

A generalized theory of acidobasic and redox behaviour

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INTRODUCTION

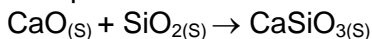
As it is known, for the definition of acids and bases many definitions have been proposed. The definitions that are commonly used are: the Arrhenius, the Bronsted-Lowry and the Lewis. Various publications report two more: the Lux-Flood and the Usanovitch definitions. Each definition has advantages and disadvantages. The aim of this article is to integrate the above definitions of acidic and basic behavior without exclude their advantages. The only definition that is not included in the integration is the Usanovitch definition, reasons for such a decision is stated in the next section of the article.

According to the Arrhenius definition, which was formulated in 1884, acids are the hydrogenous compounds that give H^+ cations when dissolved in water while bases are the compounds that give OH^- anions when dissolved in water.

According to the Bronsted-Lowry definition that put forth in 1923 acids are the substances (molecules or ions) that give protons (H^+), while bases are the substances that receive protons.

Moreover, according to the Lewis definition, also put forth in 1923, acids are the substances that receive an electron pair, while bases are the substances that give an electron pair.

Thus according to the definition of Lux and Flood, formulated in 1939 and in 1947, acids are the compounds that receive the O^{2-} anion, while bases are the compounds that give the O^{2-} anion. This definition is used for the characterization of certain oxides, which react in anhydrous conditions in metallurgy, as acids or bases. For example:



(Γ. Μανουσάκη, Π. Ασλανίδη, Χ. Μπόλου. Αρχές Γενικής Χημείας.

<http://www.chm.ulaval.ca/~chm19641/Notes/pertabc1/node55.html>

http://fr.encycarta.msn.com/encyclopedia_761562874/acides_et_bases.html)

Finally, according to Usanovitch, acid is any substance that gives cations or receives anions or electrons, while base is any substance that receives cations or gives anions or electrons.

EVALUATION OF EACH DEFINITION

Usanovitch's definition is not accepted by a large number of scientists, because besides the acidic and basic behavior, it also includes the oxidation-reduction (redox) one. Based on this definition, all chemical reactions can be unified and the term "redox behavior" becomes redundant. Nevertheless, this approach could be useful in cases when the boundaries between redox behavior and acidic-basic behavior become fuzzy.

The **Lux-Flood** definition, as already said, has a limited range of application as it is used for the interpretation of the acidic or basic behavior of certain oxides in anhydrous conditions in metallurgy.

The **Arrhenius** definition has the following advantages and disadvantages:

Advantages

1. It can classify acids and bases according to their strength.
2. The theory can be expanded to other solvents besides water.
3. It is characterized by simplicity.

Disadvantages

1. It is limited in polar solvents.

2. It doesn't include ions in acids and bases.
3. It is restricted in solutions.

Similarly, the **Bronsted-Lowry** definition has the following advantages and disadvantages:

Advantages

1. It can classify acids and bases according to their strength.
2. The theory can be expanded to other solvents besides water.
3. In the consideration of acids and bases it also includes ions.
4. It can make a distinction in the behavior of the same compound when this compound behaves as an acid and when it behaves as a base.

Disadvantages

1. It is restricted in solutions

The **Lewis** definition has the following advantages and disadvantages:

Advantages

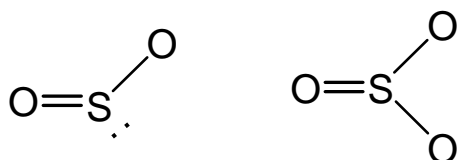
1. It is more general and includes the definitions given by Arrhenius, Bronsted-Lowry and Lux-Flood.
2. It is characterized by simplicity.
3. It combines the behavior of compounds with their electronic structure.

Disadvantages

1. It doesn't directly classify acids and bases according to their strength.
2. In many cases it confuses acidic-basic behavior with redox behavior.

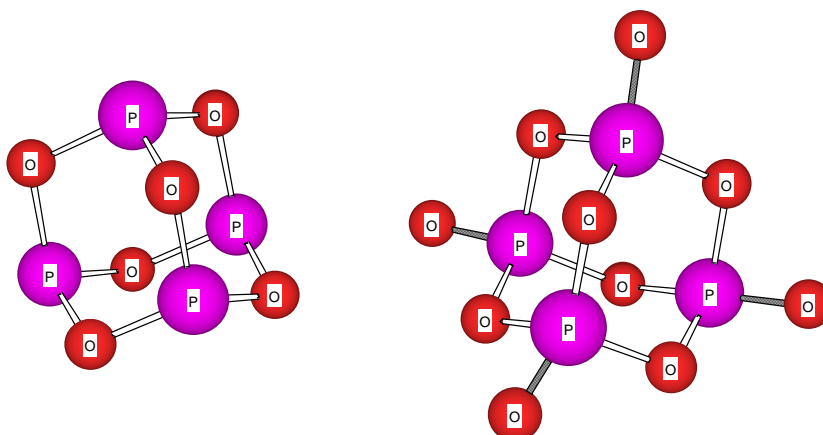
Clarifications on the second disadvantage:

According to the Lewis definition, the redox reaction $\text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{SO}_3$, is a reaction between an acid and a base, because from the SO_2 and SO_3 structures it can be seen that the S of SO_2 gives an electron pair for the creation of a bond with the O atom.



Moreover, according to the Lewis definition, the reaction $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$, is not entirely redox, because from the structure of SO_2 it can be seen that the S atom gives an electron pair for the creation of a bond with one of the two O atoms.

Furthermore, according to the Lewis definition, the redox reaction $\text{P}_2\text{O}_3 + \text{O}_2 \rightarrow \text{P}_2\text{O}_5$, is a reaction between an acid and a base, because from the structures of P_2O_3 and P_2O_5 it is obvious that the P gives an electron pair for the creation of a bond with the O atom. The aforementioned two oxides are in the form of the P_4O_6 and P_4O_{10} dimers, as seen in the following three-dimensional structures:



The definition proposed as follows, aims at including all the above mentioned ones, except for the Usanovitch definition, without eliminating their advantages. Moreover, it makes a clear distinction between acid-basic behavior and redox behavior.

SUGGESTED DEFINITION FOR THE MANIFESTATION OF ACIDOBASIC BEHAVIOUR

The demonstration of acidobasic behavior results from the transfer of a pair of electrons from an element of higher electronegativity to an element with lower electronegativity.

For such a transfer to take place: the more electronegative element must either be in the form of an anion, mainly O^{-2} , or it must possess a free electron pair, like N in NH_3 and the more electropositive element must either exist in the form of a cation, mainly H^+ , or it must be capable of receiving an electron pair in order to form a more stable structure, as does B in BF_3 . As a result, the reactions in which acidic and basic behavior is observed are always displacement reactions.

The substance that receives the electron pair acts as an acid and the substance that gives the electron pair acts as a base. The transfer of the electron pair could be direct or indirect through the transfer of the O^{-2} anion or the H^+ cation.

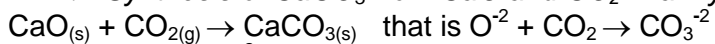
Examples:

1. *Neutralization of NaOH from HCl in aqueous solution*



in this case, there is a transfer of H^+ from the HCl to the OH^- and then the H^+ accepts an electron pair from the O of the OH^- (this interpretation is similar to that by Arrhenius, Bronsted-Lowry and Lewis).

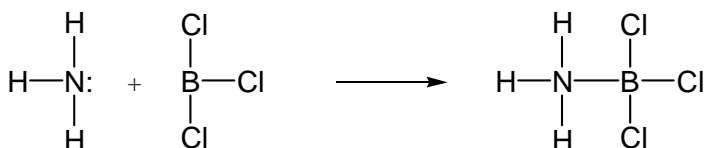
2. *Synthesis of $CaCO_3$ from CaO and CO_2 in anhydrous conditions*



in this case the O^{-2} anion is transferred to the CO_2 and offers an electron pair to the C atom (interpretation similar to that by Lux-Flood)

3. *Reaction of NH_3 with BCl_3 .*

In this case, the N offers an electron pair to the B (like in the Lewis theory)



NOTICE

With this definition we can't characterize as acidic or basic the behavior of the reactants in the following reactions:

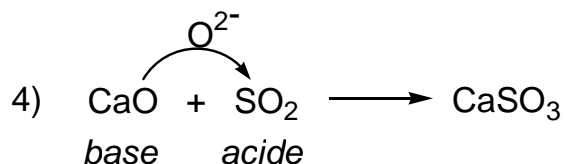
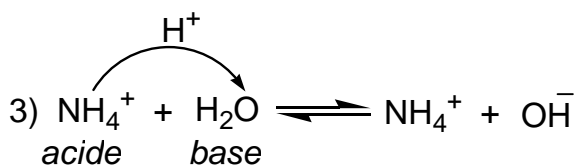
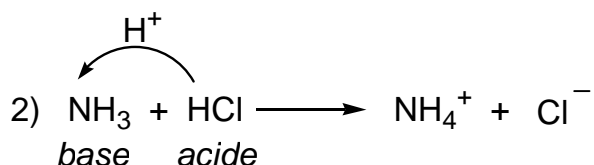
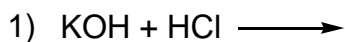
$SO_{2(g)} + 1/2O_{2(g)} \rightarrow SO_{3(g)}$ and $Ca_{(s)} + S_{(s)} \rightarrow CaS_{(s)}$, in which the transfer of the electrons and in this particular case, of an electron pair--is brought about by an element of low electronegativity towards an element of higher electronegativity. The two reactions mentioned above are redox reactions and not displacement reactions, as predicted by the mentioned definition.

THE MOST COMMON CASES

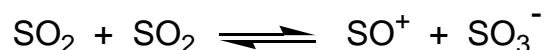
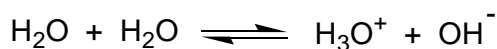
The majority of cases, in aqueous solutions, in gaseous phase and anhydrous conditions, the demonstration of the acidic or basic character results from the transfer of H^+ or O^{-2} between two substances. In these cases, every substance (molecule or

ion) that gives H^+ or receives O^{2-} behaves as an acid, while every substance that receives H^+ or gives O^{2-} behaves as a base.

Examples:



The interpretation of the electrical conductivity of several pure liquid substances is also classified in such a case as is evident in the following examples:

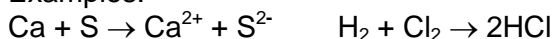


CONTRADISTINCTION WITH THE REDOX REACTIONS DEMONSTRATION OF REDOX BEHAVIOUR

After the definition of acidobasic behavior it is appropriate to make an accession in the definition of redox as well.

The demonstration of redox behavior results from the transfer of one or more electrons from an element with lower electronegativity towards an element with higher electronegativity. The result of this transfer is the change of the oxidation number.

Examples:

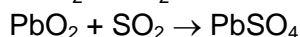
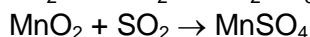
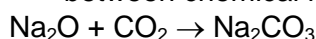


INNOVATION

The basic novelty of the suggested definition of acidobasic behavior consists in the addition of the clarification that the transfer of the electron pair must take place from the more electronegative to the more electropositive element. The transfer of an electron pair from an element of lower electronegativity towards an element of higher electronegativity is classified in the cases of redox behavior.

ADVANTAGES

1. This definition includes all the previous ones without great alterations but with additions. In fact, it is a completion to the Lewis definition.
2. Concerning the already existing definition of redox behavior, there is no essential innovation because the change of the oxidation number, which is a characteristic feature of these reactions, excludes the transfer of an electron pair, in the way that this transfer is mentioned in the proposed definition of acidic and basic behavior.
3. It clearly distinguishes acidic and basic behavior from redox behavior.
4. Using the criterion of the change in oxidation number, we can differentiate between chemical reactions, such as the following:



The last two in particular, even though they are reactions between the oxide of a metal and the oxide of a nonmetal, are redox reactions and consequently we can conclude that in these reactions no acidic or basic behavior is observed. This, according to the suggested definition, can be verified even by High School students, who are not familiar with the structure of the MnO_2 and PbO_2 oxides.

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