

1.12: LEWIS ACIDS AND BASES

Learning Objective

- Use the definition of Lewis Acids and Bases to recognize electron movement in reactions

Acids and bases are an important part of chemistry. One of the most applicable theories is the Lewis acid/base motif that extends the definition of an acid and base beyond H^+ and OH^- ions as described by Brønsted-Lowry acids and bases.

INTRODUCTION

The Brønsted acid-base theory has been used throughout the history of acid and base chemistry. However, this theory is very restrictive and focuses primarily on acids and bases acting as proton donors and acceptors. Sometimes conditions arise where the theory doesn't necessarily fit, such as in solids and gases. In 1923, G.N. Lewis from UC Berkeley proposed an alternate theory to describe acids and bases. His theory gave a generalized explanation of acids and bases based on structure and bonding. Through the use of the Lewis definition of acids and bases, chemists are now able to predict a wider variety of acid-base reactions. Lewis' theory used electrons instead of proton transfer and specifically stated that an acid is a species that accepts an electron pair while a base donates an electron pair.

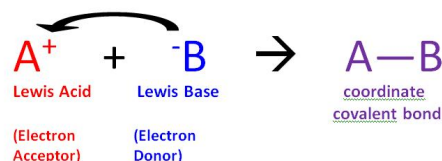


Figure 1.12.1: Above: A Lewis Base (B) donates its electrons to a Lewis Acid (A) resulting in a coordinate covalently bonded compound, also known as an adduct.

The reaction of a Lewis acid and a Lewis base will produce a coordinate covalent bond, as shown in Figure 1.12.1 above. A coordinate covalent bond is just a type of covalent bond in which one reactant gives its electron pair to another reactant. In this case the Lewis base donates its electrons to the Lewis acid. When they do react this way the resulting product is called an addition compound, or more commonly an adduct.

- Lewis Acid:** a species that accepts an electron pair (i.e., an electrophile) and will have vacant orbitals
- Lewis Base:** a species that donates an electron pair (i.e., a nucleophile) and will have lone-pair electrons

LEWIS ACIDS

Lewis acids accept an electron pair. Lewis Acids are Electrophilic meaning that they are electron attracting. When bonding with a base the acid uses its lowest unoccupied molecular orbital or LUMO (Figure 2).

- Various species can act as Lewis acids. All cations are Lewis acids since they are able to accept electrons. (e.g., Cu^{2+} , Fe^{2+} , Fe^{3+})
- An atom, ion, or molecule with an incomplete octet of electrons can act as a Lewis acid (e.g., BF_3 , AlF_3).
- Molecules where the central atom can have more than 8 valence shell electrons can be electron acceptors, and thus are classified as Lewis acids (e.g., $SiBr_4$, SiF_4).
- Molecules that have multiple bonds between two atoms of different electronegativities (e.g., CO_2 , SO_2)

LEWIS BASES

Lewis Bases donate an electron pair. Lewis Bases are Nucleophilic meaning that they "attack" a positive charge with their lone pair. They utilize the highest occupied molecular orbital or HOMO (Figure 2). An atom, ion, or molecule with a lone-pair of electrons can thus be a Lewis base. Each of the following anions can "give up" their electrons to an acid, e.g., OH^- , CN^- , CH_3COO^- , $:NH_3$, H_2O , $:CO$. Lewis base's HOMO (highest occupied molecular orbital) interacts with the Lewis acid's LUMO (lowest unoccupied molecular orbital) to create bonded molecular orbitals. Both Lewis Acids and Bases contain HOMO and LUMOs but only the HOMO is considered for Bases and only the LUMO is considered for Acids (Figure 1.12.2).

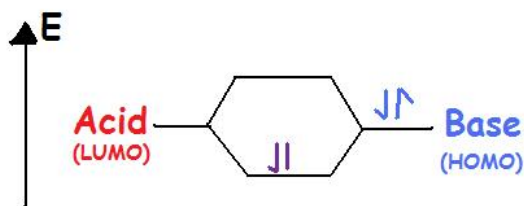


Figure 1.12.2: Lewis Acids have vacant orbitals so they are in a lower energy level. While Lewis bases have lone pair electrons to share and thus occupy a higher energy level.

COMPLEX ION / COORDINATION COMPOUNDS

Complex ions are polyatomic ions, which are formed from a central metal ion that has other smaller ions joined around it. While Brønsted theory can't explain this reaction Lewis acid-base theory can help. A Lewis Base is often the ligand of a coordination compound with the metal acting as the Lewis Acid (see Oxidation States of Transition Metals).



The aluminum ion is the metal and is a cation with an unfilled valence shell, and it is a Lewis Acid. Water has lone-pair electrons and is an anion, thus it is a Lewis Base.

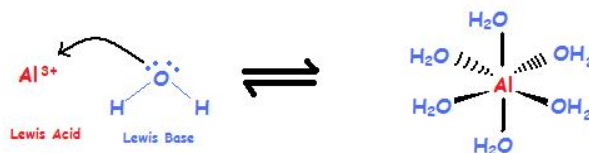
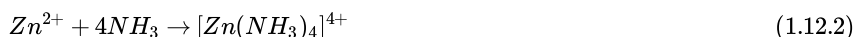


Figure 1.12.3: Aluminum ion acts as a Lewis acid and accepts the electrons from water, which is acting as a Lewis base. This helps explain the resulting hexaaquaaluminum(III) ion.

The Lewis Acid accepts the electrons from the Lewis Base which donates the electrons. Another case where Lewis acid-base theory can explain the resulting compound is the reaction of ammonia with Zn^{2+} .



Similarly, the Lewis Acid is the zinc Ion and the Lewis Base is NH_3 . Note how Brønsted Theory of Acids and Bases will not be able to explain how this reaction occurs because there are no H^+ or OH^- ions involved. Thus, Lewis Acid and Base Theory allows us to explain the formation of other species and complex ions which do not ordinarily contain hydronium or hydroxide ions. One is able to expand the definition of an acid and a base via the Lewis Acid and Base Theory. The lack of H^+ or OH^- ions in many complex ions can make it harder to identify which species is an acid and which is a base. Therefore, by defining a species that donates an electron pair and a species that accepts an electron pair, the definition of an acid and base is expanded.

AMPHOTERISM

As of now you should know that acids and bases are distinguished as two separate things however some substances can be both an acid and a base. You may have noticed this with water, which can act as both an acid or a base. This ability of water to do this makes it an amphoteric molecule. Water can act as an acid by donating its proton to the base and thus becoming its conjugate acid, OH^- . However, water can also act as a base by accepting a proton from an acid to become its conjugate base, H_3O^+ .

- Water acting as an Acid:



- Water acting as a Base:



You may have noticed that the degree to which a molecule acts depends on the medium in which the molecule has been placed in. Water does not act as an acid in an acid medium and does not act as a base in a basic medium. Thus, the medium which a molecule is placed in has an effect on the properties of that molecule. Other molecules can also act as either an acid or a base. For example,



- where $Al(OH)_3$ is acting as a Lewis Base.



- where $Al(OH)_3$ is acting as an Lewis Acid.

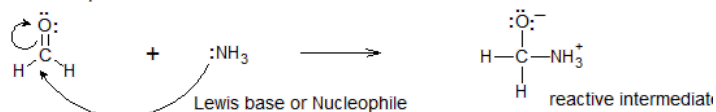
Note how the amphoteric properties of the $Al(OH)_3$ depends on what type of environment that molecule has been placed in.

LEWIS BASES & ACIDS AS NUCLEOPHILES & ELECTROPHILES

The emphasis on electron flow in the Lewis Theory of acids and bases is an important foundation for learning and predicting reaction mechanisms. The electron rich Lewis base can be described as a nucleophile. Nucleophiles are attracted to and can react with compounds or ions that have full or partial positive charge (like the nucleus). The electron poor Lewis acids can be described as electrophiles. Electrophiles attract nucleophiles until orbital overlap occurs between them triggering a reaction. At this point in the course, we can indicate electron flow using curved arrows when both the reactant(s) and product(s) are given.

Example

Lewis acid or Electrophile

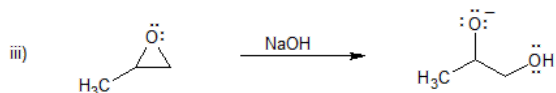
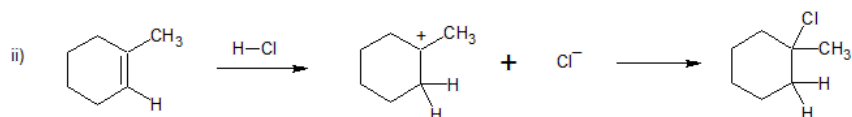
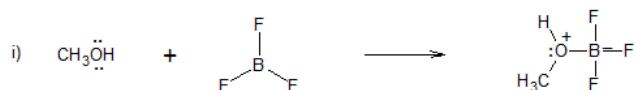


EXERCISES

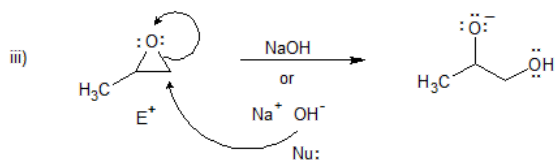
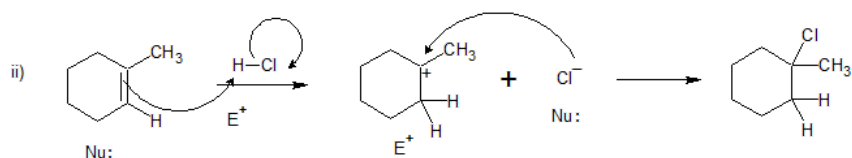
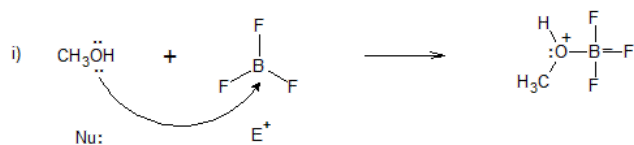
For the following reactions,

a) add curved arrows to indicate the electron flow

b) label each reactant as the Nu (nucleophile) or E⁺ (electrophile).



SOLUTIONS



OUTSIDE LINKS

- Very Detailed review of Lewis Acids and Bases, covering all topics of this type of chemistry
- Very Complex and Detailed "Lewis Acid and Base Interaction Matrix"
- Youtube Video about Lewis Acids/Bases

REFERENCES

1. Cycloaddition on Ge(100) of the Lewis Acid AlCl_3 . Soon Jung Jung,, Young-Sang Youn,, Hangil Lee,,, Ki-Jeong Kim,,, Bong Soo Kim, and, Sehun Kim,. *Journal of the American Chemical Society* 2008 130 (11), 3288-3289
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3. Harwood, William S., F. G. Herring, Jeffry D. Madura, and Ralph H. Petrucci. General Chemistry Principles and Modern Applications. 9th ed. New Jersey: Prentice Hall, 2007. 695-96.

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