Chemistry 1000 Lecture 20: Lewis acids and bases

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Historical ideas about acids and bases

Arrhenius theory: based on the behavior of acids and bases in water

Arrhenius acid: dissociates in water, producing H^+

Examples: HCl, CH_3COOH

Arrhenius base: dissociates in water, producing OH^-

Examples: $NaOH$, $Ba(OH)_2$

Brønsted theory: puts the emphasis on proton transfer

Brønsted acid: proton donor

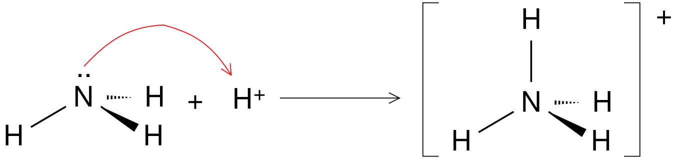
Examples: HCl, CH_3COOH, H_2O

Brønsted base: proton acceptor

Examples: OH^-, NH_3, H_2O

Ammonia as a base

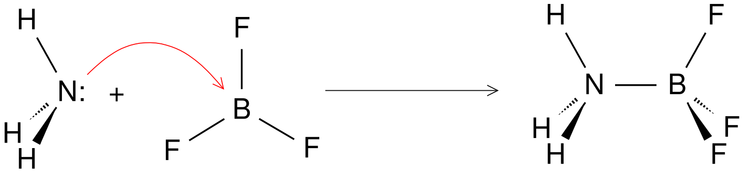
Ammonia is a Brønsted base:



Thinking of ammonia as a Brønsted base, we would say that it is accepting a proton.

An alternative viewpoint is that ammonia is donating an electron pair to H^+.

Now consider



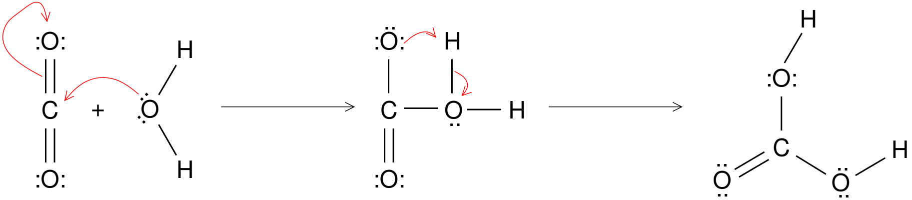
This reaction and the reaction of NH_3 with H^+ are clearly of the same kind, even though one is a Brønsted acid-base reaction, and the other isn't.

Lewis acids and bases

Lewis acid: electron pair acceptor

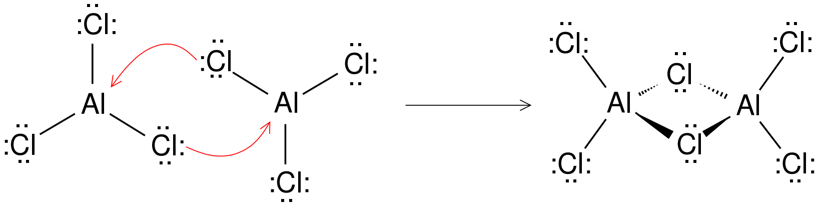
Lewis base: electron pair donor

CO_2 as a Lewis acid



Note that this Lewis acid-base reaction makes CO_2 into the Brønsted acid H_2CO_3.

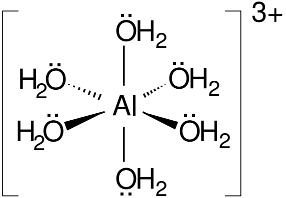
In the gas phase, many group 13 metal halides exist as Lewis dimers:



Metal ions as Lewis acids

Metal ions often act as Lewis acids.

Example: hydrated Al^{3+} ion



$[Al(H_2O)_6]^{3+}$ is a Brønsted acid:

$$[Al(H_2O)_6]^{3+}_{(aq)} + H_2O_{(l)} \rightarrow [Al(H_2O)_5(OH)]^{2+}_{(aq)} + H_3O^+_{(aq)}$$

$$pK_a = 4.85$$

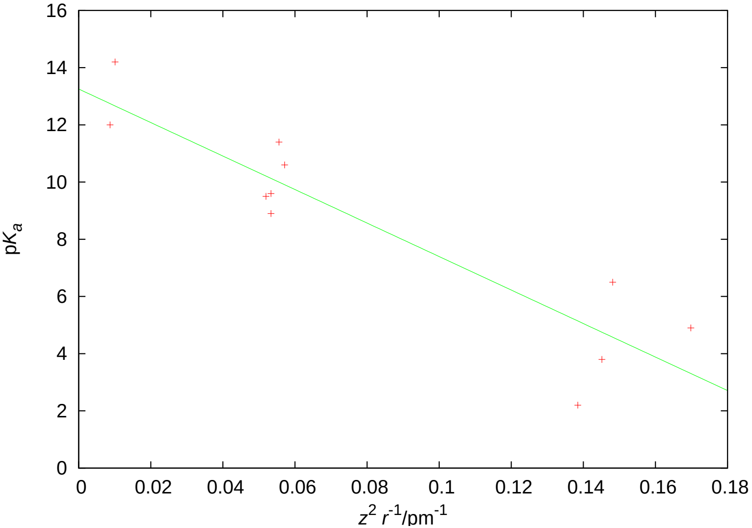
Factors that affect the acidity of aqua ions

- Acidity of aqua ions is due to the weakening of bonds between O and H when a new bond is formed between O and a metal ion.
- What makes metal-water bonds strong?

  Ion charge (z): Lewis acidity is based on attraction of (in this case) an ion for one lone pair on the oxygen atom.
  - All other things being equal, we might think that the force of attraction increases with z.
  - However, the polarization of the O-H bond also increases with z, so the force between the ion and water molecule increases as z^2.

  Ion radius (r): A smaller radius increases the electrostatic potential energy of the bond.

  Overall: The acidity should increase with z^2/r.


16
14
12
10
8
6
4
2
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
pK_a
$z^2\, r^{-1}$/pm^{-1}

Consequence: Ions with small z and/or relatively large r have aqua ions with little or no acidity in water (e.g. alkali metal ions).

Additional consideration: All other things being equal, more electronegative metals tend to give more acidic complexes. Why?

Acidity and solubility

- We can sometimes think of the dissolution of ionic compounds in terms of acid-base concepts, at least for simple ionic compounds.
- Take, e.g. oxides, i.e. compounds of O^{2-} with metal ions.
  We can think of these compounds as products of the reaction of a Lewis acidic metal ion with the Lewis basic oxide ion.
- The oxide ion is a strong Lewis base.
- If the metal ion is a strong Lewis acid, then the product is hard to break up and will not dissolve.
- Examples:

  Na^{+} is a very weak Lewis acid so its compounds (including oxides) are very soluble.

  Ti^{4+} is a very strong Lewis acid, so its oxide (in particular) is insoluble in water.

Acidity and solubility (continued)

- Solubility can often be modulated by varying the pH.
- Al^{3+} is an interesting case:
  - Near neutral pH, Al_2O_3 is insoluble because Al^{3+} is a very strong Lewis acid.
  - At low pH, the oxide ion is removed by H^+, and Al^{3+} is obtained in solution (as the solvated ion).
  - At high pH, the oxide is converted to $[Al(OH)_4]^-$, which makes it soluble.

Summary of Lewis acids and bases

- Categories of Lewis acids:

  Metal cations and H^+

  Metal-deficient species such as BX_3 and BeX_2

  Molecules containing double or triple bonds between atoms with very different electronegativities such as CO_2 and SO_3

- Lewis bases have lone pairs, as in NH_3.