

Lewis vs. Brønsted-Lowry: Acid-Base Theories

Historically, people would use taste to help distinguish between materials. Substances such as vinegar and lemon-juice were described in Latin as 'acere', or 'sour-tasting', from which the word 'acid' is derived. Early soaps were made by roasting minerals and mixing the ashes with animal fats. This introduced the term 'alkali', which is derived from the Arabic word to 'roast'. Early scientists knew very little about the properties of acids and while the ability of bases to neutralise the corrosive effects of acids were known, they were not understood. The first documented use of litmus, a dye extracted from a lichen, as a test of acidity occurred around 1300, by Spanish scholar, Arnaldus de Villa Nova. The study of acids and bases began with the work of Frenchman, Antoine Lavoisier (1743-1794), with the first concerted attempt to isolate the element that gave acids their unique properties. Lavoisier incorrectly identified oxygen as the element responsible. German scientist, Justus Frieher von Liebig (1803-1873), later isolated hydrogen as the element responsible, reasoning that it was the only element common to all acids. The Swedish chemist, Svante Arrhenius (1859-1927), later proposed that acids and bases gained their properties because of the action of ions in the solution.

Arrhenius' Theory

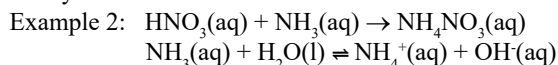
Arrhenius' theory is of historical interest and states:

- 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.

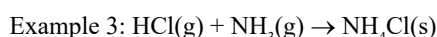
Arrhenius' theory successfully explains many familiar acid-base reactions. Example 1 describes the reaction between hydrochloric acid, HCl, and sodium hydroxide, NaOH. Hydrogen ions, H⁺, from the acid react with hydroxide ions, OH⁻, from the base, to produce water, H₂O.



Example 2 appears to describe a reaction proceeding without the hydroxide ion, OH⁻, involved. This is explained by realising that ammonia reacts with water to produce small quantities of hydroxide ions, OH⁻. Therefore, the reaction can still be described as meeting Arrhenius' theory.



Example 3 highlights limitations in Arrhenius' theory in describing the action of acids and bases. The direct reaction of hydrogen chloride and ammonia does not require hydrogen ions, H⁺, or hydroxide ions, OH⁻, in solution. This reaction cannot be fully explained by Arrhenius' theory.




Despite limitations in his theory, Arrhenius did provide the first meaningful definition of acids, which led to him receiving the Nobel Prize in Chemistry in 1903.

Brønsted-Lowry: Definition of Acids

In 1923, two chemists, Johannes Nicolaus Brønsted, from Denmark, and Thomas Martin Lowry, from England, working independently, suggested the idea of protonation. They proposed that bases are protonated and acids are de-protonated. They developed the theory that acids 'donated' hydrogen ions, H⁺, and bases 'accepted' hydrogen ions.

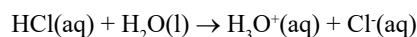
They described an acid-base reaction as the removal of a hydrogen ion, or proton, H⁺, from an acid, and its addition to a base.

The key development is that the Brønsted-Lowry definition does not refer to the formation of a salt and solvent. Instead, Brønsted-Lowry describes the formation of conjugate acids and conjugate bases.

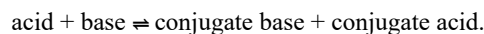
 The removal of a hydrogen ion from an acid produces its conjugate base; acid, HA → H⁺ + conjugate base, A⁻

The acceptance of a proton by a base produces its conjugate acid; base, B + H⁺ → conjugate acid, BH⁺

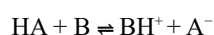
Describing the dissociation of hydrochloric acid, HCl, in aqueous solution, gives the following equation:



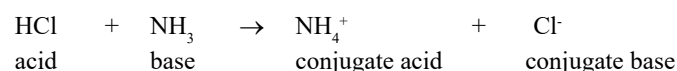
Hydrochloric acid, HCl, donates a proton, H⁺, and produces its conjugate base, the chloride ion, Cl⁻. In this example, water, H₂O, is behaving as a base by accepting a proton, H⁺, to produce its conjugate acid, the hydronium ion, H₃O⁺. The Brønsted-Lowry definition of an acid-base reaction does not produce salt plus water, rather it describes the formation of a new acid and new base. The general equation can be written as:



The equilibrium sign, ⇌, is used because the reaction can occur in the forward and reverse directions. This is applicable for the action of weak acids, where an acid, HA, can lose a proton to become its conjugate base, A⁻. The base, B, can accept a proton to become its conjugate acid, BH⁺:



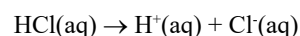
Review Example 3, above: the direct reaction between hydrogen chloride and ammonia is better defined using the Brønsted-Lowry theory. This describes how the action of acids and bases may be independent of any solvent. Hydrogen chloride is described acting as an acid by donating a proton and forming its conjugate base, Cl⁻. Conversely, ammonia gas acts as a base by accepting a proton and forming its conjugate acid, NH₄⁺:



The Brønsted-Lowry theory provides a more encompassing explanation for acid-base behaviour than the Arrhenius theory.

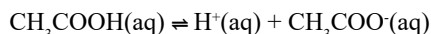
Strong/Weak Acids

When describing Brønsted-Lowry acids, the strength of an acid is determined by how successful the original acid molecule dissociates in aqueous solution. Substances that fully dissociate are described as strong acids, e.g. hydrochloric acid, HCl.

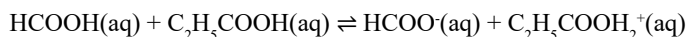


Acidic substances that partially dissociate in aqueous solution to produce an equilibrium mixture are described as weak acids, such as ethanoic acid, CH₃COOH.

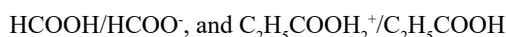
Typically the position of equilibrium lies to towards the original unionised acid, i.e. the concentration of hydrogen ions produced in aqueous solution is very small.



When two acids are mixed, the stronger acid dissociates to a greater extent compared to the weaker acid. For example, methanoic acid, HCOOH, is a stronger acid than propanoic acid, C₂H₅COOH. In solution, methanoic acid, HCOOH, is more successful in donating its proton. As the weaker of the two acids, propanoic acid, C₂H₅COOH, will act as a Brønsted-Lowry base by accepting a proton. i.e.,

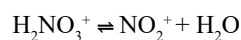
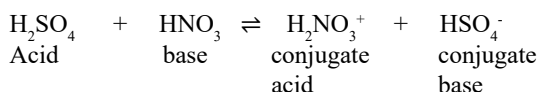


The solution contains competing acid-base conjugate pairs:



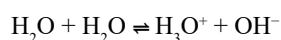
This seems peculiar, an acid (propanoic acid) acting as a base, but under the definition of Brønsted-Lowry theory it is perfectly reasonable. Another, interesting example involves the formation of the electrophilic nitronium cation, NO₂⁺, in the nitration of benzene.

Benzene is reacted with a hot mixture of concentrated nitric and sulfuric acids. Sulfuric acid is stronger than nitric acid and donates a proton to the nitric acid.



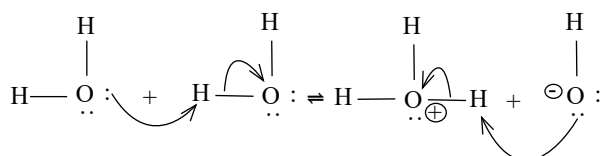
Brønsted-Lowry Model of Water

Water is amphoteric, which means it can act as an acid and a base. It is also amphiprotic, meaning it is capable of both donating and accepting H⁺ ions. The Brønsted-Lowry model explains how water can dissociate to form hydronium ions, H₃O⁺, and hydroxide ions, OH⁻.

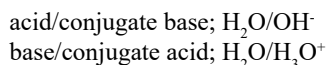


The acid-base behaviour of water can be illustrated as follows, see Fig. 1. One water molecule acts as an acid, donating a proton, the second water molecule acts as a base, accepting a proton.

Fig. 1



In terms of its Brønsted-Lowry acid/conjugate base behaviour, the acid/conjugate base pairs can be represented as:



Lewis: Definition of Acids

Figure 1, above, illustrates how acid-base behaviour can be described in terms of protonation and de-protonation, that is, the loss and gain of a proton. It also describes how acid-base behaviour might be explained in terms of availability of electron-pairs.

One water molecule is shown donating an electron pair to the second water molecule.

Likewise, in the reverse reaction, the hydroxide ion, OH⁻, is shown donating an electron-pair to the hydronium ion, H₃O⁺. That is, a base can be described as a substance that donates an electron-pair. Conversely, an acid can be described as a substance that accepts an electron-pair.

In 1923, the same year as Brønsted-Lowry independently published their theories on the nature of acids and bases, Gilbert Lewis defined an acid as a substance that accepts a lone pair of electrons from another species to complete the stable group of one of its own atoms. The two theories are complementary; Brønsted-Lowry acids exhibit Lewis acid activity and Brønsted-Lowry bases act as Lewis bases. However, the converse is not necessarily true; not all Lewis acids and bases are Brønsted-Lowry acids and bases, e.g., AlCl₃.

Figure 2 describes the reaction between hydrogen chloride gas, HCl, and ammonia, NH₃. An ammonia molecule, NH₃, behaves as a Lewis base by donating an electron-pair to a hydrogen chloride molecule, HCl. This behaves as a Lewis acid, by accepting an electron-pair.

Fig. 2

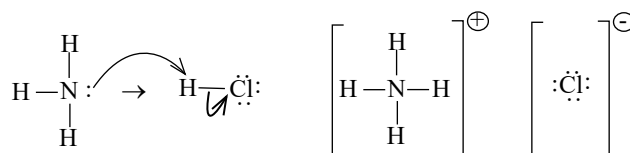
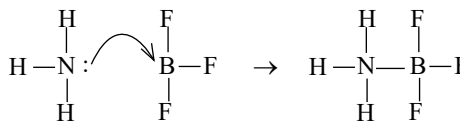
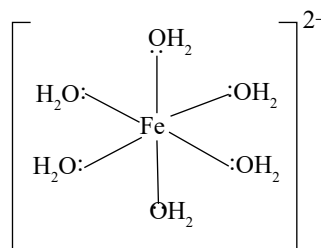
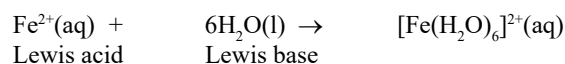


Figure 3 describes an example of Lewis acid-base behaviour that does not involve the movement of a hydrogen ion, H⁺. The reaction of ammonia, NH₃, and boron trifluoride, BF₃, is used to illustrate the formation of a dative or coordinate covalent bond, i.e. a covalent bond is formed and the participating bonding electrons both originate from the same atom. This action also describes ammonia, NH₃, as acting as a Lewis base by donating the electron-pair (lone-pair) on the nitrogen atom to the boron atom on the boron trifluoride, BF₃.

Fig. 3



Complex ion formation may also be described using Lewis acid-base behaviour. In complex ion formation, the central metal ion acts as a Lewis acid, accepting multiple pairs of electrons from the surrounding ligands, which are acting as Lewis bases. For example,



Hard/Soft Acids

Lewis acids and bases can be described in terms of whether they are hard or soft. This is given the acronym, HSAB, (Hard Soft Acid Base), and is also known as the Pearson acid base concept. Knowledge and application of HSAB is not required at A-level, but can be helpful when explaining stability, for example, comparing equilibrium constants of Lewis acids and Lewis bases.

For reference purposes, Table 1, below, provides a summary of the characteristics associated by different HSAB species.

Table 1

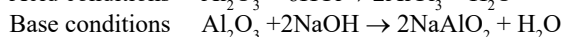
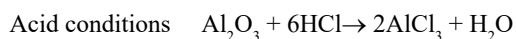
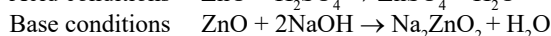
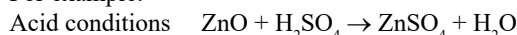
HSAB Species	Characteristics	Examples
Hard Acids	Small ionic radii High positive charge Empty orbitals in their valence shells Electropositive	H^+ , Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} Al^{3+} , Cr^{3+} , Fe^{3+} $Be(CH_3)_2$, BF_3 , BCl_3 , $Al(CH_3)_3$
Hard Bases	Small radii Electronegative atomic centres Weakly polarisable Difficult to oxidise	H_2O , OH^- , F^- , Cl^- , $CH_3CO_2^-$, PO_4^{3-} , SO_4^{2-} , CO_3^{2-} , NH_3 , RNH_2 , N_2H_4
Soft Acids	Large radii Low or partial positive charge Completely filled orbitals in their valence shells Moderately electronegative	Cu^+ , Ag^+ , Au^+ , Cs^+ Metal atoms
Soft Bases	Large atomic/ionic radii Moderately electronegative High polarizability Easily undergo oxidation	I^- , CN^- , SCN^- , $S_2O_3^{2-}$, C_2H_4 , C_6H_6 , H^-

Note that hard acids will tend to react more readily with hard bases, forming stronger bonds. Soft acids will react more readily and form stronger bonds with soft bases.

Amphoteric Behaviour

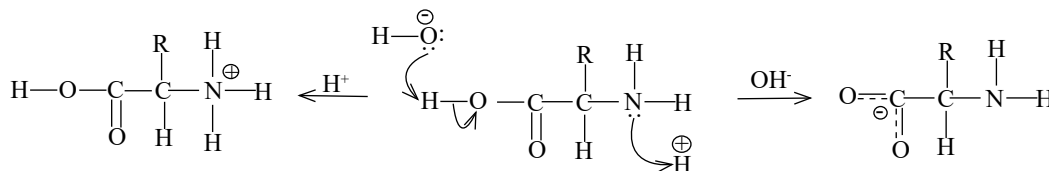
There are substances, molecules or ions, that can behave as an acid and a base. For example, many metals form amphoteric oxides or hydroxides. These will exhibit acid or base behaviour depending on conditions.

For example:



Amphiprotic molecules include self-ionising compounds, such as water, H_2O , or molecules containing amine and carboxylic acid functional groups, such as amino acids and proteins that can either donate or accept a proton (H^+). Figure 4, gives a simple summary on the behaviour of a generic amino acid in acid and in basic conditions.

Fig. 4



In acidic conditions, amino acids act as a base by accepting a proton, H^+ , to form an ammonium ion, $R'NH_3^+$.

In basic conditions, amino acids behave as acids by donating a proton and forming a carboxylate ion, $R''CO_2^-$.

Questions

- For each of the examples provided, give the most appropriate definition/theory from the following; Arrhenius, Brønsted-Lowry acid/base, Lewis acid/base:
 - Dissociates in solution to give hydroxide ions, OH⁻.
 - Electron-pair acceptor.
 - Dissociates in solution to give hydrogen ions, H⁺.
 - Proton, H⁺, acceptor.
- Perchloric acid, HClO₄, is a mineral acid that ionises in water. Complete a chemical equation describing this reaction.
What is the conjugate base of perchloric acid, HClO₄?
 - Ethanedioic acid, H₂C₂O₄, ionises in water. Complete an equation, identifying the conjugate base of ethanoic acid, H₂C₂O₄.
- Which of the following substances are Lewis acids, and which are Lewis bases?

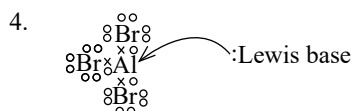
(a) BF ₃	(b) NH ₃
(c) NH ₂ NH ₂	(d) PH ₃
(e) AlCl ₃	(f) Li ⁺
(g) H ⁻	(h) H ₂ O
- Draw a dot-cross diagram of a molecule of aluminium bromide, AlBr₃, showing outer electrons only. Explain how aluminium bromide, AlBr₃, behaves as a Lewis acid.
- Both ammonia gas, NH₃, and hydrogen chloride gas, HCl, dissolve in water. Using chemical equations, explain how these two reactions illustrate water's amphoteric behaviour.

Answers

- Arrhenius' theory.
 - Lewis Theory (Lewis acid).
 - Arrhenius' theory
 - Brønsted-Lowry theory for acids.
- $$\text{HClO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^-$$

ClO₄⁻ (conjugate base)
 - $$\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HC}_2\text{O}_4^-$$

HC₂O₄⁻ (conjugate base)
- | | |
|--|--|
| (a) BF ₃ (Lewis acid) | (b) NH ₃ (Lewis base) |
| (c) NH ₂ NH ₂ (Lewis base) | (d) PH ₃ (Lewis base) |
| (e) AlCl ₃ (Lewis acid) | (f) Li ⁺ (Lewis acid) |
| (g) H ⁻ (Lewis base) | (h) H ₂ O (Lewis acid/base) |



Aluminium has three valence electrons. AlBr₃ has three covalent bonds, i.e. three bonding electron pairs and a vacant, empty p-orbital. A Lewis base can therefore donate an electron-pair, forming a dative, or coordinate, covalent bond. AlBr₃ is accepting an electron-pair and is therefore behaving as a Lewis acid.

- $$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$$

Water, H₂O, donates a hydrogen ion, H⁺, to ammonia, NH₃, thus behaving as an acid.

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

Water, H₂O, accepts a hydrogen ion, H⁺, thus behaving as a base.