Arrows in Chemistry

Abirami Lakshminarayanan

Arrows are an integral part of chemistry. What is there in an arrow? It looks insignificant yet appears in most scientific publications. These symbols which make use of 'lines' and 'heads' are perhaps the most powerful pictographic tools used in day-to-day chemistry and provide chemists a convenient way of representing their thoughts. Reactions, their states, electrons, their movement, and even processes like reflux are shown using arrows. Thus, arrows form a part of essential symbolism in chemistry.

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1. Introduction

Science makes use of a variety of symbols in order to achieve effective communication. While symbols like ψ, θ and φ play key roles in physics and math, arrows are perhaps the most fundamental and widely used symbols in chemistry. In this article, we try to explore one of the most powerful tools of chemistry, the 'arrows'.

1.1. *Origin of the Word 'Arrow'*

In Sanskrit, arrow is known as *baan* or *teer*. The word 'Arrow' derives from the Indo-European root *arkw*, which meant curve and was used to describe the 'bow' [1]. The Latin equivalent came to be known as *arcus.* The Germanic root became *arkhw* which meant 'the thing belonging to the bow' versus just 'bow'. Old English adapted it as *arw*, and perhaps that is where today's form arose from [2].

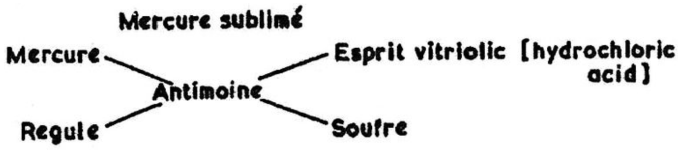
1.2. *Arrows and Chemistry*

Chemical equations and reactions make use of arrows for their representation thus avoiding a myriad array of words and sentences. Thus, arrows form an integral part in the expression of chemistry. They stand true to the old adage, "A picture speaks a thousand words". When were arrows first used in chemistry, and

Keywords
Arrows, reaction arrows, electron arrows.

who was the first one to use them.

The first chemical equation to be diagrammed was by Jean Beguin in 1615. He made the first-ever chemical equation or rudimentary reaction diagram, showing the results of reactions in which there are two or more reagents. This famous diagram found in his book *Tryocinium chymicum* (beginner's chemistry) [3], detailing the reaction of corrosive sublimate ($HgCl_2$) with sulfide of antimony (Sb_2S_3), is shown here.



Arrows in chemistry can be broadly classified as 'reaction arrows' and 'electron arrows'. While the former is used to describe the state or progress of a chemical reaction, the latter is used to represent the movement of electrons.

2. Reaction Arrows

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Arrows in chemistry can be broadly classified as 'reaction arrows' and 'electron arrows'. While the former is used to describe the state or progress of a chemical reaction, the latter is used to represent the movement of electrons.

2.1 *The Chemical Reaction Arrow*

The chemical reaction arrow is one straight arrow pointing from reactant(s) to product(s) and by-products, sometimes along with side products.

$$A \rightarrow B.$$

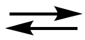
It is the most widely used arrow. The single arrow emphasizes one direction of chemical change (from A to B). Many a times, the reaction conditions, reagents and catalysts used in the chemical reaction are written on the chemical reaction arrow. For example,

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

$$N_{2(g)} + 3\,H_{2(g)} \xrightarrow[723K,\ 200\ atm]{Fe,\ Mo} 2\,NH_{3(g)}$$

2.2 *Equilibrium Arrows*

The equilibrium arrows were introduced by J H van't Hoff in his book *Étude de Dynamique Chemique* in the year 1884 [4]. Equilibrium arrows are used to depict a reversible reaction. van't Hoff used full-headed arrows pointing in opposite direction to symbolize equilibrium.



In 1902, H Marshall introduced the modified symbol with half-headed arrows pointing in opposite directions which are more commonly used today [5].

a) Dynamic Equilibrium Arrows: Half-headed double arrows pointing in opposite directions are used to represent dynamic equilibrium. The arrows are of equal length and represent a balanced equilibrium. These arrows imply that the experimental conditions that allow A to change to B, also allow the backward transformation of B into A.

The representation of a dynamic equilibrium signifies a steady state in the concentrations of A and B and that a net change no longer occurs.

Half-headed double arrows pointing in opposite directions are used to represent dynamic equilibrium.

Box 1. J H van't Hoff – The Father of Physical Chemistry [4,6,7].

Jacobus Henricus van't Hoff, along with Wilhelm Ostwald, and Svante Augustus Arrhenius are regarded as the founders of physical chemistry. J H van't Hoff was known for his epoch making publications. The one entitled "Proposal for the development of 3-dimensional chemical structural formulae" gave the impetus to the development of stereochemistry.

In 1884 he published a book *Études de Dynamique chimique* (Studies in dynamic chemistry). van't Hoff introduced the equilibrium arrows in this book (page 115). In his Nobel Lecture, he says of equilibrium arrows, while describing them, "…... This can be illustrated in the formula by introducing the sign for a reversible reaction instead of the sign of equality….."

Of the numerous distinctions to his name, J H van't Hoff was the recipient of the first Nobel Prize in Chemistry (1901).

The representation of a dynamic equilibrium signifies a steady state in the concentrations of A and B and that a net change no longer occurs.

b) Equilibrium Favouring Reactants: This equilibrium is also shown by half-headed double arrows, but the one pointing towards the products is shorter.

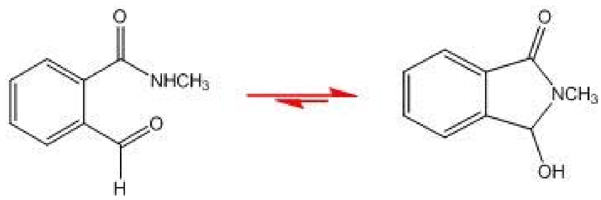
$$A \rightleftharpoons B$$

The short arrow implies that the flow of reactants to products is relatively difficult and hence equilibrium is reached when there are more reactants than products as illustrated below.

c) Equilibrium Favouring Products:

$$A \rightleftharpoons B$$

In this case, the backward reaction, i.e., conversion of product back to reactant is rather difficult and hence equilibrium is reached when there are more products than reactants. For example,



2.3 *The Upward Arrow*

Upward arrow in a chemical reaction indicates the evolution of a gas. It appears only on the product side and is written next to the gaseous product.

$$2\ KClO_{3(s)} \xrightarrow[420K]{MnO_2} 2\ KCl_{(s)} + 3\ O_2 \uparrow$$

In this example, upward arrow is placed next to oxygen to demonstrate the evolution of gas.

2.4 *The Downward Arrow*

Formation of a precipitate during a reaction is indicated by an arrow pointing downwards.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\,CaCO_3\downarrow + 2H_2O$$

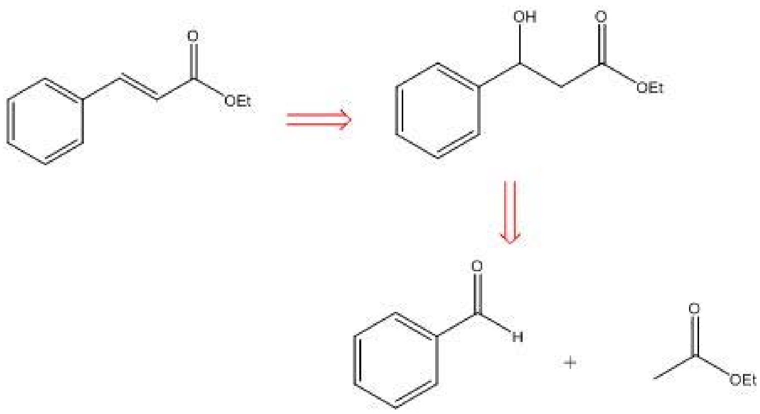
Again, this arrow appears only on the product side and is shown beside the product which precipitates.

2.5 *The Retrosynthetic Arrow*

Two straight lines and a single head constitute the retrosynthetic arrow.

$$\Longrightarrow$$

One of the widely used tools in synthetic organic chemistry, the retrosynthetic arrow literally means ‘is made from’ or functional group interconversion (FGI). The use of retosynthetic arrow is illustrated in an example shown here.



The retrosynthetic strategy was formalized by E J Corey.

2.6 *Clockwise and Anti-Clockwise Arrows*

These arrows are used in assigning the stereodescriptors ‘R’

One of the widely used tools in synthetic organic chemistry, the retrosynthetic arrow literally means ‘is made from’ or functional group interconversion (FGI). The retrosynthetic strategy was formalized by E J Corey.

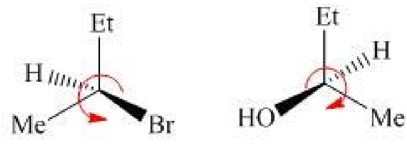
Box 2. Professor E J Corey – Father of Modern Organic Synthesis [8].

Organic chemistry is full of reactions and reagents named in honour of their discoverer, E J Corey. His profound research in organic synthesis has earned him the title 'Father of modern organic synthesis'.

E J Corey was awarded the 1990 Nobel Prize in Chemistry for his development of the theory and methodology of organic synthesis. His 1969 total syntheses of several prostaglandins are considered classics. He has authored numerous books and papers.

In his Nobel lecture, Professor Corey says, "Changes in the retrosynthetic direction are indicated by a double arrow (⟹) to distinguish them from the synthetic direction of chemical reactions (⟶) …"

(rectus, clockwise) or 'S' (sinister, anticlockwise) for confirming the absolute stereochemistry of an optically active molecule.



S-2-Bromobutane *R*-2-Butanol

The tail of these arrows begins at the group with highest priority (assigned in accordance with the priority rules give by Cahn, Ingold and Prelog [9]), travels progressively through the groups with descending priority and the head points back to the group with the highest priority.

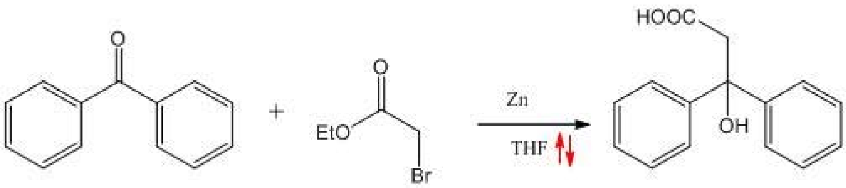
The tail of the clockwise and anti-clockwise arrows begins at the group with highest priority, travels progressively through the groups with descending priority and the head points back to the group with the highest priority.

2.7 *The Reflux Arrow*

Reflux is a technique used in chemistry to apply energy to reactions over an extended period of time. It involves boiling of a liquid in a vessel attached to a condenser so that the vapours continuously condense for reboiling [10].

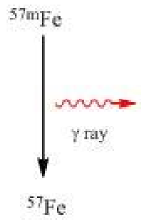
Many a time, organic chemists prefer to show the 'reflux' of a mixture using two full-headed arrows, one pointing upwards and the other downwards.

These arrows are written on the reaction arrows. If a solvent is used in the reaction, then they are shown next to the solvent.

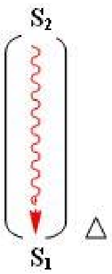


2.8 *The Wavy Arrow*

Any energy transfer or emission can be represented using the wavy arrow. For example, the emission of γ-radiation is shown by the use of a wavy line with an arrow head.



A wavy arrow pointing downwards is widely used in photochemistry to show non-radioactive decay which is a result of dissipation of energy as the molecule moves from a higher energy level to a lower one [9].



In the above diagram, S_1 and S_2 are singlet excited states of a photochemical reaction. The wavy arrow indicates a non-radioactive energy dissipation by which a molecule in higher excited singlet state S_2 comes down to lower singlet excited state S_1.

Any energy transfer or emission can be represented using the wavy arrow.

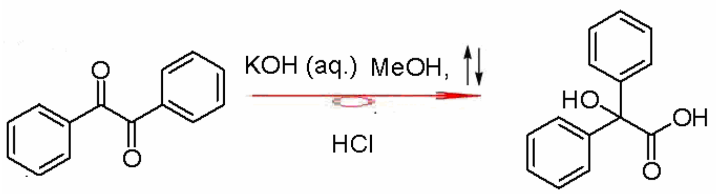
A rearrangement reaction is a broad class of organic reactions where the skeleton of the molecule is rearranged to give a structural isomer of the original molecule. Rearrangements can be shown by using a special type of arrow, 'the rearrangement arrow'.

2.9 *The Rearrangement Arrow*

A rearrangement reaction is a broad class of organic reactions where the skeleton of the molecule is rearranged to give a structural isomer of the original molecule [9]. In many rearrangements, an atom or a group of atoms moves from one atom to another, intramolecularly or intermolecularly. Rearrangements can be shown by using a special type of arrow, 'the rearrangement arrow'.

The distinguishing feature of this arrow is a small 'knot' present mid-way between its tail and head which implies that rearrangement has occurred during the reaction.

The first rearrangement reaction to be reported was the 'Benzilic Acid Rearrangement' which was discovered by Justus von Liebig, a German chemist, in 1838 [3]. It is depicted using the rearrangement arrow.



Benzil

Benzilic acid

Mechanistically, the representation of such a movement may be shown by using the conventional curved arrow protocol (refer Section 3.1).

3. Electron Arrows

Electron arrows are used to indicate movement of electrons during a chemical reaction.

3.1. *The Curved or Curly Arrow*

This arrow is one of the most important and widely used electron

Box 2. Robert Robinson – The Introducer of Curved Arrows [11].

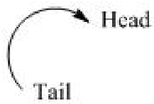
Sir Robert Robinson was born at Rufford, Derbyshire on September 13, 1886. He graduated from Manchester University in 1906 and obtained DSc in 1910. His 1917 landmark one-step synthesis of tropinone made him the forerunner of modern biomimetic synthesis. He developed a general method for constructing a six-membered ring onto a ketone with enolizable hydrogen (Robinson annulation).

In the mid-1920s, Robinson introduced the curved arrow in his paper 'An explanation of the property of Induced Polarity of Atoms and Interpretation of Theory of Partial Valances on an electronic basis'.

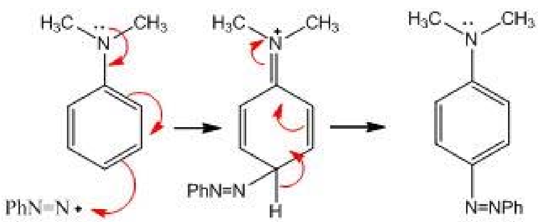
Sir Robinson was awarded the 1947 Nobel Prize in Chemistry for his work on the synthesis of natural products, especially the alkaloids.

He authored over 500 papers and several books on natural products. He was an avid chess player and his hobbies included mountaineering, photography and music.

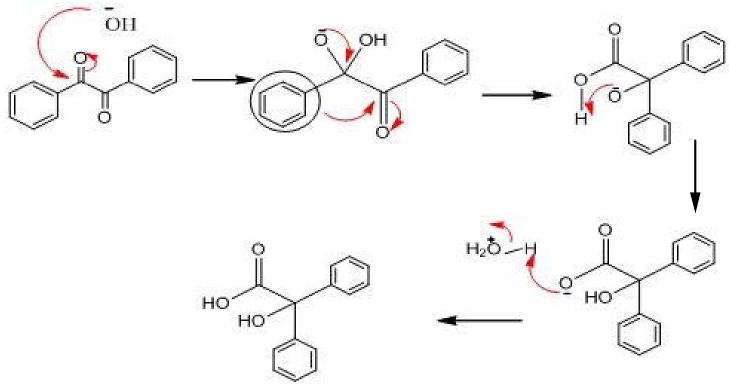
arrows and was introduced by Sir Robert Robinson in 1922 [11]. A curved arrow is used to write a reaction mechanism by indicating the movement of electrons.



The tail of a curly arrow 'starts' at a mobile electron pair and its head points to the 'destination' of the electron pair.



The benzilic acid rearrangement reaction can be mechanistically represented using the curved arrow.



The benzilic acid rearrangement reaction can be mechanistically represented using the curved arrow as follows.

The reaction involves nucleophilic attack of hydroxide ion on carbonyl carbon followed by migration of phenyl group along with its bonding electrons to the neighboring carbonyl group. The migration of the phenyl group rearrangement is shown by encircling the phenyl group and using a curved arrow beginning at the migrating phenyl group and terminating at its destination, the carbonyl carbon.

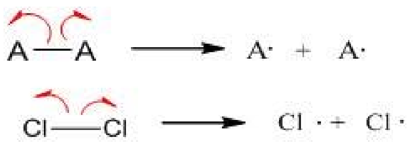
The process of writing a reaction mechanism using curved arrows is called 'electron pushing'.

3.2 *Fishhook Arrow*

Fishhook arrows indicate cleavage or movement of a single electron shown as a single-headed curved arrow. They are widely used in radical chemistry to represent the hemolytic cleavage and reactions of radicals. They always occur in pairs.

Fishhook arrows indicate cleavage or movement of a single electron shown as a single-headed curved arrow.

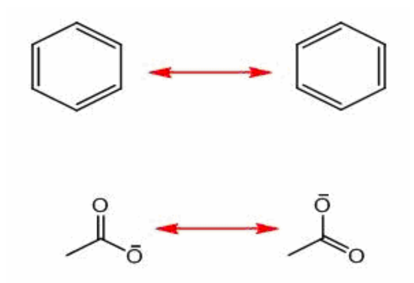
For example,



3.3 *The Resonance Arrow*

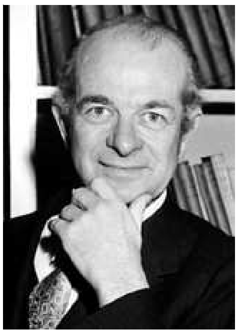
A resonance arrow is one straight double-headed arrow pointing between two equivalent structures of the same molecule. Although the concept of resonance was given by Linus Pauling in 1928, the resonance arrow was introduced by the German chemist Fritz Arndt [3]. It connects two structures of the same molecule but with different electron distribution patterns. The resonance structures of benzene and carboxylate ion are shown below.

A resonance arrow is one straight double-headed arrow pointing between two equivalent structures of the same molecule. The resonance arrow was introduced by the German chemist Fritz Arndt.



While equilibrium arrows are a pair of half-headed arrows connecting two different, distinguishable compounds, the resonance

Box 4. Linus Pauling – The Greatest Chemist of the 20th Century [7,12].



Arguably the greatest scientist of all times, Linus Carl Pauling's life presents a chronology of events that made a great impact not only on science but on mankind.

In 1928, Pauling introduced the concept of 'resonance'. This concept was the main area of attack by the Russians during the days of the Cold War who labeled the concept 'pseudo-scientific'. The fight was about arrows rather than with arrows. Pauling successfully responded to these allegations and resonance has emerged one of the most powerful concepts today.

His 1939 publication *The Nature of the Chemical Bond*, compiles forty years of his Nobel Prize work on devising molecular structure using quantum mechanics.

He was awarded the Nobel Peace Prize (1963) for his efforts to curb the use of radioactive weapons.

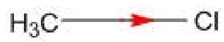
The inductive effect arrow is a special type of arrow in which the bond between two atoms acts as the straight line of the arrow.

arrow is a single arrow with two heads connecting indistinguishable structures of the same molecule.

3.4 *The Mid-Head Arrow*

This arrow is used to represent inductive effect or bond-polarization in a molecule. Bond polarization or 'induction' is a redistribution of electric charge in an object caused by the influence of nearby charges. Induction was discovered by the British scientist John Canton in 1753 [13].

The inductive effect arrow is a special type of arrow in which the bond between two atoms acts as the straight line of the arrow, while the arrow head is inserted in between the bond and points towards the more electronegative element.

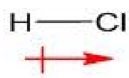


For instance, chlorine being more electronegative than carbon, the mid-head arrow points towards chlorine in the above example.

3.5 *The Dipole Moment Arrow*

This arrow is used to indicate the direction of the resultant dipole moment in a molecule. It is represented by a straight arrow with the head pointing towards the direction of net dipole moment. A special feature of this arrow is that at the tail of the arrow is a '+' sign.

Usually the dipole moment vector points towards the more electronegative atom in the molecule. The '+' sign is placed at the electron-deficient or the less electronegative atom as illustrated below.



3.6 *Electrons Occupying an Orbital*

Electrons occupying an orbital are routinely shown with the help of arrows. The arrows may be half-headed or full-headed. The direction of the arrowhead symbolizes the spin of the electron. The half-head is known to designate half-integer spin and hence is more commonly used.

Electrons occupying an orbital are routinely shown with the help of arrows. The direction of the arrowhead symbolizes the spin of the electron.

4. Conclusion

Arrows are the most frequent symbols used in everyday chemistry. An arrow may simply mean an indicator or pointer to some. But in chemistry, this humble icon represents change and all aspects associated with it. Chemistry without arrows would be like a flower without fragrance. The simple yet powerful and elegant expression using arrows has made chemistry much simpler to comprehend.

Suggested Reading

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Acknowledgement

I would like to express my sincere gratitude to Professor Shridhar R Gadre, Department of Chemistry, University of Pune, who inspired, encouraged and guided me to write this article.

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