

History of acids, Conjugates and Salts

- *outline the historical development of ideas about acids, including those of Lavoisier, Davy and Arrhenius*

Historical development of ideas of acids and bases

| Chemist | Proposal | Drawback |
|----------------------------------|---|--|
| Antoine Lavoisier (1743-1794) | <ul style="list-style-type: none"> Many non metal compounds containing oxygen produced acids when dissolved in water. Acids contain oxygen. Oxygen (acid former) | <ul style="list-style-type: none"> Many oxygen containing substances were bases. Some acidic substances(HCl) did not contain oxygen. |
| Humphry Davy (1778-1829) | <ul style="list-style-type: none"> Electrolysed HCl to produce H₂ and Cl₂. Proved that no oxygen was essential. Proposed that Hydrogen gave acids their acidic properties. Acids contained 'replaceable hydrogen.' | <ul style="list-style-type: none"> NO₂ forms when concentrated nitric acid attacked metal. |
| Svante Arrhenius (1859-1927) | <ul style="list-style-type: none"> Electrolysis of aqueous solutions of acids produce H₂ at the cathode. This means that hydrogen ions in the water is converted into hydrogen molecules. All acidic solutions are formed when acids ionise when they dissolve in water. A base produces OH⁻ when dissolved in water. Important in the development of the pH scale (it recognised the importance of the conc of H⁺ in a water solution). During neutralisation the H⁺ and OH⁻ react to form H₂O. | <ul style="list-style-type: none"> Metallic oxides and carbonates do not contain OH⁻ but are basic. Solutions of various salts are acidic or basic rather than neutral. |

**Bronsted-Lowry
(1879-1947) -(1874-
1939)**

- **Acids are proton donors.**
- **Bases are proton acceptors.**
- **Related the properties of an acid relative to those of the solvent.**
- **Provided a sound basis for the quantitative treatment of acid-base equilibria and pH calculations.**
- **Hydrolysis of salts to produce a pH different from 7.0 was an acid-base reaction.**

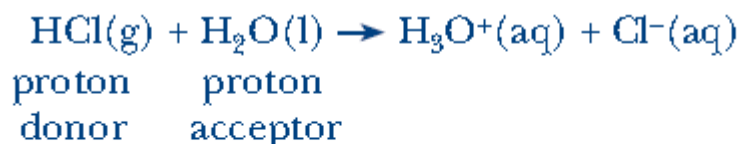
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- *outline the Bronsted–Lowry theory of acids and bases*

THE BRÖNSTED–LOWRY CONCEPT OF ACIDS AND BASES

An **acid** is a substance that, in solution, tends to give up protons (hydrogen ions), and a **base** is a substance that tends to accept protons

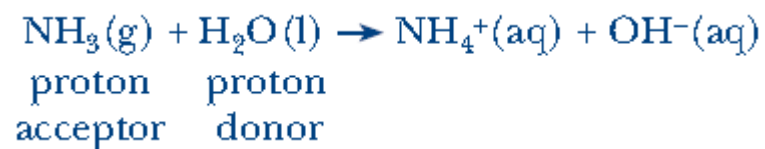
An acid is a proton donor.



Thus the HCl is a Bronsted–Lowry acid (B–L acid) as it is the proton donor. Water is the Bronsted–Lowry base as it is the proton acceptor.

Water = Bronsted –Lowry base

A base is a proton acceptor.

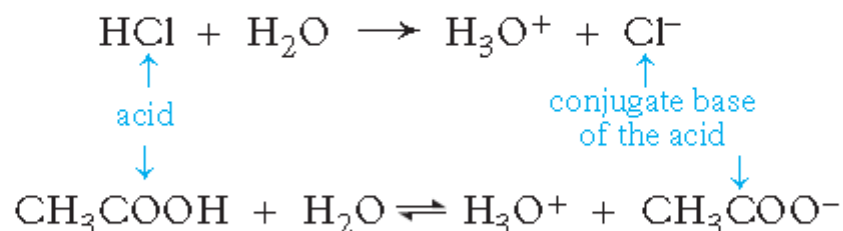


Water = Bronsted –Lowry acid

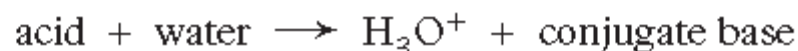
- *describe the relationship between an acid and its conjugate base, and a base and its conjugate acid*

Conjugates

An acid gives up a proton to form what is called its **conjugate base**:



That is:



The reaction product is called a conjugate *base* because in solution it tends to gain (accept) a proton:

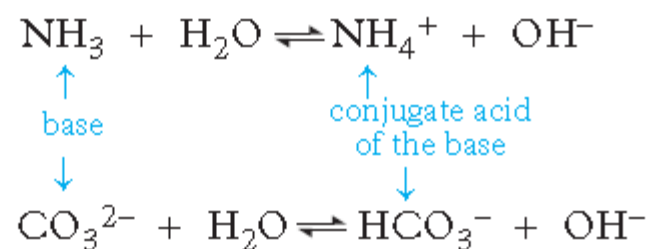


HF = Bronsted–Lowry acid; F[−] = conjugate base of HF

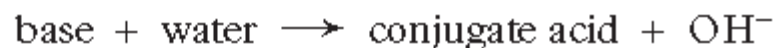
H₂O = Bronsted–Lowry base; H₃O⁺ = conjugate acid of H₂O

‘Conjugate’ means ‘linked with’—

Similarly, a base accepts a proton to form what is called its **conjugate acid**:



That is:



The reaction product is called a conjugate *acid* because in solution it tends to give up (donate) a proton:



- *identify conjugate acid–base pairs*

Conjugate acid base pairs

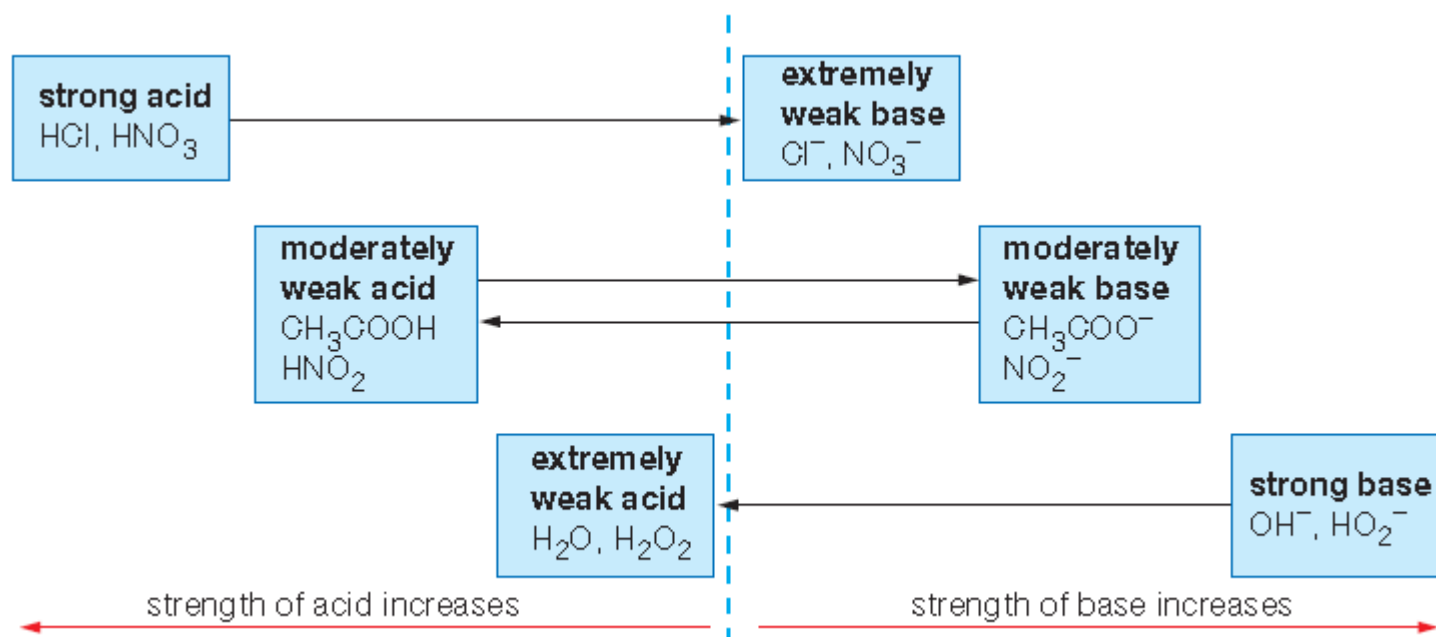
| Acid | Conjugate base | Base | Conjugate acid |
|--------------------------|---------------------------|--------------------------|--------------------------|
| HCl | Cl^- | O^{2-} | OH^- |
| HNO_3 | NO_3^- | OH^- | H_2O |
| H_3O^+ | H_2O | S^{2-} | HS^- |
| HSO_4^- | SO_4^{2-} | CO_3^{2-} | HCO_3^- |
| HF | F^- | NH_3 | NH_4^+ |
| HNO_2 | NO_2^- | HCO_3^- | H_2CO_3 |
| CH_3COOH | CH_3COO^- | HS^- | H_2S |
| H_2CO_3 | HCO_3^- | CH_3OO^- | CH_3COOH |
| NH_4^+ | NH_3 | F^- | HF |
| HCO_3^- | CO_3^{2-} | SO_4^{2-} | HSO_4^- |

Relative strengths of acid–base conjugates

The conjugate base of a strong acid is an extremely weak base

The conjugate base of a weak acid is a weak base

The conjugate acid of a strong base is an extremely weak acid

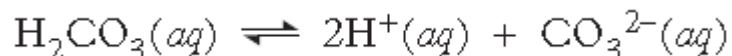


MONOPROTIC, DIPROTIC AND TRIPROTIC ACIDS

A monoprotic acid is one that forms one proton (hydrogen ion) per molecule.



A diprotic acid is one that gives up two protons per molecule of acid.



A triprotic acid is one that gives up three protons per molecule of acid.

Diprotic and triprotic acids and the anions they form

| Acid | | Anions formed | | Typical salt |
|-----------------|-------------------------|---|--|---|
| sulfuric acid | H_2SO_4 | sulfate hydrogen sulfate | SO_4^{2-} HSO_4^- | Na_2SO_4 KHSO_4 |
| carbonic acid | H_2CO_3 | carbonate hydrogen carbonate | CO_3^{2-} HCO_3^- | CaCO_3 NaHCO_3 |
| sulfurous acid | H_2SO_3 | sulfite hydrogen sulfite | SO_3^{2-} HSO_3^- | MgSO_3 KHSO_3 |
| phosphoric acid | H_3PO_4 | phosphate hydrogen phosphate dihydrogen phosphate | PO_4^{3-} HPO_4^{2-} H_2PO_4^- | Na_3PO_4 K_2HPO_4 NaH_2PO_4 |

- *identify amphiprotic substances and construct equations to describe their behaviour in acidic and basic solutions*

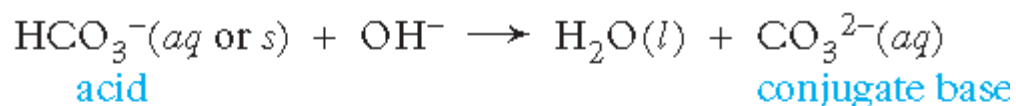
AMPHIPROTIC SUBSTANCES

A substance that can act both as a proton donor and as a proton acceptor is called an **amphiprotic** substance (*amphi* means 'both').

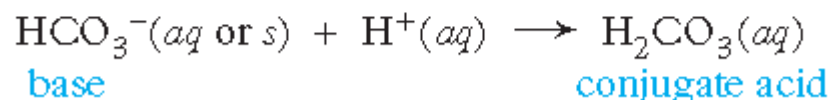
The hydrogen carbonate ion is amphiprotic, because in aqueous solution it reacts with water in two ways:



However if placed in alkaline (basic) solution, hydrogen carbonate acts as an acid:



If placed in acid solution hydrogen carbonate acts as a base:



The hydrogen sulfite ion, HSO_3^- , is also amphiprotic.

Another amphiprotic substance is water.

- *identify a range of salts which form acidic, basic or neutral solutions and explain their acidic, neutral or basic nature*

SALTS AS ACIDS AND BASES

Salt solutions with pH greater than 7.0

The nitrite ion therefore accepts a proton from water and so hydroxide ion is formed and pH is greater than 7.0:



In a salt formed from a weak acid and a strong base (e.g. sodium acetate from acetic acid and sodium hydroxide), the anion is a weak base and so the salt in aqueous solution has a pH greater than 7.

WEAK ACID + STRONG BASE → BASIC SALT + WATER

Salt solutions with pH less than 7.0



In a salt formed from a weak base and strong acid (e.g. ammonium nitrate from ammonia and nitric acid), the cation is a weak acid and so the salt in aqueous solution has a pH less than 7.

WEAK BASE + STRONG ACID → ACIDIC SALT + WATER

A salt formed from a strong acid and a strong base

This salt has a pH close to 7.0.

This is because the conjugate base of a strong acid (eg. Cl^- from HCl) does not react with water to any significant extent and so does not alter its pH. Similarly, the conjugate acid of a strong base (H_2O from OH^-) does not sufficiently react with water to alter its pH. Hence the pH of such salts is just the pH of pure water, 7.0.

STRONG ACID + STRONG BASE \rightarrow NEUTRAL SALT + WATER

A salt formed from a weak acid and a weak base

Such a salt, (for example, ammonium acetate from ammonia and acetic acid) also has a pH close to 7.0, because both the anion and the cation react with water to small extents and so approximately cancel each other.

Hydrolysis is a chemical reaction in which a substance reacts with water.

pH of solutions of salts formed from different types of acids and bases

| | Strong base (NaOH, KOH) | Weak base (NH ₃) |
|---|--|--|
| Strong acid (HCl, HNO ₃) | pH = 7 (NaCl, KNO ₃) | pH < 7 (NH ₄ Cl, NH ₄ NO ₃) |
| Weak acid (CH ₃ COOH, HNO ₂) | pH > 7 (CH ₃ COONa, KNO ₂) | pH = 7 (CH ₃ COONH ₄) |

pH of 0.25 mol/L aqueous solutions of some common salts

| Salt | pH |
|---|------------------|
| sodium chloride, NaCl | 7.0 ^a |
| potassium nitrate, KNO ₃ | 7.0 ^a |
| sodium sulfate, Na ₂ SO ₄ | 7.0 ^a |
| sodium hydrogen sulfate, NaHSO ₄ | 1.3 |
| potassium hydrogen oxalate, KHC ₂ O ₄ | 2.4 |
| ammonium nitrate, NH ₄ NO ₃ | 4.8 |
| potassium nitrite, KNO ₂ | 8.3 |
| sodium hydrogen carbonate, NaHCO ₃ | 8.3 |
| sodium acetate, CH ₃ COONa | 9.1 |
| potassium cyanide, KCN | 11.3 |
| sodium carbonate, Na ₂ CO ₃ | 11.8 |
| ammonium acetate, CH ₃ COONH ₄ | 7.0 |

NEUTRALISATION AND SAFETY

Sodium carbonate is widely used to neutralise acidic spills or effluents because:

- it is a stable solid which is easily and safely handled and stored
- it is the cheapest alkali available and
- if too much of it is used there is less danger than from excess sodium hydroxide or lime (calcium hydroxide).

These examples illustrate the factors that need to be considered in choosing a substance to neutralise acid or alkali spills in factories or laboratories, namely:

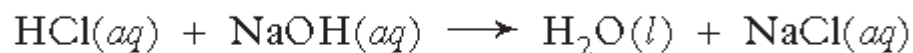
- the speed of the reaction for neutralising the spilt material
- the need for a reagent that will not have any harmful effect if an excess of it is used (since it is hard to determine exact quantities for neutralising spills)
- the safety in handling and storing the reagent
- the cost of the reagent
- the possibility of the one reagent being able to neutralise both acid and alkali spills.

- *gather and process information from secondary sources to trace developments in understanding and describing acid–base reactions*

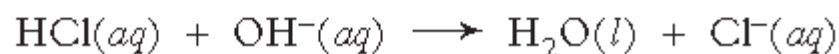
NEUTRALISATION



For example:



or



Neutralisation reactions are **proton transfer reactions**



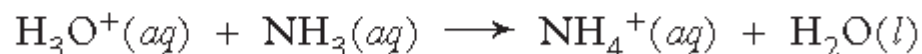
or using the more accurate formula for the hydrogen ion,



In the neutralisation of ammonia by nitric acid:

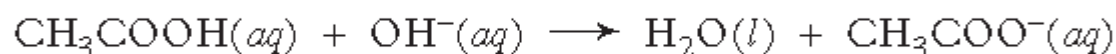


or in net ionic form (since HNO_3 is completely ionised):



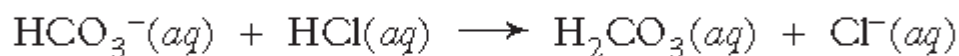
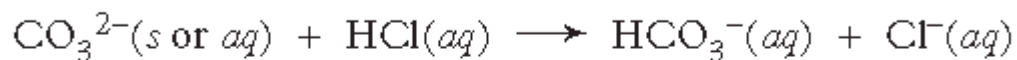
the acid transfers a proton to ammonia (to form the NH_4^+ ion).

Similarly when sodium hydroxide solution neutralises acetic acid:



a proton is transferred from the acetic acid to the base, OH^- (to form H_2O).

Sodium carbonate reacts with hydrochloric acid: we can consider this as a three-step process:



or write it as one overall reaction:



Heat of reaction

Neutralisation is an exothermic reaction

Heat is liberated as it occurs and the enthalpy change ΔH , for neutralisation reactions is -56 kJ/mol .

It varies by a few kJ/mol depending upon whether the acid or base involved is weak or strong and upon the concentration of the solutions.