

Analytical Chemistry

*Reference :- Fundamentals of Analytical Chemistry
by skoog and West.*

What is Analytical Chemistry?

study of methods for determining the composition of substances

Qualitative Analysis

-What is the chemical component in a given sample?

Quantitative Analysis

-What is the concentrations of the component in a given sample?

Quantitative analysis :

Classical methods

- Gravimetric analysis - mass
- Volumetric analysis - volume titrimetry

Instrumental methods

- Spectrophotometry - light
- Potentiometry - voltage

Volumetric analysis /General principles

Titration : one of the quantitative volumetric analysis , it used to determine the analyte by find the volume of standard reagent(solution) required to completely react with it .



where : A = titrant (st. sol.)

B = titrate (analyte)

a,b = no. of moles

Equivalent point : The point in which the amount of standard sol. Is chemically equivalent to the substance that is to be determined.

End point : is based upon the physical changes in a solution in titration method . the that occur end point detection including change in color , electrical potential , current and conductivity.

Best titration , when that the volume difference between end point and equivalent point is small. (when the end point is exactly same the equivalent point) .

Primary standard : a highly purified substance that required as a reference material in titration , and the accuracy of volumetric analysis is dependent on it .

Primary standard should be includes :

- a) Highest purity. b) Stability.
- c) Absence of hydrate water. d) High equivalent weight.

Standard solution : Is the solution whose its concentration is known exactly.

There are two ways for prepare standard solution :

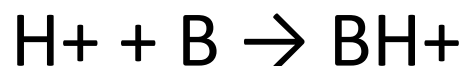
- 1) Directly , by dissolving a carefully weight quantity of pure reagent and diluting to an exactly known volume .
- 2) Indirectly , by titrating a weighed quantity of pure substance with the reagent solution .

Standard solution should be :

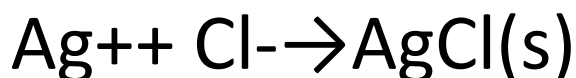
- a) Remain stable for months .
- b) Rapid and completely react with analyte .
- c) Observed satisfactory end point .
- d) Balanced chemical equation .

Types of titration reactions :

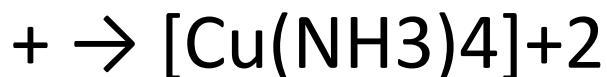
1) Acid-base titration(neutralization titration):



2) Precipitation titration :



3) Complex formation :



4) Oxidation-reduction reaction :



Calculation associated with titrimetric methods



where : A = titrant (st. sol.)

B = titrate

(analyte)

$$R = \frac{b}{a} =$$

m.mole of analyte/m.mole of titrant

1) no. of m.moles of A :

$$M = \text{m.moles} / \text{ml} = \text{mole} / \text{L}$$

$$\text{m.mole A} = M_A \cdot V_A$$

2) no. of m.moles of B :

$$\text{m.moles of B} = M_A \cdot V_A \cdot R$$

3) weight of B :

$$\text{m.moles B} = \text{mg(B)} / \text{M.wt.(B)}$$

$$\text{mg of B} = M_A \cdot V_A \cdot R \cdot \text{M.wt. B}$$

4) percentage of B :

$$\% \text{ B} = \text{mg(B)} / \text{mg of sample} \times 100$$

EX. Calculate the percentage of Na_2CO_3 in 1gm of sample dissolved in water and titrated with standard sol. of 0.1M HCl ,volume of HCl required is 36.5ml ?

EX. Calculate weight of acetic acid found in 5ml of vinegar titrated with 0.1M of NaOH , vol. required = 35ml , M.wt. acetic acid = 60 ?

EX. Prepare 250ml of 0.05N HCl , from a sol. of 0.1N ?

THEORIES OF ACIDS AND BASES

Acid-Base Equilibrium

The Arrhenius Theory of acids and bases

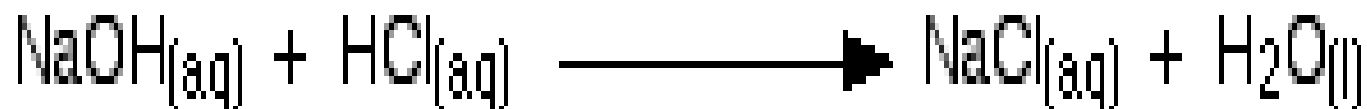
- Acids are substances which produce hydrogen ions in solution.
- Bases are substances which produce hydroxide ions in solution.

Neutralisation happens because hydrogen ions and hydroxide ions react to produce water.



Limitations of the theory

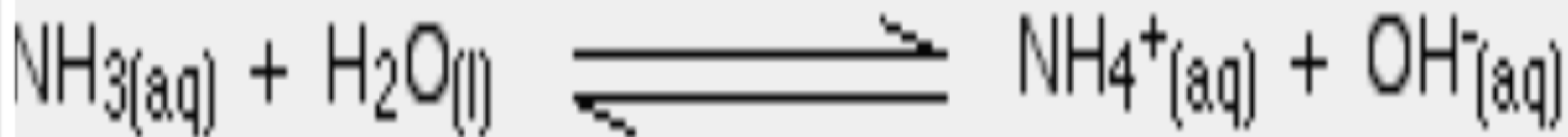
- Hydrochloric acid is neutralised by both sodium hydroxide solution and ammonia solution. In both cases, you get a colourless solution which you can crystallise to get a white salt - either sodium chloride or ammonium chloride.
- These are clearly very similar reactions. The full equations are:



In the sodium hydroxide case, hydrogen ions from the acid are reacting with hydroxide ions from the sodium hydroxide - in line with the Arrhenius theory.

However, in the ammonia case, there don't appear to be any hydroxide ions!

You can get around this by saying that the ammonia reacts with the water it is dissolved in to produce ammonium ions and hydroxide ions:



This is a reversible reaction, and in a typical dilute ammonia solution, about 99% of the ammonia remains as ammonia molecules. Nevertheless, there are hydroxide ions there, and we can squeeze this into the Arrhenius theory.

However, this same reaction also happens between ammonia gas and hydrogen chloride gas. $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{s})$

In this case, there aren't any hydrogen ions or hydroxide ions in solution - because there isn't any solution. The Arrhenius theory wouldn't count this as an acid-base reaction, despite the fact that it is producing the same product as when the two substances were in solution. That's silly!

The Bronsted-Lowry Theory of acids and bases

- An acid is a proton (hydrogen ion) donor.
- A base is a proton (hydrogen ion) acceptor.

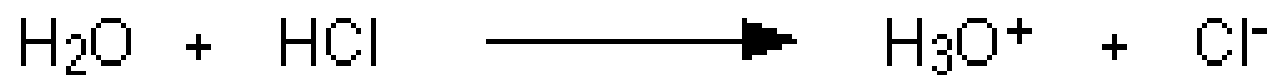
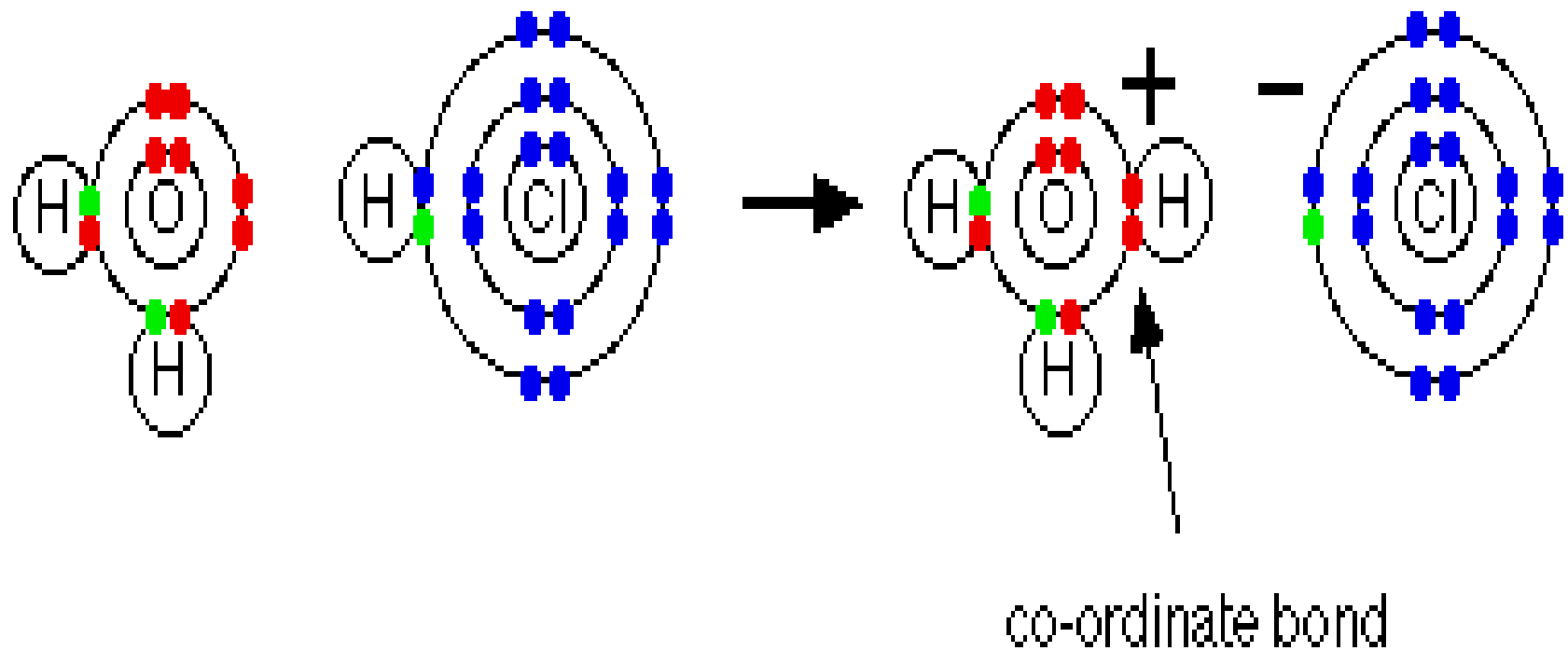
The relationship between the Bronsted-Lowry theory and the Arrhenius theory

The Bronsted-Lowry theory doesn't go against the Arrhenius theory in any way - it just adds to it.

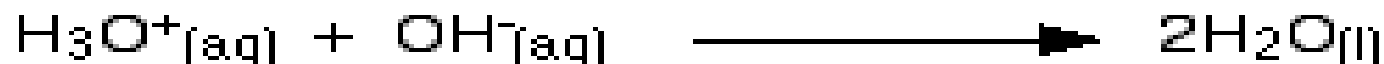
Hydroxide ions are still bases because they accept hydrogen ions from acids and form water.

An acid produces hydrogen ions in solution because it reacts with the water molecules by giving a proton to them.

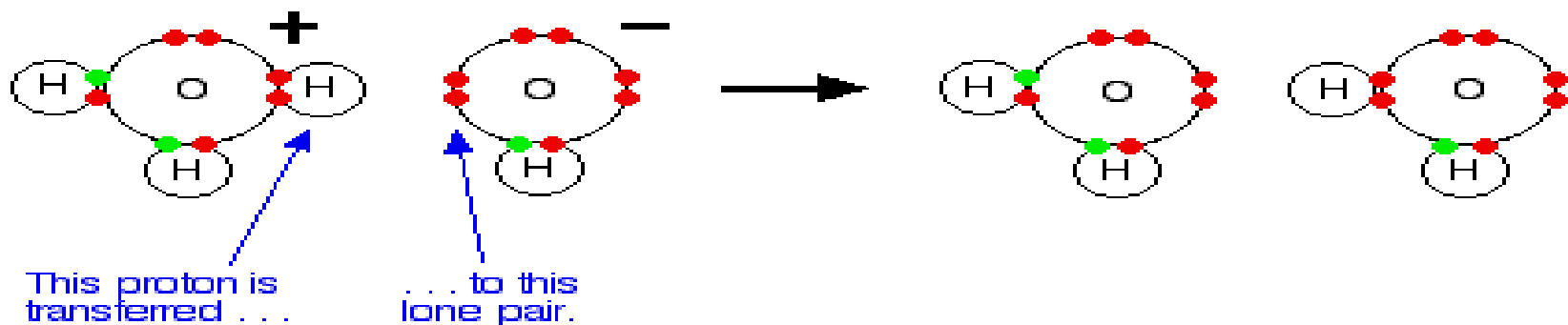
When hydrogen chloride gas dissolves in water to produce hydrochloric acid, the hydrogen chloride molecule gives a proton (a hydrogen ion) to a water molecule. A co-ordinate (dative covalent) bond is formed between one of the lone pairs on the oxygen and the hydrogen from the HCl. Hydroxonium ions, H_3O^+ , are produced



When an acid in solution reacts with a base, what is actually functioning as the acid is the hydroxonium ion. For example, a proton is transferred from a hydroxonium ion to a hydroxide ion to make water.



Showing the electrons, but leaving out the inner ones:



It is important to realise that whenever you talk about hydrogen ions in solution, $\text{H}^+(\text{aq})$, what you are actually talking about are hydroxonium ions.

The Lewis Theory of acids and bases

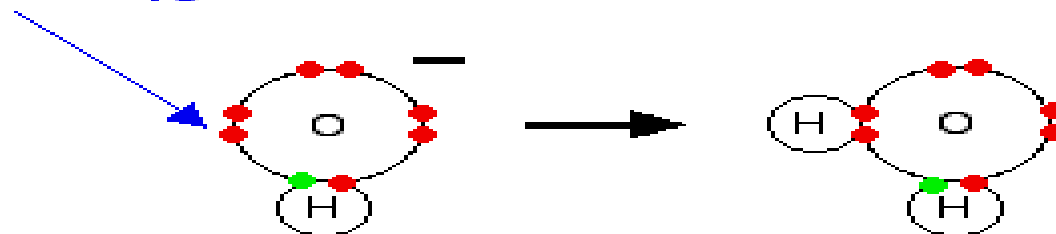
- An acid is an electron pair acceptor.
- A base is an electron pair donor.

The relationship between the Lewis theory and the Bronsted-Lowry theory

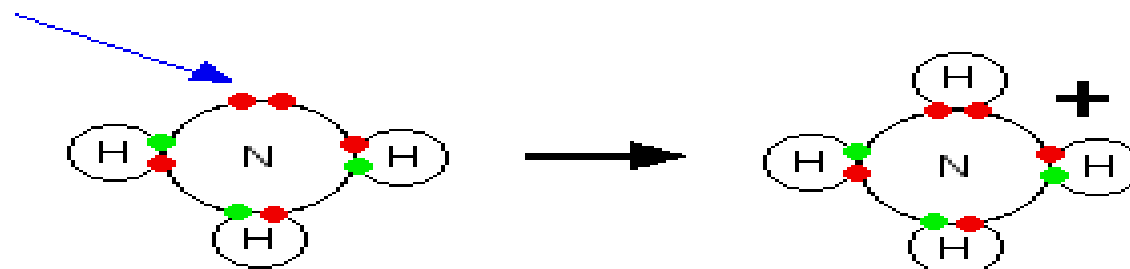
Lewis bases

It is easiest to see the relationship by looking at exactly what Bronsted-Lowry bases do when they accept hydrogen ions. Three Bronsted-Lowry bases we've looked at are hydroxide ions, ammonia and water, and they are typical of all the rest.

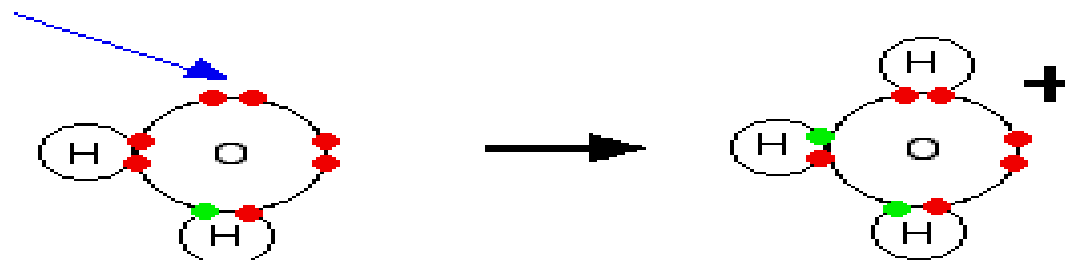
A hydroxide ion picks up a hydrogen ion by attaching it to one of the lone pairs on the oxygen.



Ammonia picks up a hydrogen ion by attaching it to the lone pair on the nitrogen.



Water picks up a hydrogen ion by attaching it to one of the lone pairs on the oxygen.

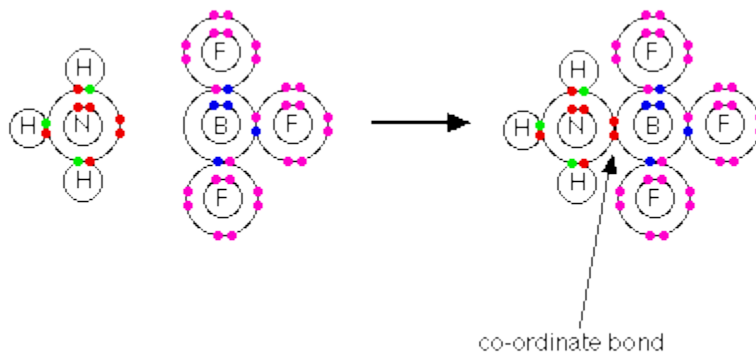


The Bronsted-Lowry theory says that they are acting as bases because they are combining with hydrogen ions. The reason they are combining with hydrogen ions is that they have lone pairs of electrons - which is what the Lewis theory says. The two are entirely consistent.

So how does this extend the concept of a base? At the moment it doesn't - it just looks at it from a different angle.

But what about other similar reactions of ammonia or water, for example? On the Lewis theory, *any* reaction in which the ammonia or water used their lone pairs of electrons to form a co-ordinate bond would be counted as them acting as a base.

Here is a reaction which you will find talked about on the page dealing with co-ordinate bonding. Ammonia reacts with BF_3 by using its lone pair to form a co-ordinate bond with the empty orbital on the boron.



As far as the ammonia is concerned, it is behaving exactly the same as when it reacts with a hydrogen ion - it is using its lone pair to form a co-ordinate bond. If you are going to describe it as a base in one case, it makes sense to describe it as one in the other case as well.

Lewis acids

Lewis acids are electron pair acceptors. In the above example, the BF_3 is acting as the Lewis acid by accepting the nitrogen's lone pair. On the Bronsted-Lowry theory, the BF_3 has nothing remotely acidic about it.

This is an extension of the term acid well beyond any common use.

What about more obviously acid-base reactions - like, for example, the reaction between ammonia and hydrogen chloride gas?

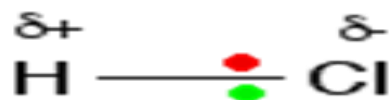


What exactly is accepting the lone pair of electrons on the nitrogen. often write this as if the ammonia is donating its lone pair to a hydrogen ion - a simple proton with no electrons around it.

That is misleading! You don't usually get free hydrogen ions in chemical systems. They are so reactive that they are always attached to something else. There aren't any uncombined hydrogen ions in HCl.

There isn't an empty orbital anywhere on the HCl which can accept a pair of electrons. Why, then, is the HCl a Lewis acid?

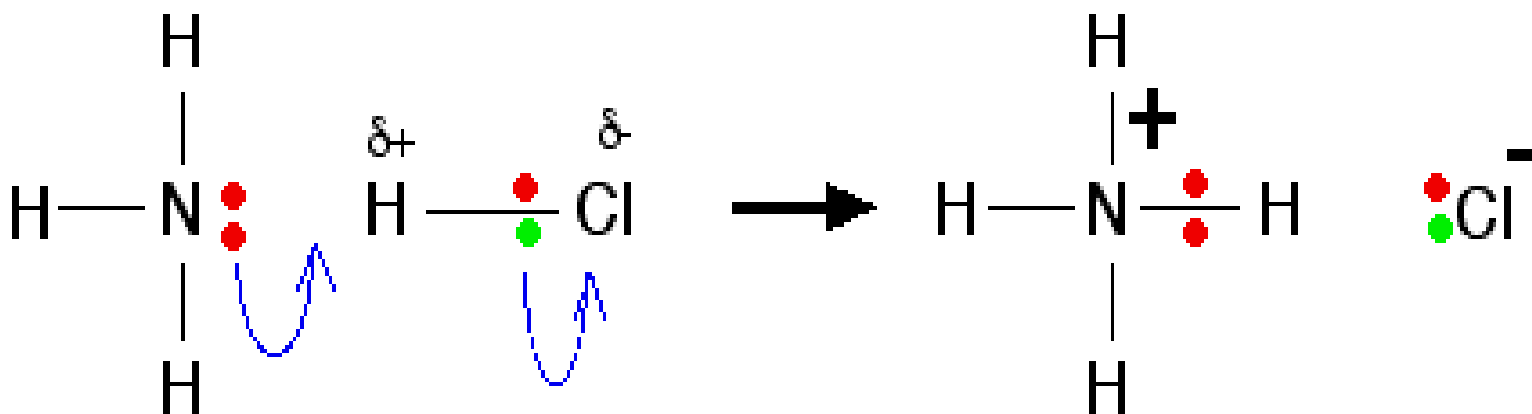
Chlorine is more electronegative than hydrogen, and that means that the hydrogen chloride will be a polar molecule. The electrons in the hydrogen-chlorine bond will be attracted towards the chlorine end, leaving the hydrogen slightly positive and the chlorine slightly negative.



The lone pair on the nitrogen of an ammonia molecule is attracted to the slightly positive hydrogen atom in the HCl. As it approaches it, the electrons in the hydrogen-chlorine bond are repelled still further towards the chlorine.

Eventually, a co-ordinate bond is formed between the nitrogen and the hydrogen, and the chlorine breaks away as a chloride ion.

This is best shown using the "curly arrow" notation commonly used in organic reaction mechanisms.



The whole HCl molecule is acting as a Lewis acid. It is accepting a pair of electrons from the ammonia, and in the process it breaks up. Lewis acids don't necessarily have to have an existing empty orbital.