO_2), $K_a = 4.0 \times 10^{-4}$
2. nitric acid (HNO_3), $K_a = 22$
3. bicarbonate (HCO_3^-), $K_a = 6.3 \times 10^{-11}$
4. hydrogen cyanide (HCN), $K_a = 7.9 \times 10^{-10}$
5. formic acid (HCOOH), $K_a = 2.0 \times 10^{-4}$

24. Which is the stronger base?

a. HS^- or HO^- **b.** CH_3O^- or $CH_3\bar{N}H$ **c.** CH_3OH or CH_3O^- **d.** Cl^- or Br^-

25. Locate the three nitrogen atoms in the electrostatic potential map of histamine, the compound that causes the symptoms associated with the common cold and allergic responses. Which of the two nitrogen atoms in the ring is the most basic?

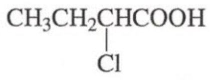
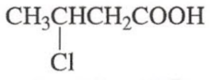


histamine

26. Using the table of pK_a values given in Appendix II, answer the following:
a. Which is the most acidic organic compound in the table?
b. Which is the least acidic organic compound in the table?
c. Which is the most acidic carboxylic acid in the table?

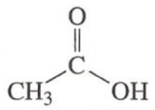
27. As long as the pH is greater than __________, more than 50% of a protonated amine with a pK_a of 10.4 will be in its neutral, nonprotonated form.

28. **a.** List the following carboxylic acids in order of decreasing acidity:

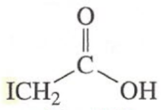
1. $CH_3CH_2CH_2COOH$ $K_a = 1.52 \times 10^{-5}$
2. 
$CH_3CH_2\underset{\underset{Cl}{|}}{C}HCOOH$ $K_a = 1.39 \times 10^{-3}$
3. $ClCH_2CH_2CH_2COOH$ $K_a = 2.96 \times 10^{-5}$
4. 
$CH_3\underset{\underset{Cl}{|}}{C}HCH_2COOH$ $K_a = 8.9 \times 10^{-5}$

b. How does the presence of an electronegative substituent such as Cl affect the acidity of a carboxylic acid?
c. How does the location of the substituent affect the acidity of a carboxylic acid?
d. Why does the electronegative substituent affect the acidity of the carboxylic acid?

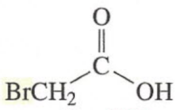
29. Explain the difference in the pK_a values of the following compounds:



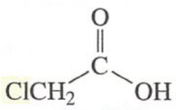
pK_a = 4.76



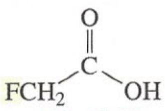
pK_a = 3.15



pK_a = 2.86



pK_a = 2.81



pK_a = 2.66

30. a. List the following alcohols in order of decreasing acidity:

CCl_3CH_2OH $K_a = 5.75 \times 10^{-13}$

CH_2ClCH_2OH $K_a = 1.29 \times 10^{-13}$

$CHCl_2CH_2OH$ $K_a = 4.90 \times 10^{-13}$

b. Explain their relative acidities.

31. Ethyne has a pK_a value of 25, water has a pK_a value of 15.7, and ammonia (NH_3) has a pK_a value of 36. Draw the equation, showing equilibrium arrows that indicate whether reactants or products are favored, for the reaction of ethyne with

a. HO^-

b. $^-NH_2$

c. Which would be a better base to use if you wanted to remove a proton from ethyne, HO^- or $^-NH_2$?

32. For each of the following pairs of reactions, indicate which one has the more favorable equilibrium constant (that is, which one most favors products):

a. $CH_3CH_2OH + NH_3 \rightleftharpoons CH_3CH_2O^- + {}^+NH_4$

or

$CH_3OH + NH_3 \rightleftharpoons CH_3O^- + {}^+NH_4$

b. $CH_3CH_2OH + NH_3 \rightleftharpoons CH_3CH_2O^- + {}^+NH_4$

or

$CH_3CH_2OH + CH_3NH_2 \rightleftharpoons CH_3CH_2O^- + CH_3\overset{+}{N}H_3$

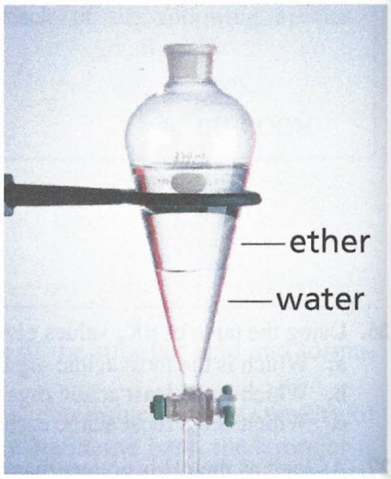
33. Carbonic acid has a pK_a of 6.1 at physiological temperature. Is the carbonic acid/bicarbonate buffer system that maintains the pH of the blood at 7.3 better at neutralizing excess acid or excess base?

34. Water and diethyl ether are immiscible liquids. Charged compounds dissolve in water, and uncharged compounds dissolve in ether (Section 3.7). $C_6H_{11}COOH$ has a pK_a of 4.8 and $C_6H_{11}\overset{+}{N}H_3$ has a pK_a of 10.7.

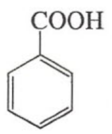
a. What pH would you make the water layer in order to cause both compounds to dissolve in it?

b. What pH would you make the water layer in order to cause the acid to dissolve in the water layer and the amine to dissolve in the ether layer?

c. What pH would you make the water layer in order to cause the acid to dissolve in the ether layer and the amine to dissolve in the water layer?

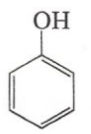


35. How could you separate a mixture of the following compounds? The reagents available to you are water, ether, 1.0 M HCl, and 1.0 M NaOH. (*Hint:* See Problem 34.)

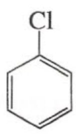


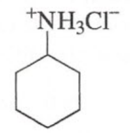
pK_a = 4.17

pK_a = 4.60



pK_a = 9.95





pK_a = 10.66