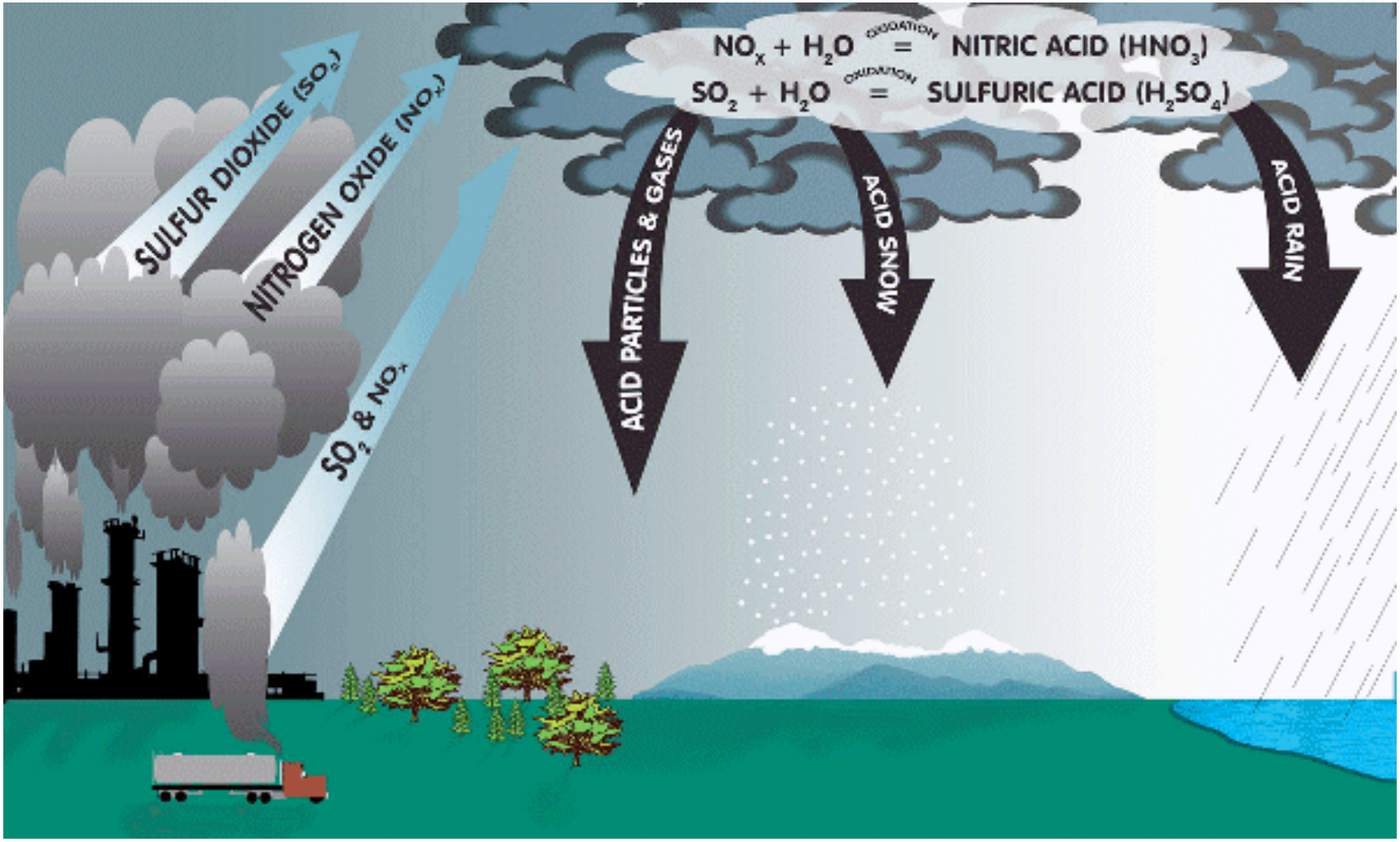
Acid Rain: Non-metal oxides



Element oxides

Various element oxides can combine with water to produce acids or bases

Basic oxides – upon reaction with water form materials that are stronger Brønsted bases than water (decrease $[H^+]$).

Acidic oxides – upon reaction with water form materials that are stronger Brønsted acids than water (increase $[H^+]$)

Amphoteric oxides – upon reaction with water form materials that can react with both bases and acids

Examples: Li_2O, CaO, and BaO react with water to form basic solutions and can react with acids directly to form salts.

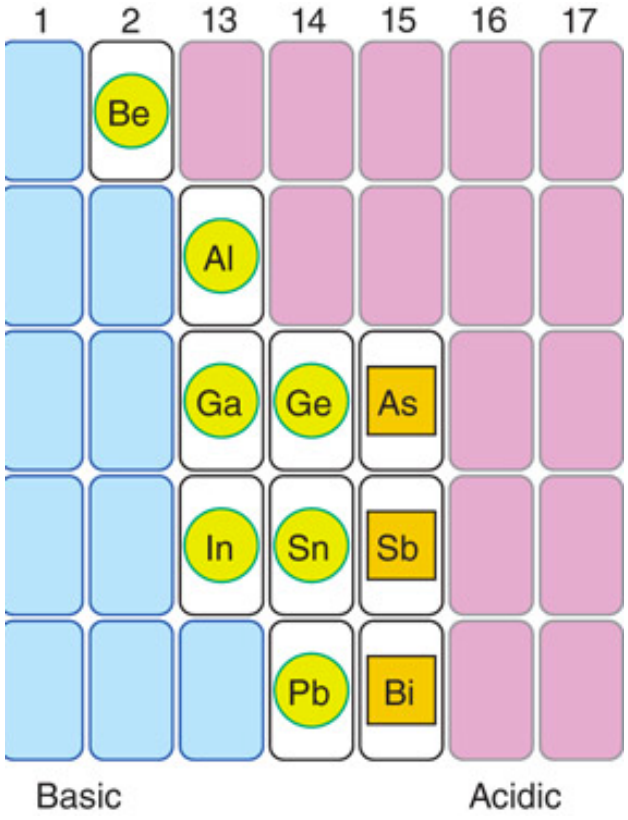
Likewise, SO_3, SO_2, CO_2, N_2O_5, P_2O_3 and P_2O_5 form acidic aqueous solutions and can react directly with bases to give salts.

Element oxides:
Which react with water to give $E^+(OH)^-$ and which give EO^-H^+

Basic oxides – typically metal oxides (oxides of the more **electropositive** elements: Na_2O, MgO, CaO, etc.)

Acidic oxides – typically non-metal oxides (oxides of the more **electro-negative** elements)

Amphoteric oxides – typically oxides of the elements of intermediate electronegativity



**For the same element, the higher the oxidation state, the more acidic the oxide is.

Amphoteric is not to be confused with *amphiprotic* – a substance that can act as both a Brønsted acid and base

Oxides as Acid and Basic Anhydrides

Basic Oxides (usually "ionic")

$CaO + 2\ H_2O \longrightarrow Ca^{2+} + 2\ OH^-$, a moderately strong base

$[O^{2-}] + H_2O \longrightarrow 2OH^-$ $\quad K > 10^{22}$

Alkali metal and alkaline earth oxides are basic (dissolve in acid).
Or, they react directly with acidic oxides:

$CaO + SO_3 \longrightarrow Ca^{2+}\ SO_4^{2-}$

$CaO + CO_2 \longrightarrow Ca^{2+}\ CO_3^{2-}$

Examples of Acidic Oxides, or Acid Anhydrides, reactions with water give "oxy-acids"

$SO_3 + H_2O \longrightarrow H_2SO_4$

$CO_2 + H_2O \longrightarrow H_2CO_3$

$SO_2 + H_2O \longrightarrow H_2SO_3$

$\xrightarrow{H_2O}$ Ionization into protons and anions

Note: The non-metal element-oxygen (E–O) bond is not broken on dissolution.

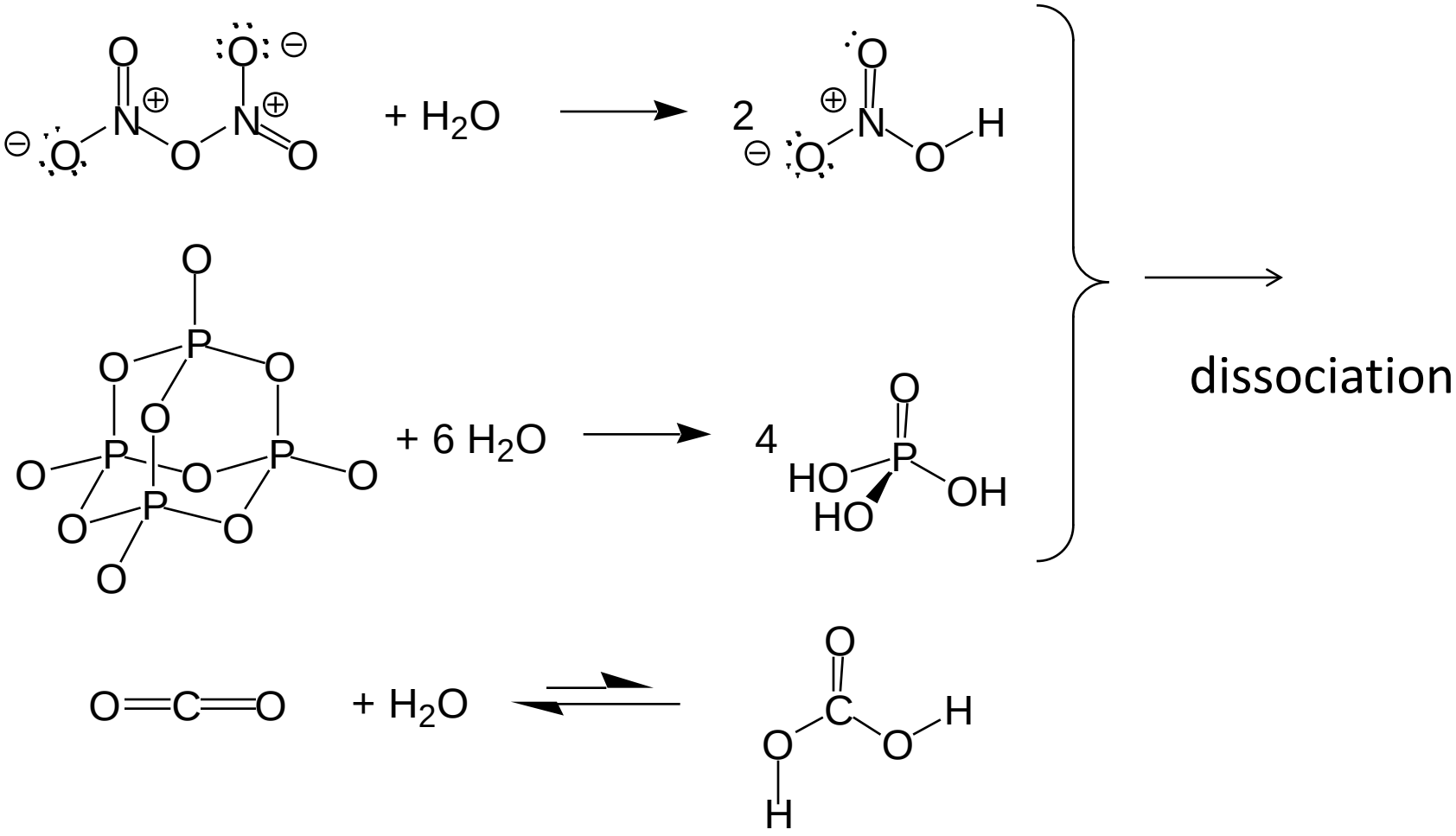
either

an E – O – E group is hydrolyzed by water (as in P_4O_{10});

or

water is added across the E=O double bond (as in CO_2).

Examples of Acidic Oxides, or Acid Anhydrides, reactions with water give "oxy-acids"



Acidic Oxides (Non-metal Oxides or Acid Anhydrides)

element-oxygen (E–O) bond is not broken on dissolution

either

an E – O – E group is hydrolyzed by water

or

water is added across a double bond

Acidic Oxides not soluble in water will dissolve in basic aqueous solutions to produce salts

eg. $As_2O_3 + 2NaOH(aq) \longrightarrow 2NaH_2As\ O_3$

(Often seen for anhydrides of weaker acids.)

Amphoteric Oxides

Dissolve in acids or bases - if strong enough.

Eg., BeO, SnO, certain forms of Al_2O_3

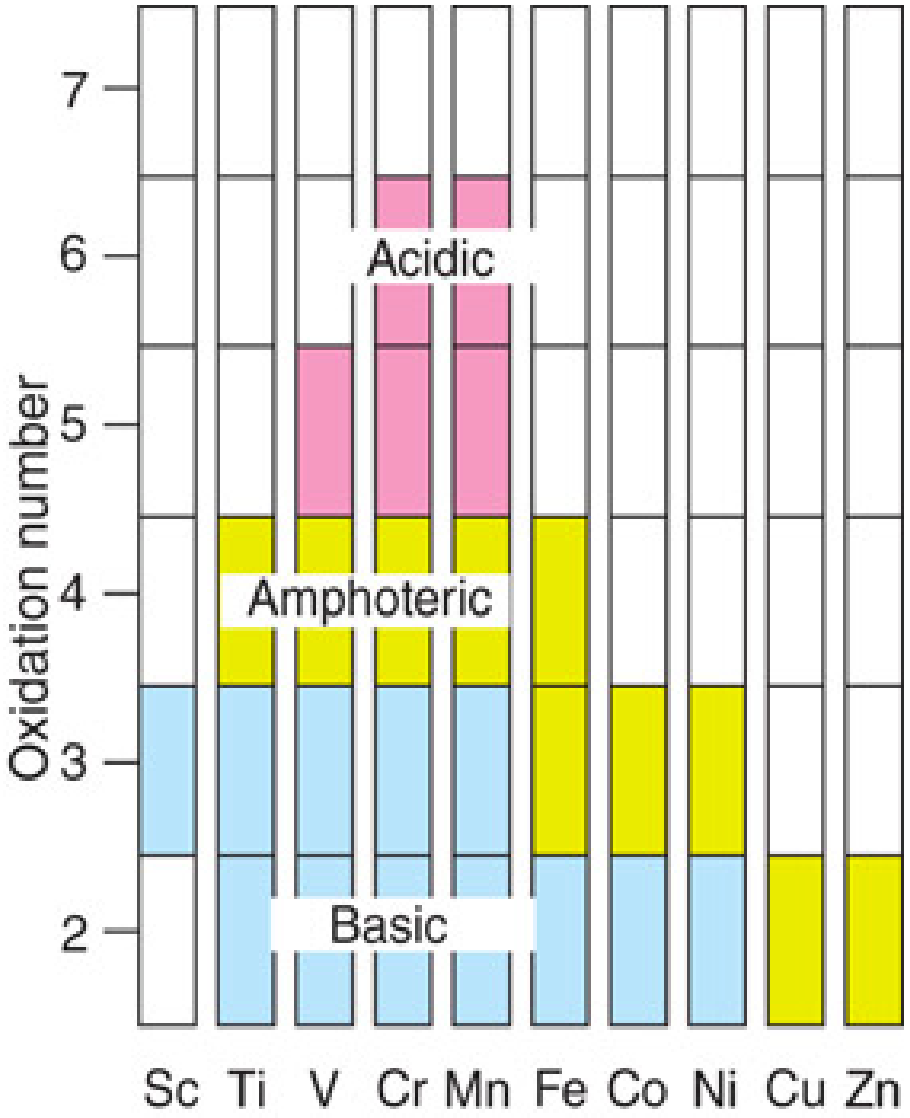
In strong acids:

$ZnO + 4\ HCl(aq) \longrightarrow H_3O^+ \quad [ZnCl_4]^{2-}$

$ZnO + \quad 2HNO_3(aq) \longrightarrow Zn(OH_2)_6^{2+} + NO_3^-$

In strong base: $ZnO + 2NaOH(aq) \longrightarrow 2Na^+(aq) + [Zn(OH_4)]^{2-}(aq)$

Transition Metal Oxides Acidity or Basicity Depends on Oxidation Number (State)

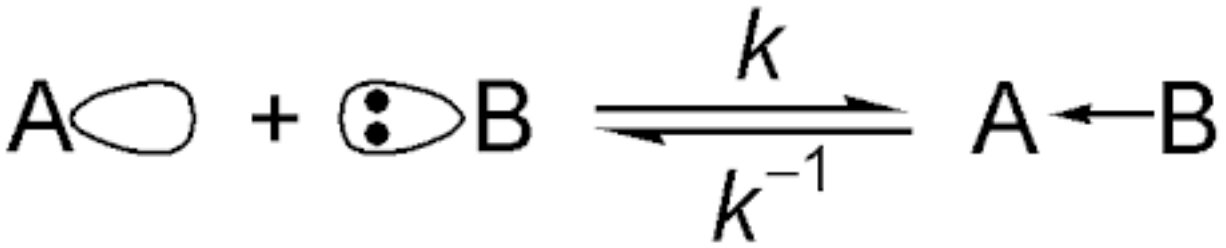


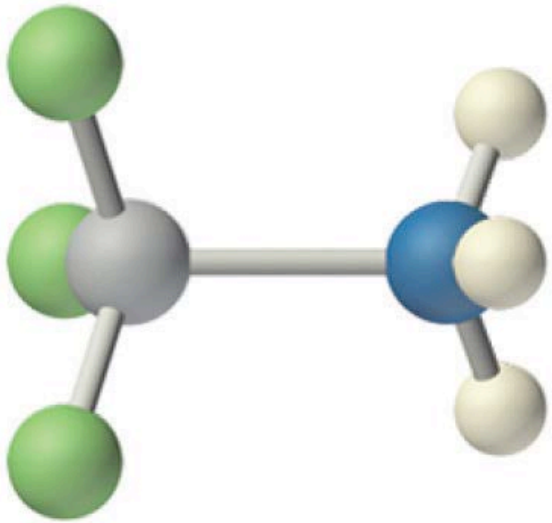
MnO is basic;
MnO_2 is amphoteric
MnO_3 is acidic

Figure 4.6 Shriver, et al.

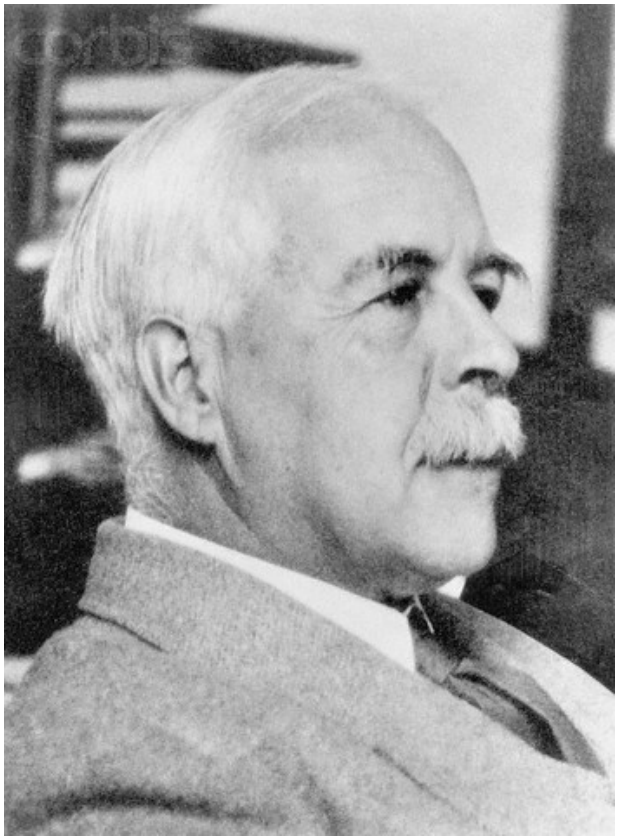
What determines aqueous acid “strength”?

Lewis approach to acid/base interactions



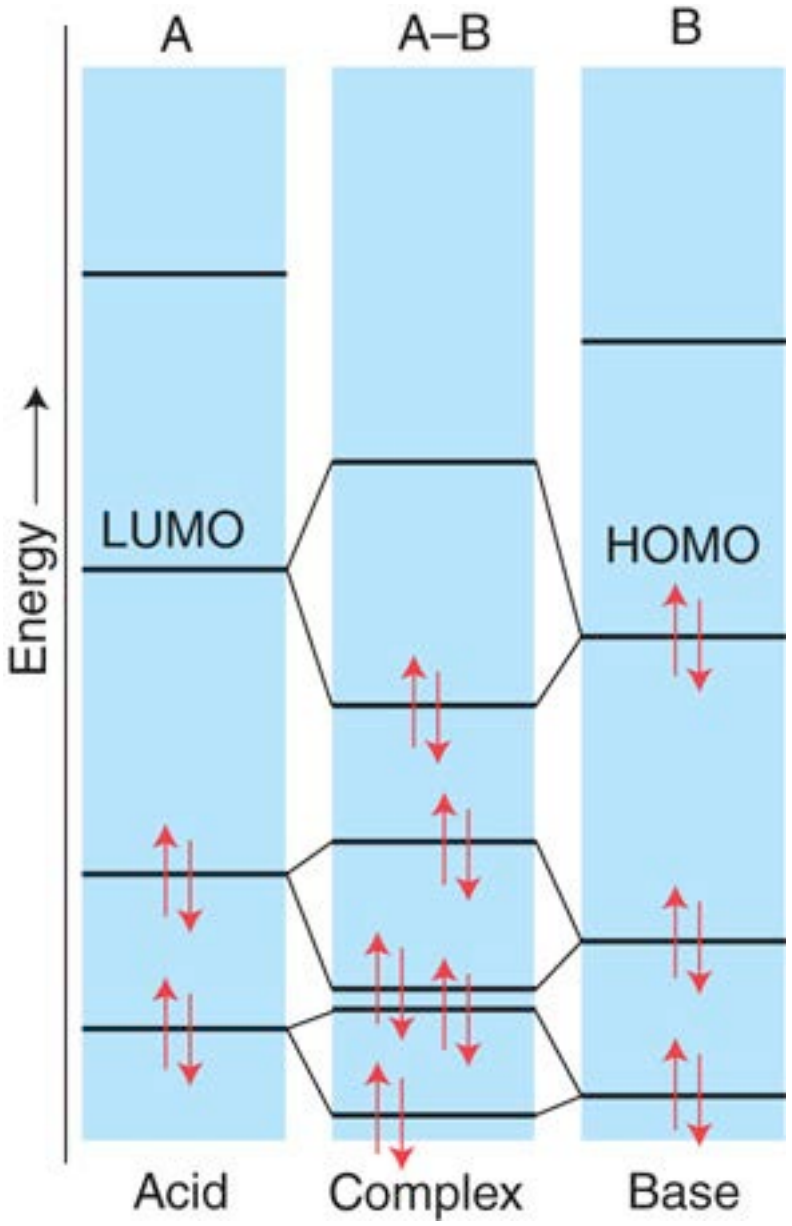


Boron trifluoride-ammonia adduct



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 Continued

A more general view also classifies compounds that can generate a species with an empty orbital as Lewis acids. Then we can include **B_2H_6, 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 are 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:

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

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