# Acid-base Concepts

There are three widely used definitions for acids and bases. Each definition or concept is useful for certain applications. You must know each of them and be able to apply each when appropriate. One often uses the first two definitions for acid-base titrations. The last definition helps explain the formation of complex ions and other compounds.

With each definition, is the proper reaction between acids and bases.
The definitions and reactions are for water (aqueous) solutions. One can extent these concepts and definitions to other solvents. First learn what they mean with water.
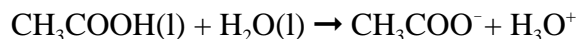
Arrhenius Acids and Bases[1]

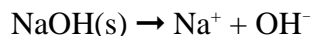The following are the Arrhenius definitions of acids and bases.

Acid - An acid when dissolved in water produces hydronium, H_3O^+, ions. For example, when $HCl(g)$[2] dissolves in water, the following reaction occurs.
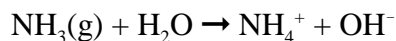
$$HCl(g) + H_2O(l) \rightarrow Cl^- + H_3O^+$$
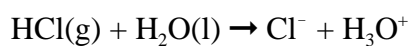
When $CH_3COOH(l)$ dissolves in water, the following reaction occurs.

$$CH_3COOH(l) + H_2O(l) \rightarrow CH_3COO^- + H_3O^+$$

Base - A base when dissolved in water produces hydroxide, OH^-, ions.
For example, when $NaOH(s)$ dissolves in water, the following reaction occurs.

$$NaOH(s) \rightarrow Na^+ + OH^-$$

When $NH_3(g)$ dissolves in water, the following reaction occurs.

$$NH_3(g) + H_2O \rightarrow NH_4^+ + OH^-$$

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[1] The Arrhenius definition is here historically not accurate. The choice has been made here to modify it to reflect modern understanding of the chemistry.

[2] The following standard symbols will be used:
(s) ° solid; (l) ° liquid; (g) ° gas; (aq) ° dissolved in water. When referring to water solutions, ions are understood to be aqueous (dissolved) ions.

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How to recognize an Arrhenius acid or base:

You may wonder at this point how you would know if a compound is a Arrhenius acid or base, or it does not even fit within the Arrhenius definition. Much of this comes with experience, however for now, we can say in general (the exceptions we will not worry about at this point) that:

1) An Arrhenius acid will be written in the following fashion:

      a) the compound will begin with an H and there will follow atoms that are non-metals
            Examples: HCl H_2SO_4 H_3PO_4
            These acids are referred to as "mineral acids".

      b) the compound is written with the signature "COOH" (IUPAC convention[3])
            Examples: CH_3COOH HCOOH   HOOCCOOH
            These acids are referred to as "organic acids" or "carboxylic acids". This latter name refers to the carboxylic acid group "--COOH".

2) An Arrhenius base will be written in the following fashion:

      a) the compound will begin with a metal ion followed by one or more hydroxyl groups
            Examples: NaOH $Ca(OH)_2$ $Fe(OH)_3$
   These are referred to as the metal hydroxides.

      b) the compound will have nitrogen in it, but it is not an acid (like HNO_3 or HNO_2)
            Examples: NH_3 CH_3NH_2 $(CH_3)_3N$ C_5H_5N
            These are referred to as amines. After being proficient in Lewis structures it will become more obvious what compounds qualify as amines.

The **Arrhenius acid-base reaction** yields a **salt**. In the Arrhenius definition, if one reacts an acid with a base, the product is a salt. The reaction may also produce water. The Arrhenius reaction is an **overall** reaction, since it include ions, called spectator ions. Spectator ions do not contribute to the chemistry of the reaction. For more details see below.
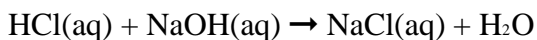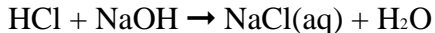
Examples:
       $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$
       acid + base $\rightarrow$ salt + water(optional)

At this point, since one should be able to recognize an acid and a base, the (aq) for the acid and base need not be written. Thus the reaction written as:

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[3] Sometimes organic acids are written without the COOH obvious, e.g. $CH_3COOH \Rightarrow HC_2H_3O_2$. This should be avoided today. The IUPAC convention will be followed throughout this course.

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$$HCl + NaOH \rightarrow NaCl(aq) + H_2O$$

has lost no important information. The (aq) for the salt will be left on at this point since the solubility rules have not been discussed.

$$HCl + NH_3 \rightarrow NH_4Cl(aq)$$
$$acid + base \rightarrow salt$$
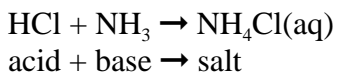
Notice that in the example above, no water is written in the balanced reaction. An acid that has more than one acidic H is referred to as "polyprotic".

$$H_2SO_4 + 2NaOH ® Na_2SO_4 + 2H_2O$$

polyprotic (diprotic) acid + base → salt
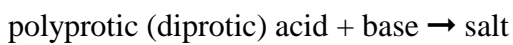
The **Arrhenius acid-base** definitions are useful for **measurements and weighings**. For example, if one is given a **titration** or **neutralization** problem, one must use the Arrhenius definition to determine the amounts of acid, base or salt in the solution.

Example 1:

A lab person titrates a standard 0.1015 M solution of HCl with NaOH to determine the NaOH concentration. A 25.00 mL pipet was used to measure out the HCl solution. The endpoint of the titration occured after the addition of 31.53 mL of NaOH solution. What is the concentration of the NaOH solution?

The definition of molarity, C with unit symbol M, is given by the equation:

$$C = \frac{n}{V}$$

where n is the number of moles, mol, and V is the solution volume in liters, L. The reaction involved is:

$$HCl + NaOH \rightarrow NaCl + H_2O$$
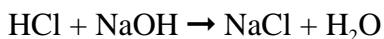
For the above reaction, the following equation gives the molar relationship between HCl and NaOH.

$$\frac{n_a}{v_a} = \frac{n_b}{v_b}$$

This equation uses subscript "a" for acid and subscript "b" for base. The letters,   (Greek neu) are the standard symbols for the stoichiometric coefficients. One also has from above the following:

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$$\frac{C_a V_a}{V_a} = \frac{C_b V_b}{V_b}$$

The unknown quantity in the problem above is C_b. Using the last two equations, solve for C_b. (Remember the stoichiometry relationship in the second equation, even though this is here 1 to 1.

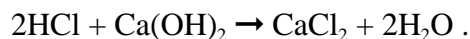I. E., in this instance: $\dfrac{C_a V_a}{1} = \dfrac{C_b V_b}{1}$)

Substituting: $\dfrac{(0.1015 \text{ M})(25.00 \text{ mL})}{1} = \dfrac{C_b (31.53 \text{ mL})}{1}$

$C_b = (0.1015 \text{ M})(25.00 \text{ mL})/(31.53 \text{ mL})$
$C_b = 0.8048 \text{ M}$

Example 2:
A lab person titrates a standard 0.1015 M solution of HCl with $Ca(OH)_2$ to determine the $Ca(OH)_2$ concentration. The Arrhenius reaction for this is:

$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$.

A 25.00 mL pipet was used to measure out the HCl solution. The endpoint of the titration occured after the addition of 31.53 mL of $Ca(OH)_2$ solution. What is the concentration of the $Ca(OH)_2$ solution?

The stoichiometry for this reaction is not the same as for the first problem. The stoichiometry equation is:

$$\frac{n_a}{2} = \frac{n_b}{1}$$

Solving in a similar fashion: $\dfrac{(0.1015 \text{ M})(25.00 \text{ mL})}{2} = \dfrac{C_b (31.53 \text{ mL})}{1}$

and therefore:

$C_b = (0.1015 \text{ M})(25.00 \text{ mL})/[2(31.53 \text{ mL})]$
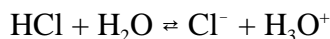$C_b = 0.4024 \text{ M}$

Do not forget the stoichiometry equation!

**Acid-base Concepts**

Brønsted-Lowry Acid and Base

The following are the Brønted-Lowry definitions of acids and bases.

**Acid** - An acid is a proton donor in a reaction.

For example, for HCl dissolved in water, the following reaction exists.

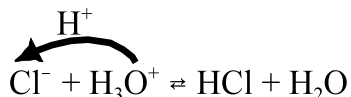$$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$$

Notice HCl is an acid because it transfers its proton to water. What other differences do you detect from the example above in the Arrhenius definition? The reaction arrow has been change from a $\rightarrow$ to a $\rightleftharpoons$. This indicates that the reaction is valid for both the forward and reverse directions. In other words the reaction written as:

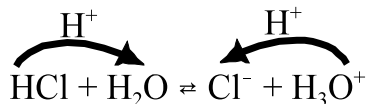$$Cl^- + H_3O^+ \rightleftharpoons HCl + H_2O$$
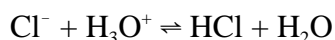
is also valid. Indeed, the reaction as written with the $\rightleftharpoons$ implies that both directions are happening. This is referred to as a (dynamic) equilibrium. To see the Brønted-Lowry definition better, the transfer of the proton, H^+, is shown in the following fashion. For the first reaction:

$$\overset{H^+}{\overset{\frown}{HCl + H_2O}} \rightleftharpoons Cl^- + H_3O^+$$
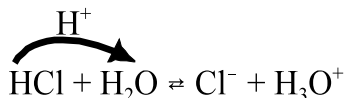
and for the second reaction:

$$\overset{H^+}{\overset{\frown}{Cl^- + H_3O^+}} \rightleftharpoons HCl + H_2O$$

or more simply to express both:

$$\overset{H^+}{\overset{\frown}{HCl + H_2O}} \rightleftharpoons \overset{H^+}{\overset{\frown}{Cl^- + H_3O^+}}$$.

Notice then that there is both an acid and a base for the "reactant" and for the "product".

An important definition. (You don't think so now but you will be confused later if you don't know it.)

Notice that on the opposite sides of the reaction, that the species differ by only an H^+. Thus, HCl and Cl^- differ by an H^+ and H_2O and H_3O^+ differ by an H^+. These are call **conjugate acid-base pairs**. HCl is the conjugate of Cl^- (and vis-a-verse) and H_2O is the conjugate of H_3O^+ (and vis-a-verse). This is sometimes illustrated as follows:

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$$\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{Cl}^- + \text{H}_3\text{O}^+$$

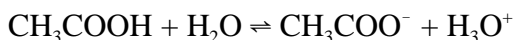conjugate pair

acid   base   base   acid
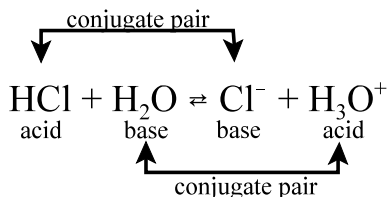
conjugate pair

Summary for this reaction:

1)   HCl and H_3O^+ are the Brønsted-Lowry acids
2) H_2O and Cl^- are the Brønsted-Lowry bases
3)   HCl and Cl^- is a conjugate pair.
4) H_2O and H_3O^+ is a conjugate pair.

Notice the only recognizable Arrhenius acid in this reaction is HCl. All the other species are defined by the reaction. (In water, H_3O^+ is always a Brønsted-Lowry acid.)

Example 2:

When CH₃COOH is in water solution, the following reaction exists[4].

$$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$$

1) CH_3COOH and H_3O^+ are the Brønsted-Lowry acids
2) H_2O and CH_3COO^- are the Brønsted-Lowry bases
3) CH_3COOH and CH_3COO^- is a conjugate pair.
4) H_2O and H_3O^+ is a conjugate pair.

Notice that the Brønsted-Lowry definition is for a condition that exists in equilibrium. It is not for a change due to addition, weighing etc.

Base - A base is a proton acceptor in a reaction. The example of NaOH has no equivalent example (except autoionization) in the Brønsted-Lowry definition. NaOH is a strong soluble base and is totally ionized. Thus, the Na₊ is a spectator ion and is not normally shown in the Brønsted-Lowry notation. With NH₃ in water solution, the following reaction exists.

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$
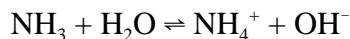
Notice that ammonia, NH_3, is a base. It accepts a proton to become NH_4^+, the ammonium ion.

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[4] Notice that for the Brønsted-Lowry reaction starting with an Arrhenius acid/base the water is written in the reactant as the second reactant and the H_3O^+ and OH^- are written in the products as the second reactant. This is not a rule, it's only traditional and you need not worry about it.

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To summarize the reaction $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$:

1) H_2O and NH_4^+ are the Brønsted-Lowry acids
2) NH_3 and OH^- are the Brønsted-Lowry bases
3) H_2O and OH^- is a conjugate pair.
4) NH_3 and NH_4^+ is a conjugate pair.

The **Brønsted-Lowry** definition describes the chemistry of the solution. It tells what species are active. It can be derived from the overall reaction, and is called the **net ionic reaction**. For example, given the reaction between the strong base NaOH and the weak acid CH_3COOH, the overall or Arrhenius reactions is:

$$CH_3COOH + NaOH \rightarrow NaCH_3COO(aq) + H_2O$$
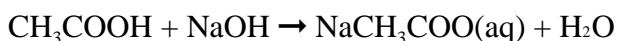
All (well, nearly all) salts are ionized completely if they are in water solution. Thus, $NaCH_3COO(aq)$ is actually Na^+ and CH_3COO^-. Since NaOH is a strong soluble base, it is also totally ionized in water. NaOH is actually Na_+ and OH_-. The above reaction can be written as:

$$CH_3COOH + Na^+ + OH^- \rightarrow Na^+ + CH_3COO^- + H_2O$$
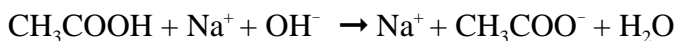
Notice, however that Na^+ is on both sides, and can be cancelled. The cancellation shows which ions have no meaning for the chemistry. Ions of the type are called **spectator ions**. This yields:

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$
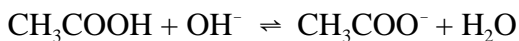
which is the Brønsted-Lowry formulation. By similar reasoning, one can transform other acid-base reactions. For example:

$$HCl + NH_3 \rightarrow NH_4Cl(aq)$$
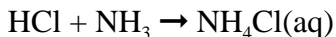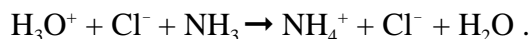
is the same as:
$H_3O^+ + Cl^- + NH_3 \rightarrow NH_4^+ + Cl^- + H_2O$.
(Note that H_2O has to be added since H^+ is the short form for the chemical species H_3O^+.)
and finally by eliminating the spectator ion, Cl^-:

$$H_3O^+ + NH_3 \rightleftharpoons NH_4^+ + H_2O$$
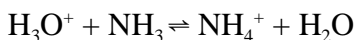
Acid-base Concepts

Lewis Acid and Base

The Lewis acid and base concept is very important for a variety of reactions, especially for organic chemistry. This concept becomes clearer after one learns the Lewis dot system of determining compound structure. For the early stages of General Chemistry, one does not use the Lewis acid-base concept much but it is presented here for future reference.

A Lewis **acid** is an **electron acceptor** for the formation of a compound or a complex ion.
A Lewis **base** is an **electron donor** for the formation of a compound or a complex ion.

Examples:

BF_3 is a good example of a Lewis acid. If one draws the Lewis dot structure for this compound, then boron is electron deficient. The Lewis structure is as shown in the following

$$
\begin{array}{c}
\text{F} \\
| \\
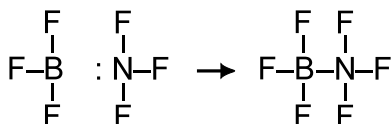\text{F--B} \quad \longleftarrow \\
| \\
\text{F}
\end{array}
$$
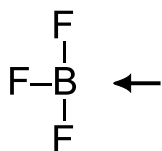
The arrow points to the position where the electrons are missing. This compound will seek electrons and react. By doing so the rule of 8 is fulfilled. For example, it will react with NF_3 which has a lone pair of electrons and is a Lewis base. This reaction is (writing BF_3 backward to emphasize the bonding):

$$F_3B + :NF_3 \rightarrow F_3B\leftarrow NF_3$$
acid + base $\rightarrow$ compound
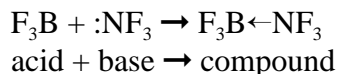
The arrow, $\leftarrow$, means that both electrons in the bonding originally came from the NF_3. (Electrons, like dollars, really don't have tags. This is only for humans' accounting system.) Graphically:

$$
\begin{array}{ccc}
\text{F} \quad \text{F} & & \text{F} \ \text{F} \\
| \quad\quad | & & | \ \ | \\
\text{F--B} \quad :\text{N--F} & \longrightarrow & \text{F--B--N--F} \\
| \quad\quad | & & | \ \ | \\
\text{F} \quad \text{F} & & \text{F} \ \text{F}
\end{array}
$$

Another example is the reaction in water between metal ions and Lewis bases such as NH_3, $H_2NCH_2CH_2NH_2$, H_2O or OH^- (or many others). (Hint: A recognizable Brønsted-Lowry base is also a Lewis base. The opposite is not necessarily true although often is. Often there is not hint as to what the Lewis acid is other than the electron accounting.)

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Examples:

$Ag^+ + 2NH_3 \longrightarrow Ag(NH_3)^{2+}$ $(H_3N \rightarrow Ag \leftarrow NH_3)^+$

$Cu^{2+} + 2NH_3 \longrightarrow Cu(NH_3)_2{}^{2+}$ $(H_3N \rightarrow Cu \leftarrow NH_3)^{2+}$

$Zn^{2+} + 4NH_3 \longrightarrow Zn(NH_3)_4{}^{2+}$

$Zn^{2+} + 4OH^- \longrightarrow Zn(OH)_4{}^{2-}$

$Zn^{2+} + 2H_2NCH_2CH_2NH_2 \longrightarrow Zn(H_2NCH_2CH_2NH_2)_2{}^{2+}$