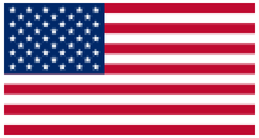
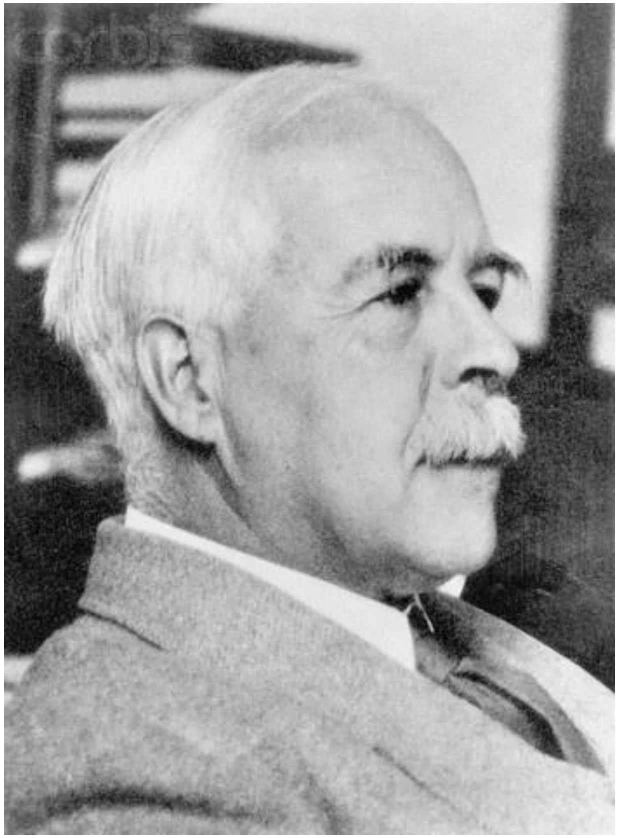
Acids and Bases—Chapter 4
Shriver et al.

MIT 3091 Video Lecture: Acids and Bases on You Tube

http://ocw.mit.edu/courses/materials-science-and-engineering/3-091sc-introduction-to-solid-state-chemistry-fall-2010/aqueous-solutions/26-acids-and-bases/

Acid-Base concepts





Gilbert Newton Lewis

1875 – 1946

Lewis Concept

Lewis, 1930s:

Base is a donor of an electron pair.

Acid is an acceptor of an electron pair.

For a species to function as a Lewis acid, it needs to have an accessible empty orbital.

For a species to function as a Lewis base it needs to have an accessible electron pair.

Examples of Lewis acids: **BF_3, $AlCl_3$, SbF_5, Na^+, H^+, S^{6+}**, etc.

Examples of Lewis bases: **F^-, H_2O, Me_3N, C_2H_4, Xe**, etc.

Lewis Concept—Connection to MO Theory

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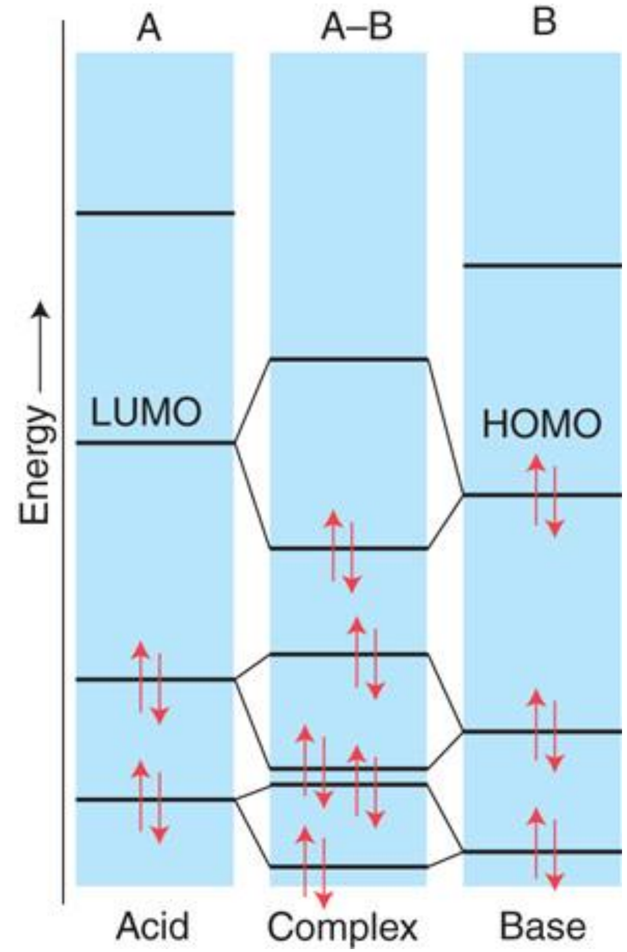

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Lewis Continued

A more general view also classifies compounds that can generate a species with an empty orbital as Lewis acids. Then we can include $\mathbf{B_2H_6}$, $\mathbf{Al_2Cl_6}$, **HCl** etc.

Since H^+ and any cation from a solvent autodissociation is a Lewis acid, and anything that can add H^+ or a solvent-derived cation is a Lewis base, the Lewis acid concept effectively includes the ones discussed previously.

Lewis Continued

Acid-base reactions under the Lewis model is the reactions of forming adducts between Lewis acids and bases.

$$BF_3 + Me_3N \rightarrow F_3B\text{-}NMe_3$$

$$HF + F^- \rightarrow FHF^-$$

$$SiF_4 + 2F^- \rightarrow SiF_6^{2-}$$

$$CO_2 + OH^- \rightarrow HCO_3^-$$

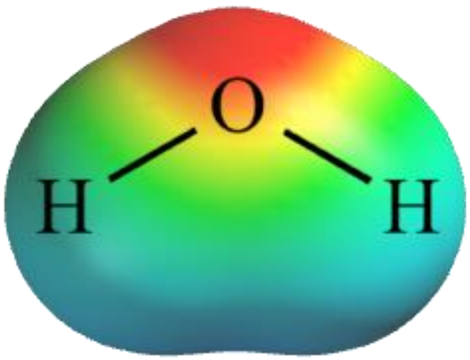
$$TiCl_4 + 2Et_2O \rightarrow TiCl_4(OEt_2)_2$$

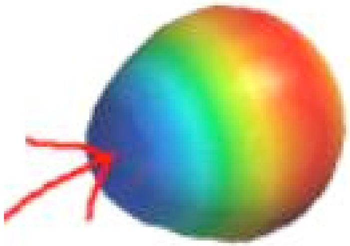
In fact, any chemical compound can be mentally disassembled into Lewis acids and bases:

$$S^{6+} + 6F^- \rightarrow SF_6$$

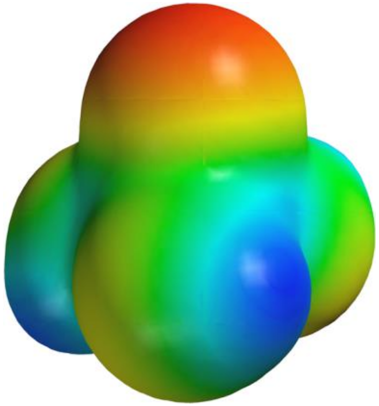
$$C^{4+} + 3H^- + NH_2^- \rightarrow CH_3^+ + NH_2^-$$

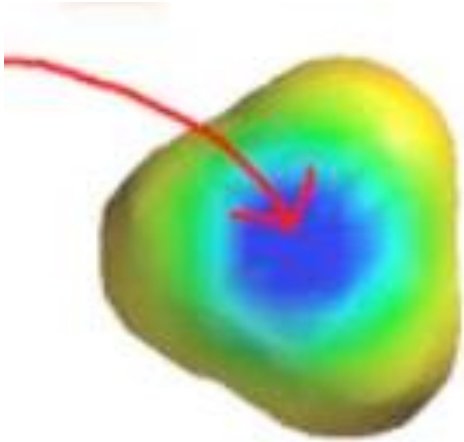
Tying this into MO Theory: Electrostatic Potential Plots: Red is negative; blue is positive



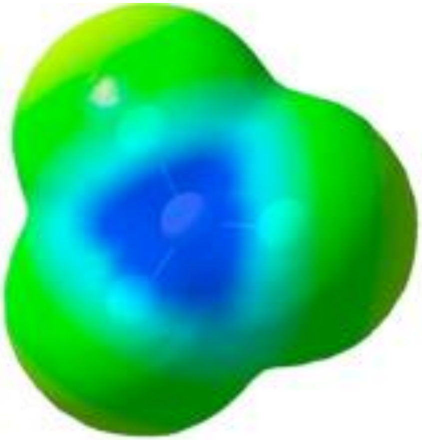


HBr

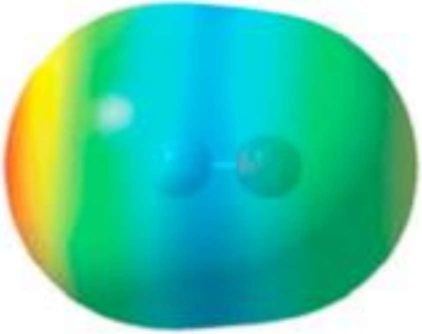




BH_3

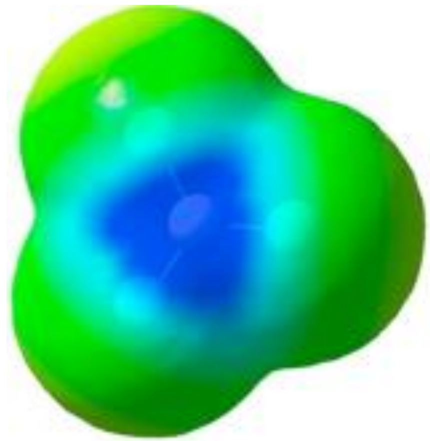


BF_3

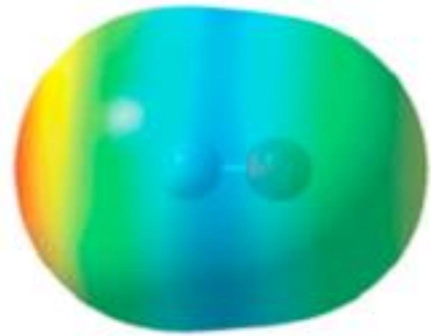


CO

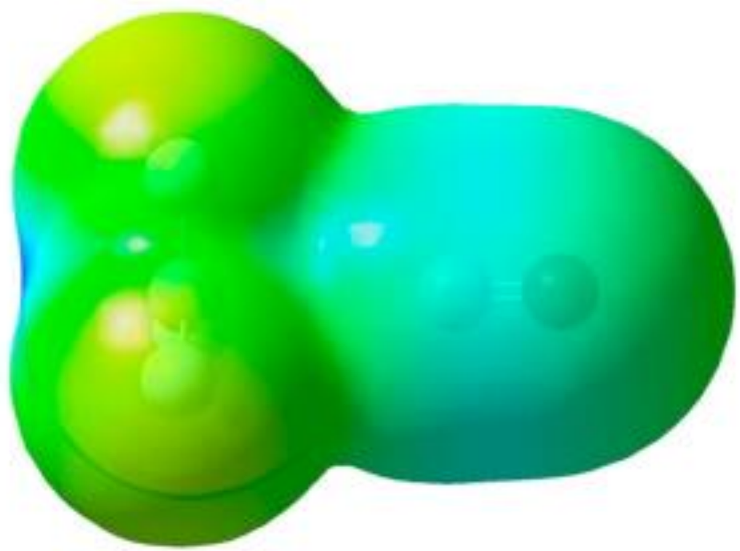
Formation of Lewis Acid-Base adduct



BF_3



CO



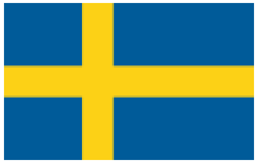
BF_3-CO

Another Look: Acid-Base concepts

pKa = -log$_{10}$ [H$^+$] $K_a = [H^+][OH^-]/[H_2O]$

Table 8.3 From Jolly, “Modern Inorganic Chemistry” Aqueous pK_a values of the binary “hydrides” of the nonmetals

CH_4 ~ 44	NH_3 39	H_2O 15.74	HF 3.15
SiH_4 ~ 35	PH_3 27 PH_3 27	H_2S 6.89	HCl -6.3
GeH_4 25	AsH_3 ≤ 23	H_2Se 3.7	HBr -8.7
		H_2Te 2.6	HI -9.3



Svante August Arrhenius

1859 – 1927

Arrhenius concept

Arrhenius, 1880s:

Acids form hydrogen ions $H^+(H_2O)_n$ in aqueous solution.

Bases form hydroxide ions in aqueous solution.

Examples of Arrhenius acids (in water): HCl, H_2SO_4, etc.

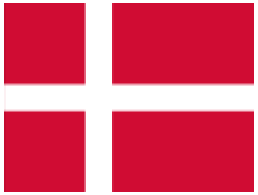
Examples of Arrhenius bases (in water): NaOH, NH_3, etc.

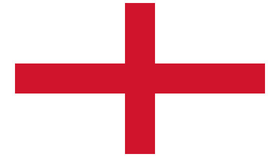
Arrhenius definitions only apply to aqueous solutions.

A general Arrhenius acid-base reaction is the reaction between H^+ and OH^- to produce water.

Acid + Base → Salt + Water

$$H^+ + NO_3^- + K^+ + OH^- \rightarrow K^+ + NO_3^- + H_2O$$



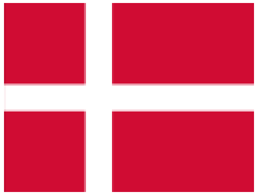


Johannes Nicolaus Brønsted

1879 – 1947

Thomas Martin Lowry

1874 – 1936



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Brønsted-Lowry concept

Brønsted and Lowry, 1923:

Acid – a species with a capability to lose H^+.

Base – a species with a capability to gain H^+.

[As often as not Lowry's name is omitted and only Brønsted's name is used.]

Brønsted's acids and bases are by and large the same acids and bases as in the Arrhenius model but the model of Brønsted and Lowry is not restricted to aqueous solutions.

Brønsted's model introduces the notion of conjugate acid-base pairs. It is logical that if something (an acid) exists and may lose a proton, then the product of such a proton loss is by definition a base since it has the capability to add a proton.

Conjugate acids and bases

Acid	Base
H_3O^+	H_2O
H_2O	OH^-
OH^-	O^{2-}
CH_3^+	CH_2
CH_4	CH_3^-
$H_2NCH_2CO_2H$	$H_2NCH_2CO_2^-$
$[H_3NCH_2CO_2H]^+$	$H_2NCH_2CO_2H$
H_2	H^-

Brønsted continued

- Likewise, any compound with a pair of electrons may behave as a Brønsted base.
- It is possible for the same compound to be able to behave as a Brønsted base *and* as a Brønsted acid.
- Usually a compound is called acid or base depending on the circumstances.
- Theoretically, any compound that has a hydrogen atom in it may behave as a Brønsted acid.

Brønsted continued

Under the Brønsted-Lowry model, an acid-base reaction is always a reaction between an acid and a base giving their conjugate base and acid, respectively.

$$\mathbf{EtOH + Me_2N^- \, Li^+ \rightarrow EtO^- \, Li^+ + Me_2NH}$$

$$\mathbf{Acid1 + Base2 \quad \rightarrow Base1 \quad + Acid2}$$

$$\mathbf{EtOH + H_2SO_4 \rightarrow EtOH_2^+ + HSO_4^-}$$

$$\mathbf{Base1 + Acid2 \rightarrow Acid1 \quad + Base2}$$

Generally, the reactions proceed to form weaker acids and bases.

Solvent system concept

The solvent system concept is applicable to solvents that undergo autodissociation:

Acids are compounds that increase the concentration of the cation.

Bases are compounds that increase the concentration of the anion.

The Arrhenius model can be viewed as a part of the solvent system model.

Solvent system concept

The Arrhenius model can be viewed as a part of the solvent system model.

For instance, BrF_3 undergoes autodissociation:

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

In BrF_3, KF will be classified as a base, and SbF_5 – as an acid.

$$KF + BrF_3 \rightleftharpoons K^+ + BrF_4^-$$

$$SbF_5 + BrF_3 \rightleftharpoons BrF_2^+ + SbF_6^-$$

An acid-base reaction in water is the reaction between H^+ and OH^-; an acid-base reaction in BrF_3 is the reaction between BrF_2^+ and BrF_4^-.