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*

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)# 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.

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

The **Arrhenius acid-base reaction** yields a **salt**. In the Arrhenius definition, if one

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* The Arrhenius definition is here historically not accurate. I have chosen to modify it to reflect modern understanding of the chemistry.

\# The following 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.

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)

$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$
acid + base $\rightarrow$ salt

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$
polyprotic acid + base $\rightarrow$ 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.

For the above reaction, the following equation gives the molar relationship between HCl and NaOH. This equation uses subscript "a" for acid and subscript "b" for base.

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

One also has from above the following.

$$C_a V_a = n_a \quad \text{and} \quad C_b V_b = n_b$$

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.)

In this instance:

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

Substituting:

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

$\boldsymbol{C_b}$ = 0.8048 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:

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

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:

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

Solving in a similar fashion:

$$C_b = \frac{C_a V_a}{2V_b}$$

and therefore:

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

$\boldsymbol{C_b}$ = 0.4024 M

Do not forget the stoichiometry equation!

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.

$$HCl(aq) + H_2O \rightleftharpoons Cl^- + H_3O^+$$

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?

When CH_3COOH is in water solution, the following reaction exists.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Notice that the Brønsted-Lowry definition is for a condition that exists. 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 NH_3 in water solution, the following reaction exists.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Notice that ammonia, NH_3, is a base. It accepts a proton to become NH_4^+, the ammonium ion.

A **Brønsted-Lowry** acid-base reaction has as its reactants an acid and a base and as its products an acid and a base. These reactions can are occuring in both directions simultaneously. The symbol ⇄ indicates this. In the reactions above, the acids and bases are given by:

$$HCl(aq) + H_2O \rightleftharpoons Cl^- + H_3O^+$$
acid + base ⇄ base + acid

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$
acid + base ⇄ base + acid

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
base + acid ⇄ acid + base[+]

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:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O$$

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:

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

is the same as:

$$H_3O^+ + Cl^- + NH_3 \rightarrow NH_4^+ + Cl^- + H_2O \quad .$$

(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^-:

$$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$$

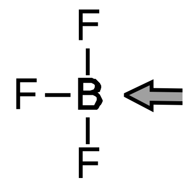
[+] Notice that usually in water solution H_2O is written second in the reactants and H_3O^+ or OH^- are written 2nd in the products, although this is not a rule.

Lewis Acid and Base

- ☺ 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 figure to the right. 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):

$$F_3B \;+\; :NF_3 \;\rightarrow\; F_3B{\leftarrow}NF_3$$
$$\text{acid} \;+\; \text{base} \;\rightarrow\; \text{compound}$$

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.)

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).

$Ag^+ + 2NH_3 \rightleftarrows Ag(NH_3)_2^+$ $(H_3N{\rightarrow}Ag{\leftarrow}NH_3)^+$

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

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

H_3N NH_3
↘ ↙
Zn
↗ ↖
H_3N NH_3

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

HO OH
↘ ↙
Zn
↗ ↖
HO OH

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