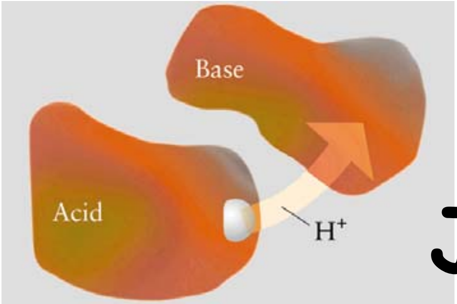
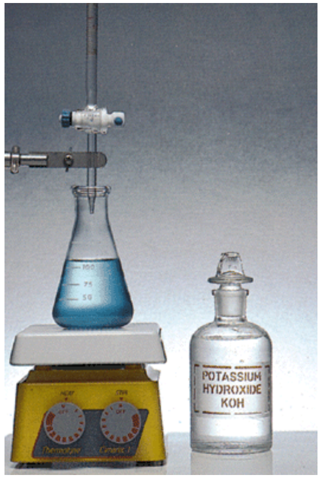


COLÁISTE NA TRÍONÓIDE, BAILE ÁTHA CLIATH | TRINITY COLLEGE DUBLIN
Ollscoil Átha Cliath | The University of Dublin

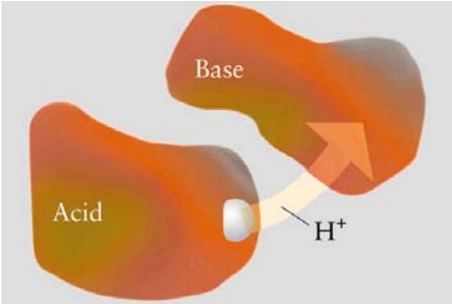
JF Chemistry 1101 2013-2014
Introduction to Physical Chemistry:
Acid Base and Solution Equilibria.

Professor Mike Lyons
School of Chemistry
melyons@tcd.ie



Required Reading Material.

- Silberberg, Chemistry, 4th edition.
  - Chapter 18.
    - Acid/base equilibria. pp.766-813.
  - Chapter 19.
    - Ionic equilibria in aqueous systems. pp.814-862.
- Kotz, Treichel and Weaver, 7th edition.
  - Chapter 17 (Chemistry of Acids and Bases) & Chapter18 (Principles of reactivity: other aspects of ionic equilibria), pp.760-859.
- Chemistry^3, Burrows et al.
  - Chapter 6, Acids & bases, pp.263-299.



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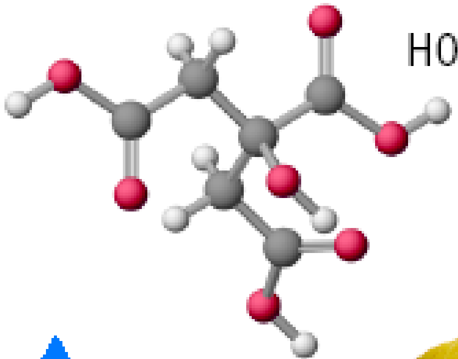
Review : Kotz Chapter 3 for simple acid/base definitions.

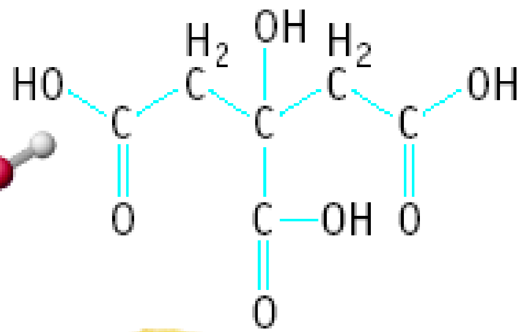
Lecture 10.

Acid/base chemistry : Simple ideas: Arrhenius, Bronsted-Lowry, Lewis.

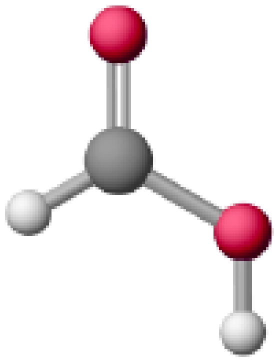
Kotz: section 3.7, pp.131-139.
Section 17.1, pp.761-762.

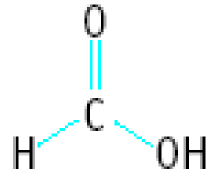
Acid and Bases





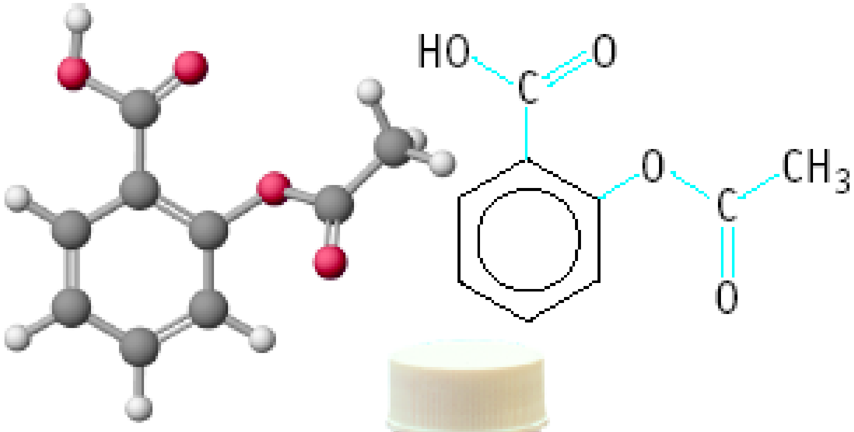
The tartness of lemons and oranges comes from the weak acid citric acid. The acid is found widely in nature and in many consumer products. *(Charles D. Winters)*



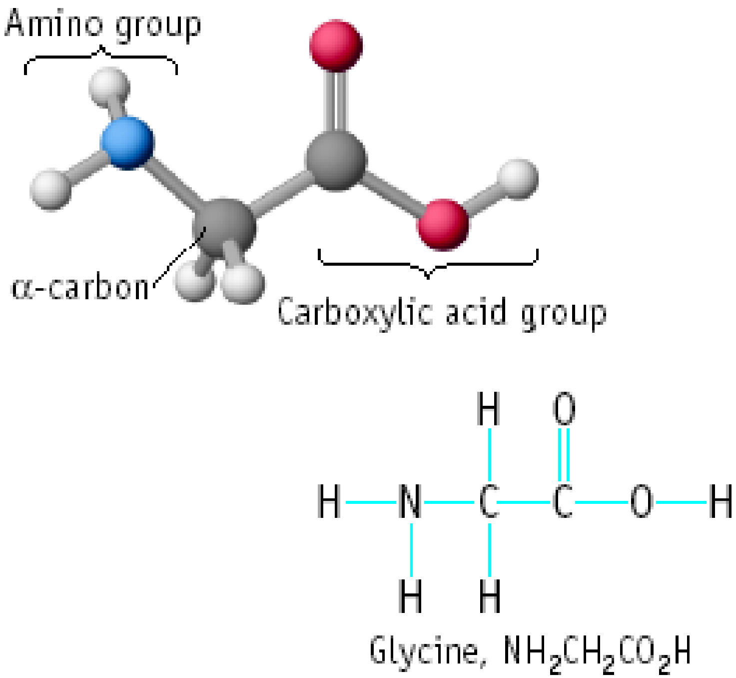


The sting of ants is due to the weak acid formic acid, HCO_2H. *(Gallo Images/@ CORBIS)*

Acid and Bases

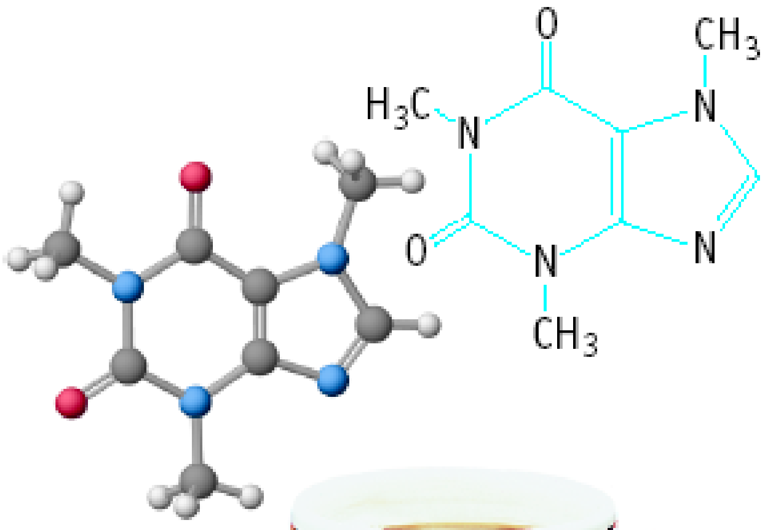


▲ Aspirin is a weak acid that has been used as an analgesic for over 100 years. *(Charles D. Winters)*

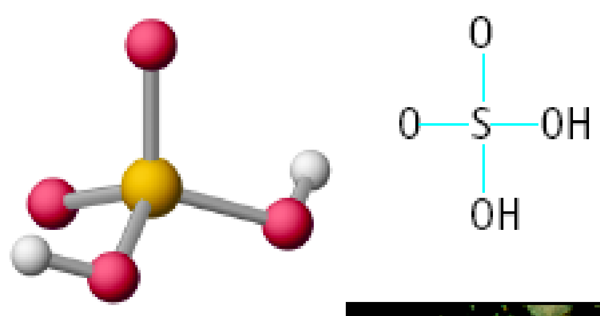


▲ Glycine is representative of the amino acids that are the basis of proteins. The $-CO_2H$ group is the acid portion of the molecule, and the $-NH_2$ group is the basic portion. *(Charles D. Winters)*

Acid and Bases



Caffeine is a well known stimulant and a weak base. *(Charles D. Winters)*



A sea slug excretes the strong acid sulfuric acid in self-defense. *(Sharksong/ M. Kazmers/Dembinski Photo Associates)*

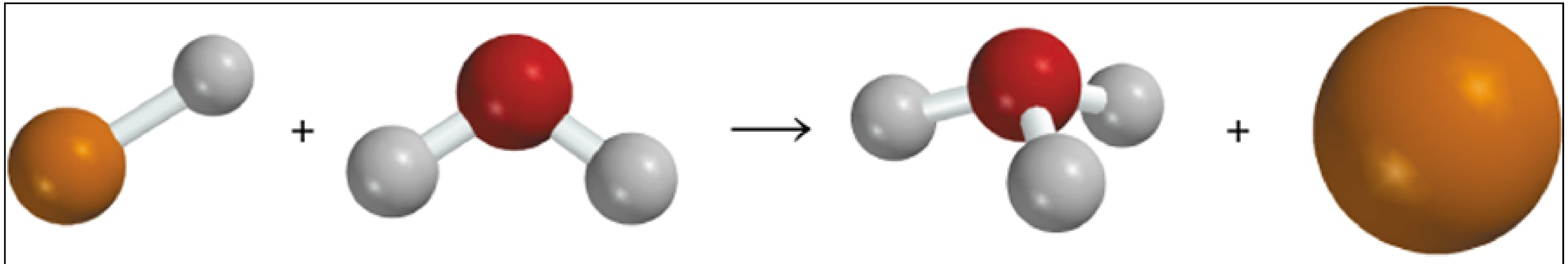
Arrhenius (or Classical) Acid-Base Definition

- An ***acid*** is a neutral substance that contains hydrogen and dissociates or ionizes in water to yield hydrated protons or hydronium ions H_3O^+.
- A ***base*** is a neutral substance that contains the hydroxyl group and dissociates in water to yield hydrated hydroxide ions OH^-.
- ***Neutralization*** is the reaction of an H^+ (H_3O^+) ion from the acid and the OH^- ion from the base to form water, H_2O.
- These definitions although correct are limited in that they are not very general and do not
- Give a comprehensive idea of what acidity and basicity entails.

$$HCl \rightarrow H^+(aq) + Cl^-(aq)$$
$$NaOH \rightarrow Na^+(aq) + OH^-(aq)$$

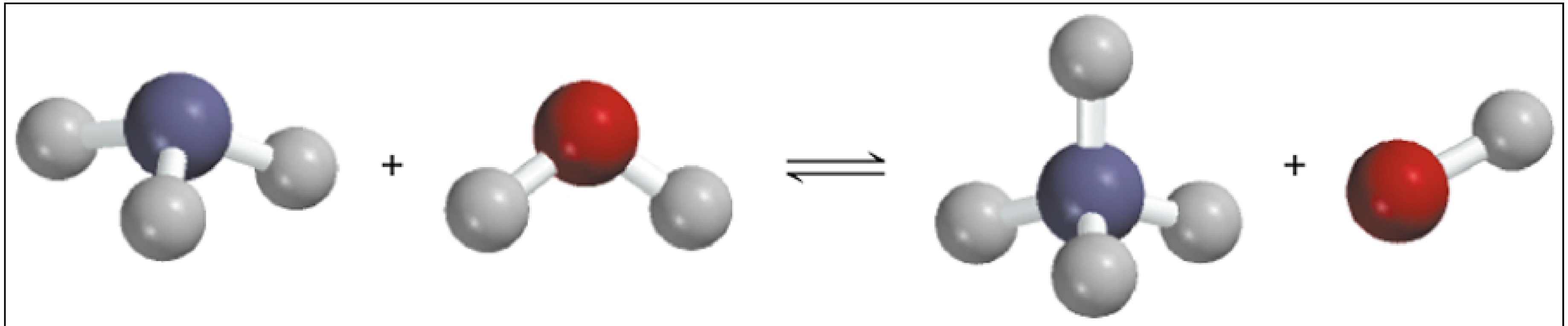
$$HCl + NaOH \rightarrow NaCl + H_2O$$

Arrhenius acid is a substance that produces H^+ (H_3O^+) in water.



$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

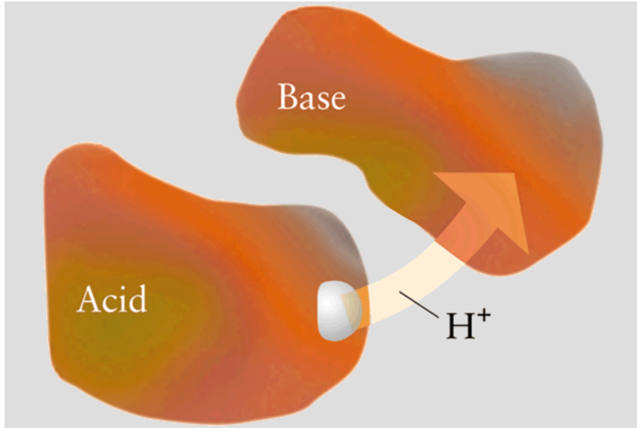
Arrhenius base is a substance that produces OH^- in water.



$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Acids and bases: Bronsted/Lowry definition.

- Bronsted/Lowry Acid (HA):
  - An acid is a species which donates a proton
- Bronsted/Lowry Base (B):
  - A base is a species which accepts a proton.
- These definitions are quite general and refer to the reaction between an acid and a base.
- An acid must contain H in its formula; HNO_3 and $H_2PO_4^-$ are two examples, all Arrhenius acids are Brønsted-Lowry acids.
- A base must contain a lone pair of electrons to bind the H^+ ion; a few examples are NH_3, CO_3^{2-}, F^-, as well as OH^-. Brønsted-Lowry bases are not Arrhenius bases, but all Arrhenius bases contain the Brønsted-Lowry base OH^-.



- In the Brønsted-Lowry perspective:

  one species donates a proton and another species accepts it: an acid-base reaction is a proton transfer process.

Chemistry[3] section 6.1. pp.264-267.

Kotz 7th ed. Section 17.1. pp.761-765

BL acid/base equilibria.

BL acid BL base

$$HA(aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq)$$

Proton transfer

BL base BL acid

$$B\ (aq) + H_2O\ (l) \rightleftharpoons HB^+\ (aq) + OH^-\ (aq)$$

Water can function both as an acid and a base depending on the circumstances.

- Proton donation and acceptance are dynamic processes for all acids and bases. Hence a proton transfer equilibrium is rapidly established in solution.
- The equilibrium reaction is described in terms of conjugate acid/base pairs.
- The conjugate base (CB) of a BL acid is the base which forms when the acid has donated a proton.
- The conjugate acid (CA) of a BL base is the acid which forms when the base has accepted a proton.
- A conjugate acid has one more proton than the base has, and a conjugate base one less proton than the acid has.
- If the acid of a conjugate acid/base pair is strong (good tendency to donate a proton) then the conjugate base will be weak (small tendency to accept a proton) and vice versa.

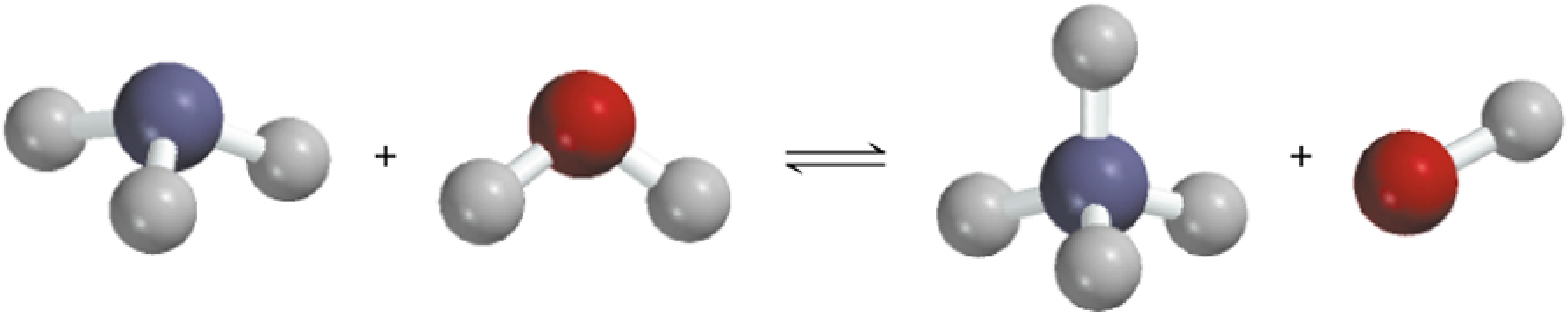
Acid : proton donor
Base : proton acceptor

Proton transfer

$$\underset{A}{HA\ (aq)} + \underset{B}{B\ (aq)} \rightleftharpoons \underset{CA}{BH^+\ (aq)} + \underset{CB}{A^-\ (aq)}$$

An acid is a proton donor, ***any species which donates a H^+.***

A base is a proton acceptor, ***any species which accepts a H^+.***



$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

NH_3	H_2O	NH_4^+	OH^-
base	acid	acid	base
base	acid	conjugate acid	conjugate base

An acid-base reaction can now be viewed from the standpoint of the reactants AND the products.

An acid reactant will produce a base product and the two will constitute an acid-base conjugate pair.

Table 18.4 The Conjugate Pairs in Some Acid-Base Reactions

Conjugate Pair

Conjugate Pair

	Acid		Base		Base		Acid
Reaction 1	HF	+	H_2O	$\rightleftharpoons$	F^-	+	H_3O^+
Reaction 2	$HCOOH$	+	CN^-	$\rightleftharpoons$	$HCOO^-$	+	HCN
Reaction 3	NH_4^+	+	CO_3^{2-}	$\rightleftharpoons$	NH_3	+	HCO_3^-
Reaction 4	$H_2PO_4^-$	+	OH^-	$\rightleftharpoons$	HPO_4^{2-}	+	H_2O
Reaction 5	H_2SO_4	+	$N_2H_5^+$	$\rightleftharpoons$	HSO_4^-	+	$N_2H_6^{2+}$
Reaction 6	HPO_4^{2-}	+	SO_3^{2-}	$\rightleftharpoons$	PO_4^{3-}	+	HSO_3^-

Table 15.2 Relative Strengths of Conjugate Acid-Base Pairs

		Acid	Conjugate Base	
Acid strength increases (↑)	Strong acids	$HClO_4$ (perchloric acid)	ClO_4^- (perchlorate ion)	Base strength increases (↓)
		HI (hydroiodic acid)	I^- (iodide ion)	
		HBr (hydrobromic acid)	Br^- (bromide ion)	
		HCl (hydrochloric acid)	Cl^- (chloride ion)	
		H_2SO_4 (sulfuric acid)	HSO_4^- (hydrogen sulfate ion)	
		HNO_3 (nitric acid)	NO_3^- (nitrate ion)	
		H_3O^+ (hydronium ion)	H_2O (water)	
	Weak acids	HSO_4^- (hydrogen sulfate ion)	SO_4^{2-} (sulfate ion)	
		HF (hydrofluoric acid)	F^- (fluoride ion)	
		HNO_2 (nitrous acid)	NO_2^- (nitrite ion)	
		HCOOH (formic acid)	$HCOO^-$ (formate ion)	
		CH_3COOH (acetic acid)	CH_3COO^- (acetate ion)	
		NH_4^+ (ammonium ion)	NH_3 (ammonia)	
		HCN (hydrocyanic acid)	CN^- (cyanide ion)	
		H_2O (water)	OH^- (hydroxide ion)	
		NH_3 (ammonia)	NH_2^- (amide ion)	

Table 6.1 The relative strengths of acids and their conjugate bases

	Conjugate acid		Conjugate base	
Strongest acid	$HClO_4$ (aq) + H_2O (l) perchloric acid	⇌	H_3O^+ (aq) + ClO_4^- (aq) perchlorate ion	Weakest base
↑	HCl (aq)+ H_2O (l) hydrochloric acid	⇌	H_3O^+ (aq) + Cl^- (aq) chloride ion	↓
	H_2SO_4 (aq) + H_2O (l) sulfuric acid	⇌	H_3O^+ (aq) + HSO_4^- (aq) hydrogensulfate ion	Increasing base strength
Increasing acid strength	H_3O^+ (aq) + H_2O (l) oxonium ion	⇌	H_3O^+ (aq) + H_2O (l) water	
	CH_3CO_2H (aq) + H_2O (l) ethanoic acid	⇌	H_3O^+ (aq) + $CH_3CO_2^-$ (aq) ethanoate ion	
	NH_4^+ (aq)+ H_2O (l) ammonium ion	⇌	H_3O^+ (aq) + NH_3 (aq) ammonia	
	H_2O (l) + H_2O (l) water	⇌	H_3O^+ (aq) + OH^- (aq) hydroxide ion	
Weakest acid	C_2H_5OH (aq) + H_2O (l) ethanol	⇌	H_3O^+ (aq) + $C_2H_5O^-$ (aq) ethoxide ion	Strongest base

Strong and weak acids.

- Strong acids dissociate completely into ions in water:

$$HA_{(g\ or\ l)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$$

In a dilute solution of a strong acid, almost no HA molecules exist: $[H_3O^+] = [HA]_{init}$ or $[HA]_{eq} = 0$

$$Q_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$ at equilibrium, $Q_c = K_c >> 1$

Nitric acid is an example: $HNO_{3\ (l)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$

- Weak acids dissociate very slightly into ions in water:

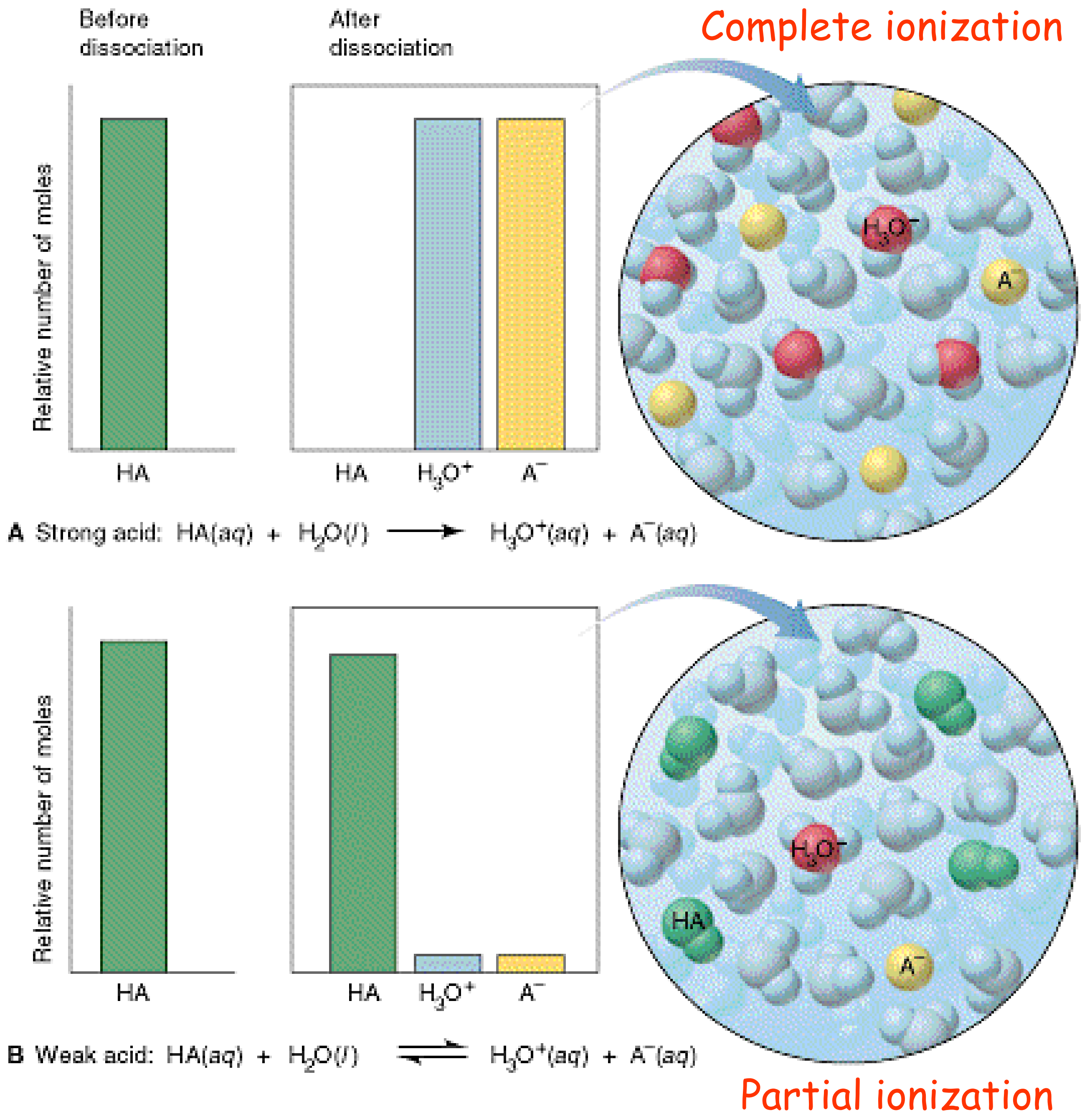
$$HA_{(aq)} + H_2O_{(aq)} \longrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$$

In a dilute solution of a weak acid, the great majority of HA molecules are undissociated: $[H_3O^+] << [HA]_{init}$ or $[HA]_{eq} = [HA]_{init}$

$$Q_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$ at equilibrium, $Q_c = K_c << 1$

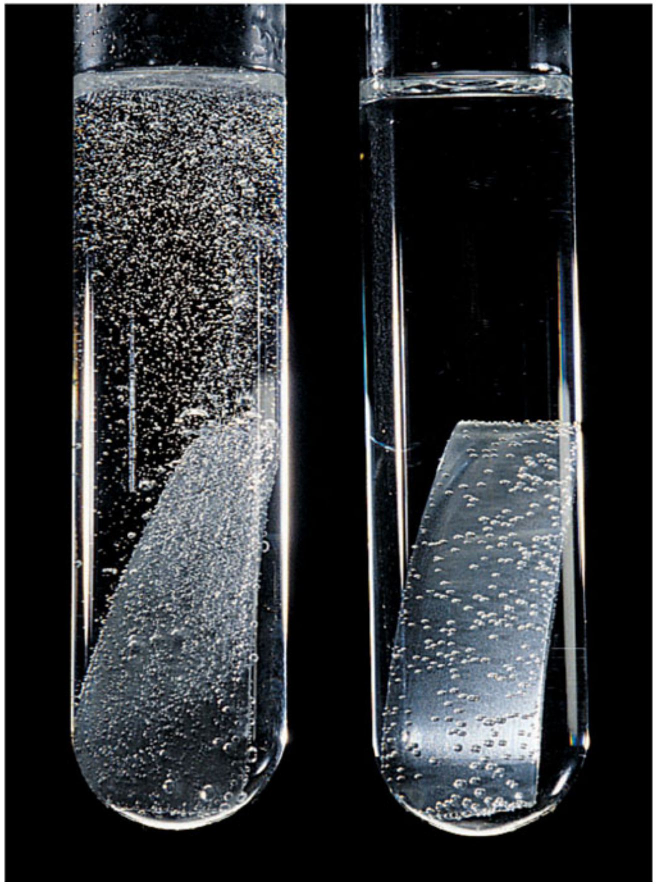
The Extent of Dissociation for Strong and Weak Acids

Key concept :
Acid/base strength quantified in terms of extent or degree of dissociation.
An acid or base is classified as strong if it is fully ionized in solution (e.g. HCl, NaOH).
An acid or base is classified as weak if only a small fraction is ionized in solution (e.g. CH_3COOH, NH_3).



Reactivity of strong and weak acids.

1M HCl(*aq*)



1M CH3COOH(*aq*)

Classifying the Relative Strengths of Acids.

Strong acids.

There are two types of strong acids:

- The hydrohalic acids HCl, HBr, and HI
- Oxoacids in which the number of O atoms exceeds the number of ionizable H atoms by two or more, such as HNO_3, H_2SO_4, $HClO_4$

Weak acids.

There are many more weak acids than strong ones. Four types, with examples, are:

- The hydrohalic acid HF
- Those acids in which H is bounded to O or to halogen, such as HCN and H_2S
- Oxoacids in which the number of O atoms equals or exceeds by one the number of ionizable H atoms, such as HClO, HNO_2, and H_3PO_4
- Organic acids (general formula RCOOH), such as CH_3COOH and C_6H_5COOH.

Classifying the Relative Strengths of Bases.

Strong bases.

- Soluble compounds containing O^{2-} or OH^- ions are strong bases. The cations are usually those of the most active metals: M_2O or MOH, where M= Group 1A(1) metals (Li, Na, K, Rb, Cs).
- MO or $M(OH)_2$, where M = Group 2A(2) metals (Ca, Sr, Ba) [MgO and $Mg(OH)_2$ are only slightly soluble, but the soluble portion dissociates completely.]

Weak bases.

- Many compounds with an electron-rich nitrogen are weak bases (none are Arrhenius bases). The common structural feature is an N atom that has a lone electron pair in its Lewis structure.
  - Ammonia (NH_3)
  - Amines (general formula RNH_2, R_2NH, R_3N), such as $CH_3CH_2NH_2$, $(CH_3)_2NH$, $(C_3H_7)_3N$, and C_5H_5N

Strong Electrolyte – 100% dissociation

$$NaCl\ (s) \xrightarrow{H_2O} Na^+\ (aq) + Cl^-\ (aq)$$

Weak Electrolyte – not completely dissociated

$$CH_3COOH \rightleftharpoons CH_3COO^-\ (aq) + H^+\ (aq)$$

Strong Acids are strong electrolytes

$$HCl\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

$$HNO_3\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + NO_3^-\ (aq)$$

$$HClO_4\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + ClO_4^-\ (aq)$$

$$H_2SO4\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + HSO_4^-\ (aq)$$

Weak Acids are weak electrolytes

$HF\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + F^-\ (aq)$

$HNO_2\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + NO_2^-\ (aq)$

$HSO_4^-\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + SO_4^{2-}\ (aq)$

$H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$

Strong Bases are strong electrolytes

$NaOH\ (s) \xrightarrow{H_2O} Na^+\ (aq) + OH^-\ (aq)$

$KOH\ (s) \xrightarrow{H_2O} K^+\ (aq) + OH^-\ (aq)$

$Ba(OH)_2\ (s) \xrightarrow{H_2O} Ba^{2+}\ (aq) + 2OH^-\ (aq)$

Weak Bases are weak electrolytes

$$F^- (aq) + H_2O (l) \rightleftharpoons OH^- (aq) + HF (aq)$$

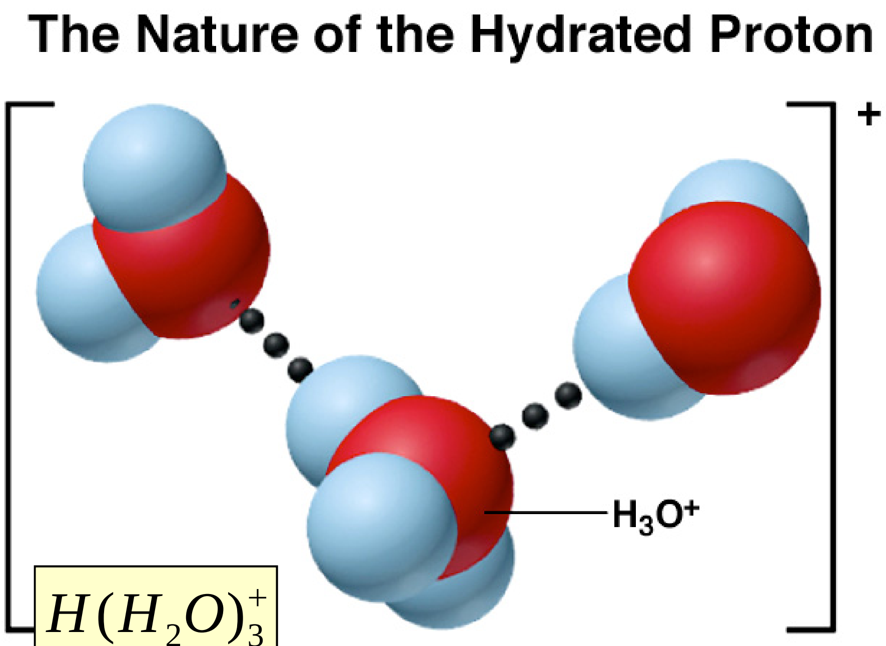
$$NO_2^- (aq) + H_2O (l) \rightleftharpoons OH^- (aq) + HNO_2 (aq)$$

Conjugate acid-base pairs:

- The conjugate base of a strong acid has no measurable strength.
- H_3O^+ is the strongest acid that can exist in aqueous solution.
- The OH^- ion is the strongest base that can exist in aqeous solution.

Representing Protons

- Both representations of the proton, $H^+(aq)$ and H_3O^+ are equivalent.
- $H_5O_2^+$ (aq), $H_7O_3^+$ (aq), $H_9O_4^+$ (aq) have been observed.
- We will use $H^+(aq)$!

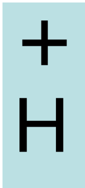


$H(H_2O)_3^+$

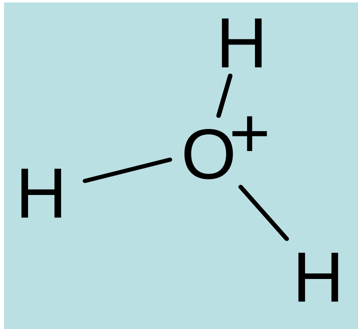
$H_7O_3^+$

The hydrated proton is quite a complex entity. It is usually represented in shorthand form as $H^+(aq)$. A better representation is in terms of the hydronium ion H_3O^+. We will adopt this representation a lot. The real situation is more complex. The H_3O^+ ion binds to other water molecules forming a mixture of species with the general formula $H(H_2O)_n^+$. In fact the structural details of liquid water is still a hot item of research.

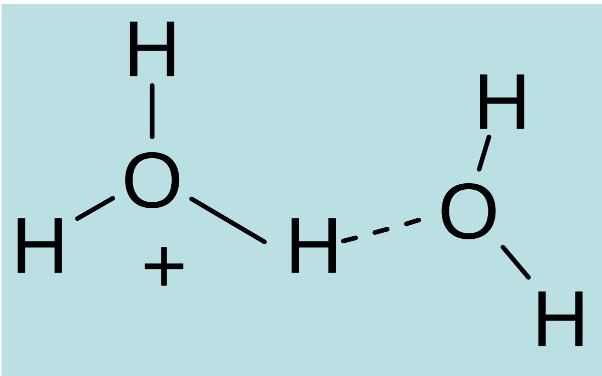
What is H^+ (aq)?



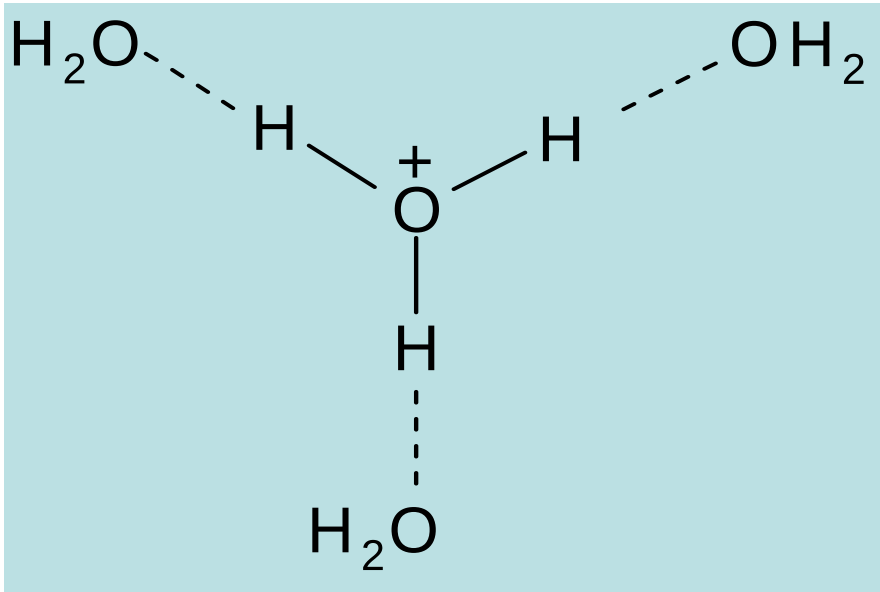
H^+



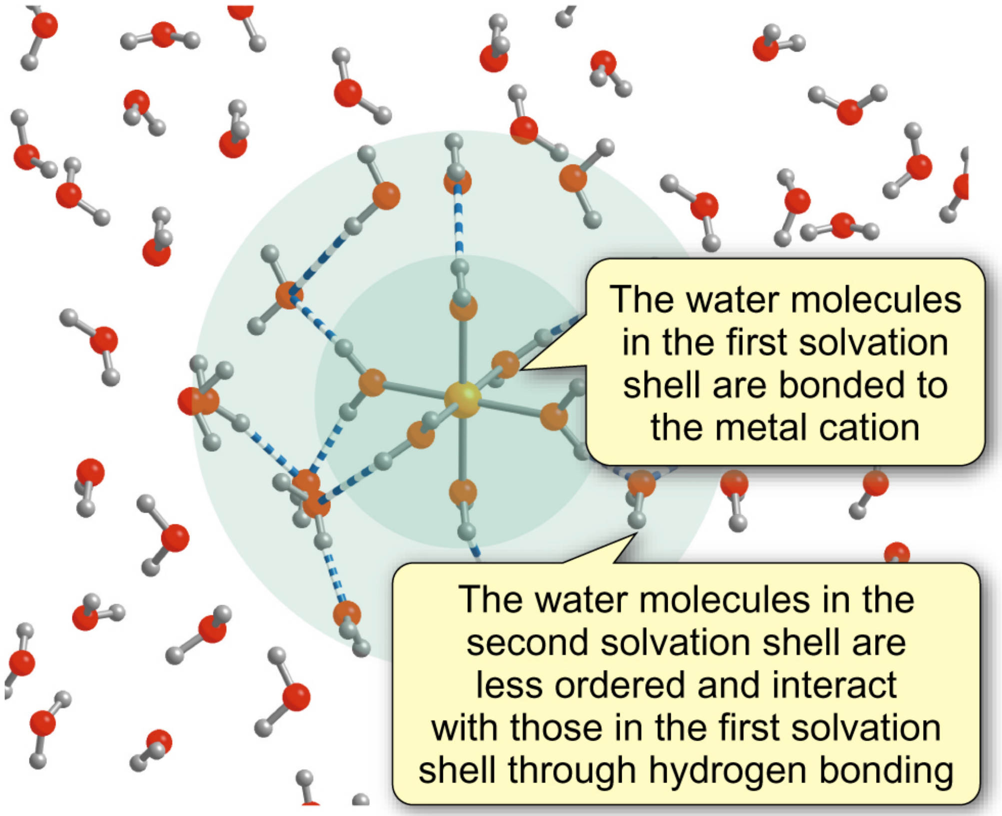
H_3O^+



$H_5O_2^+$



$H_9O_4^+$


The water molecules in the first solvation shell are bonded to the metal cation
The water molecules in the second solvation shell are less ordered and interact with those in the first solvation shell through hydrogen bonding

Yet more sophistication: Lewis acidity

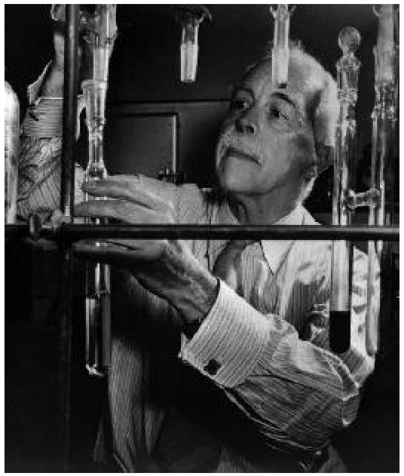
An **Arrhenius acid** is defined as a substance that produces H^+ (H_3O^+) in water.

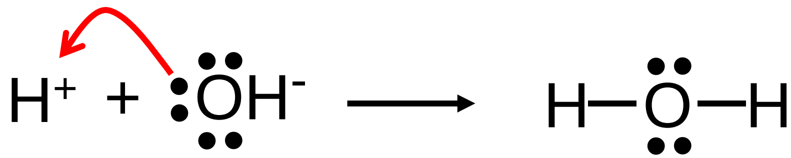
A **Brønsted acid** is defined as a proton donor

A **Lewis acid** is defined as a substance that can accept a pair of electrons.

A **Lewis base** is defined as a substance that can donate a pair of electrons

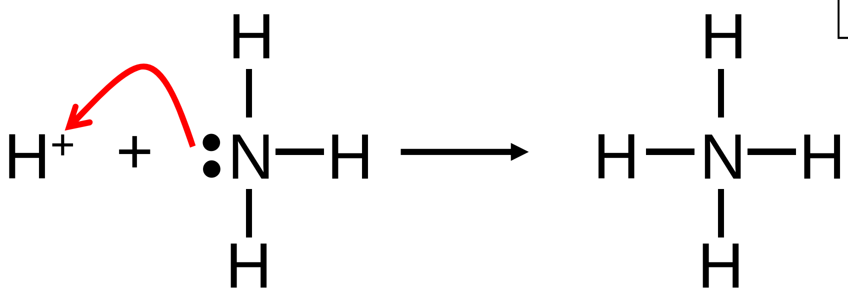
G.N. Lewis 1875-1946





acid base

See Kotz section 17.9 pp.789-798.



acid base

http://en.wikipedia.org/wiki/Gilbert_N._Lewis

Electron-Pair Donation and the Lewis Acid-Base Definition

The Lewis acid-base definition :

- A ***base*** is any species that ***donates*** an electron pair.
- An ***acid*** is any species that ***accepts*** an electron pair.

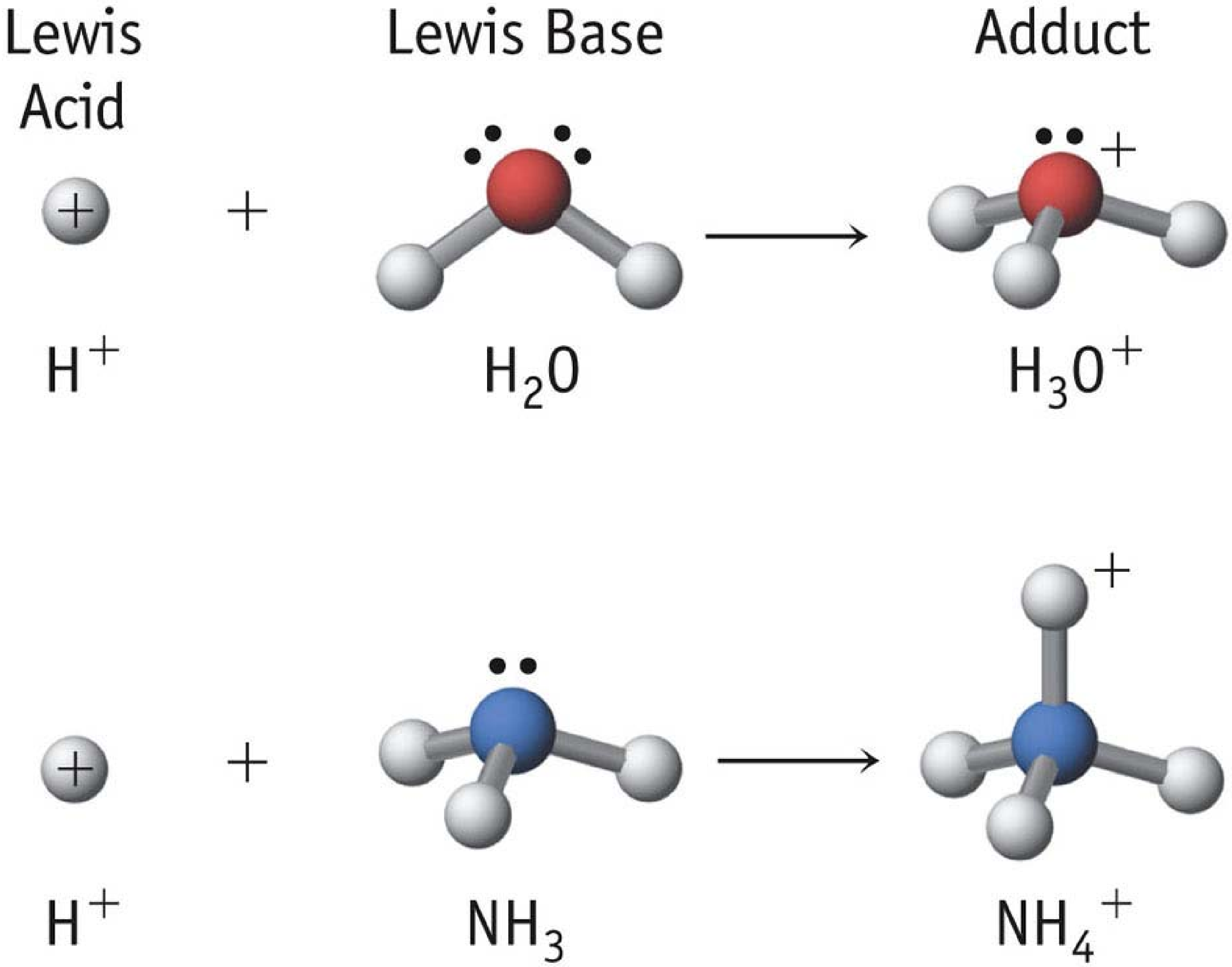
Protons act as Lewis acids in that they accept an electron pair in all reactions:

$$B: \quad + \quad H^+ \rightleftharpoons B—H^+$$

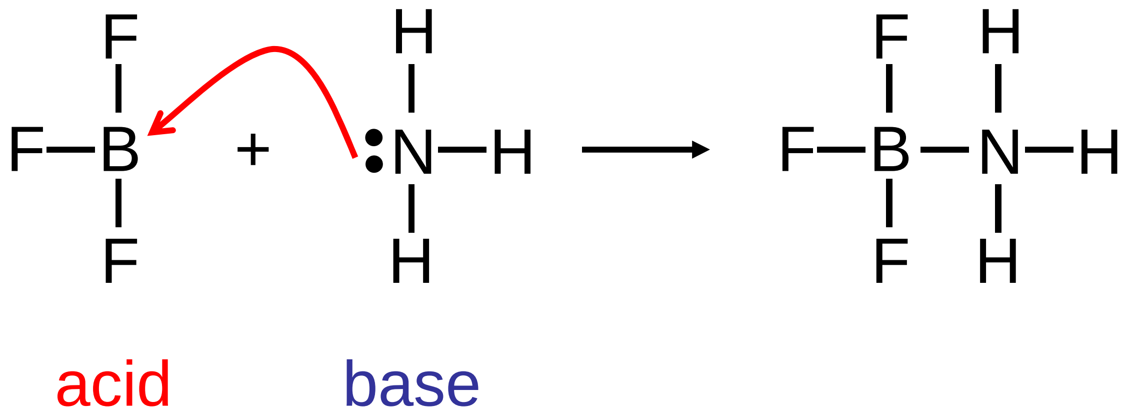
The product of any Lewis acid-base reaction is called an ***adduct,*** a single species that contains a new covalent bond.

- *A Lewis base has a lone pair of electrons to donate.*
- *A Lewis acid has a vacant orbital*

Lewis Acid/Base Reaction



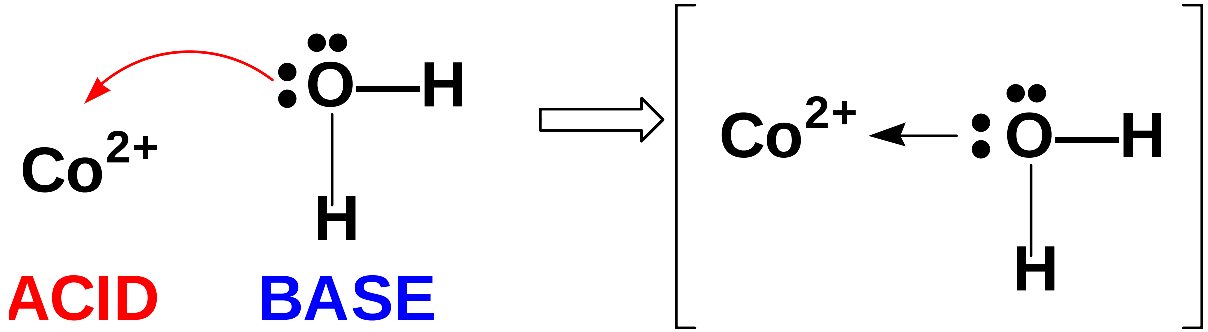
Lewis Acids and Bases

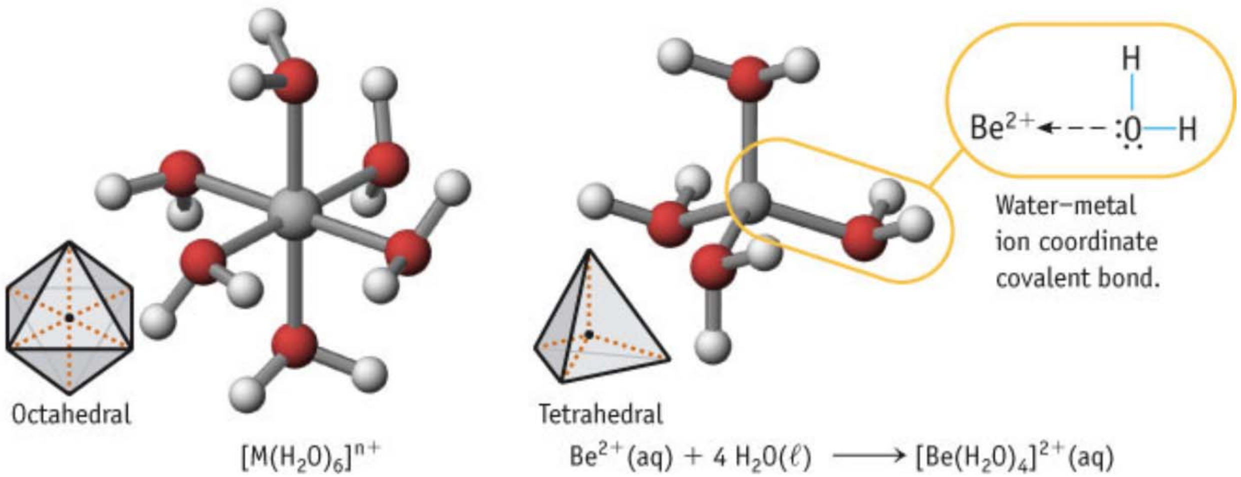


No protons donated or accepted!

Lewis Acids & Bases

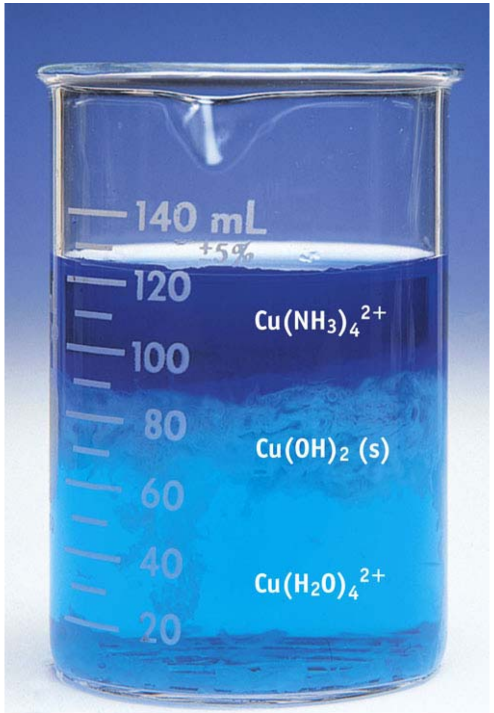
Other good examples involve metal ions.





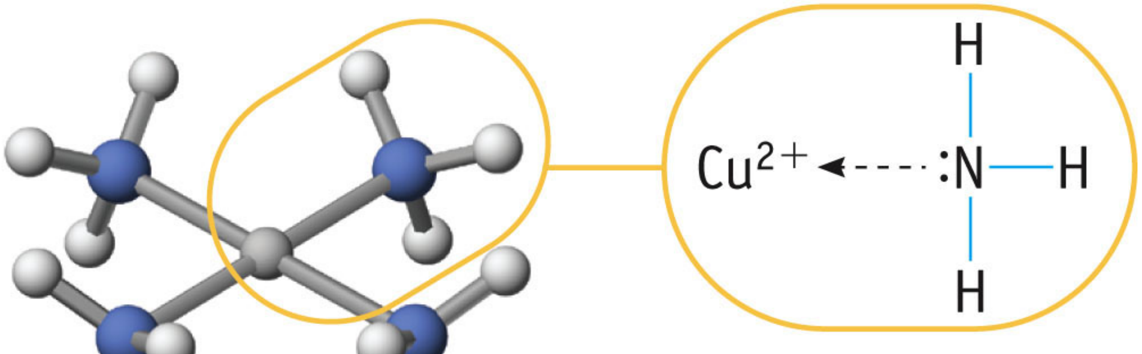
Lewis Acids & Bases

The combination of metal ions (Lewis acids) with Lewis bases such as H_2O and NH_3 leads to COMPLEX IONS



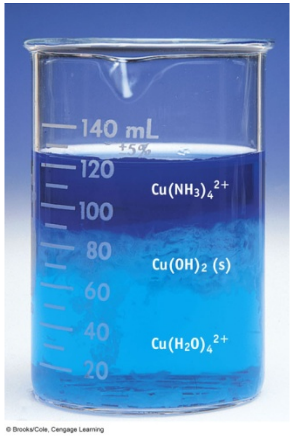
$$Cu^{2+}(aq) + 4\ NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}(aq)$$

light blue → *deep blue*



Copper–ammonia coordinate covalent bond.

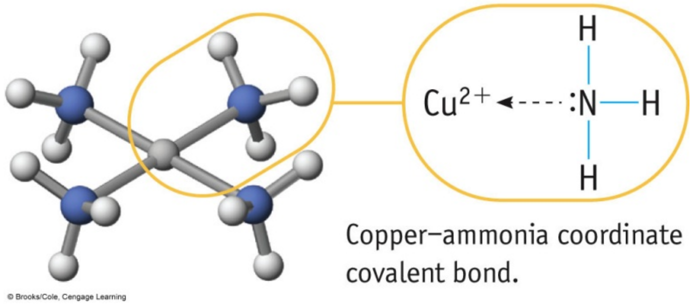
Reaction of NH_3 with $Cu^{2+}(aq)$



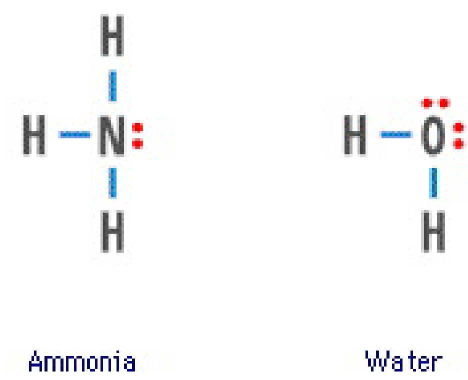
PLAY MOVIE

$$Cu^{2+}(aq) + 4\ NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}(aq)$$

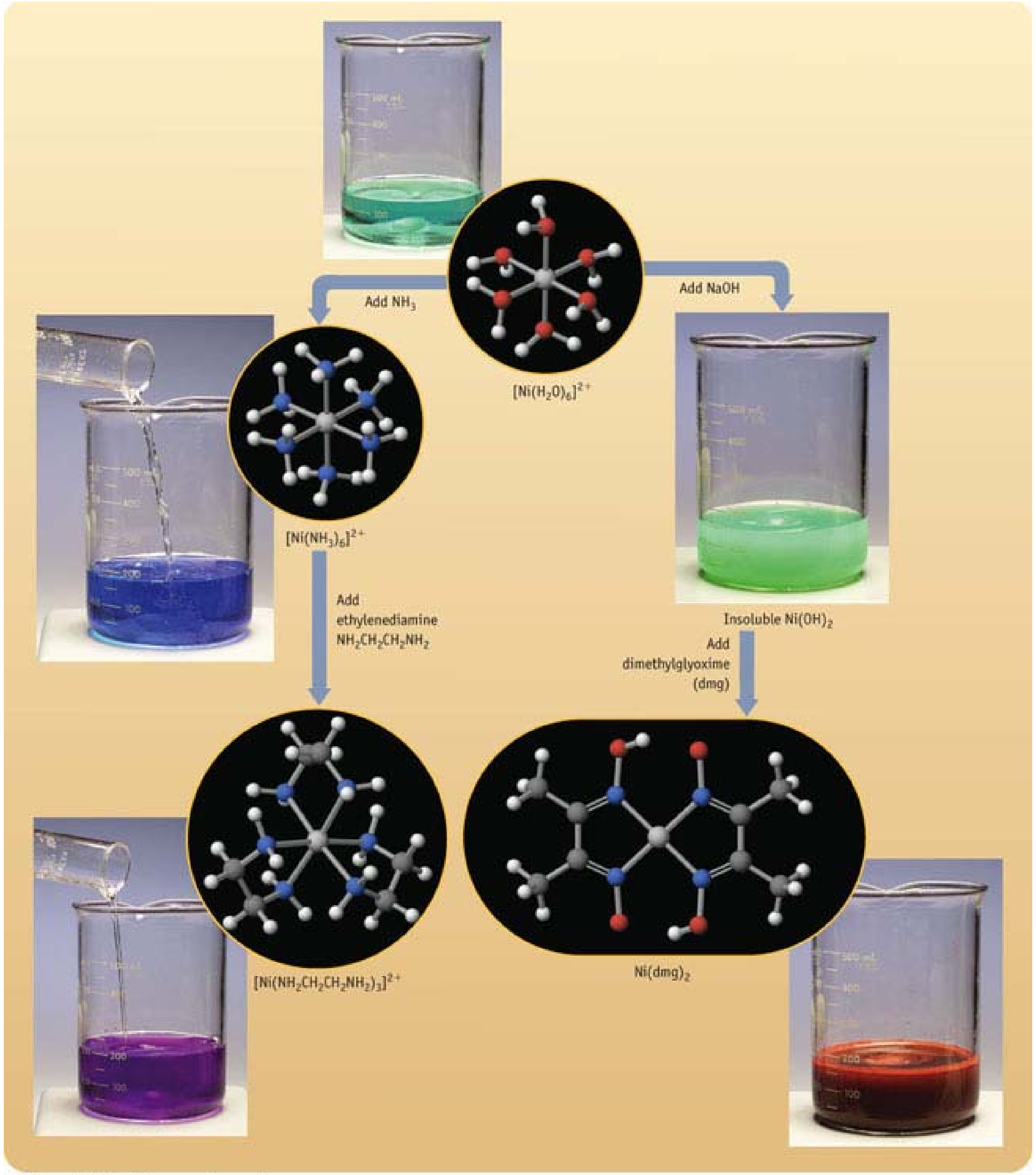
light blue — *deep blue*



Copper–ammonia coordinate covalent bond.



PLAY MOVIE

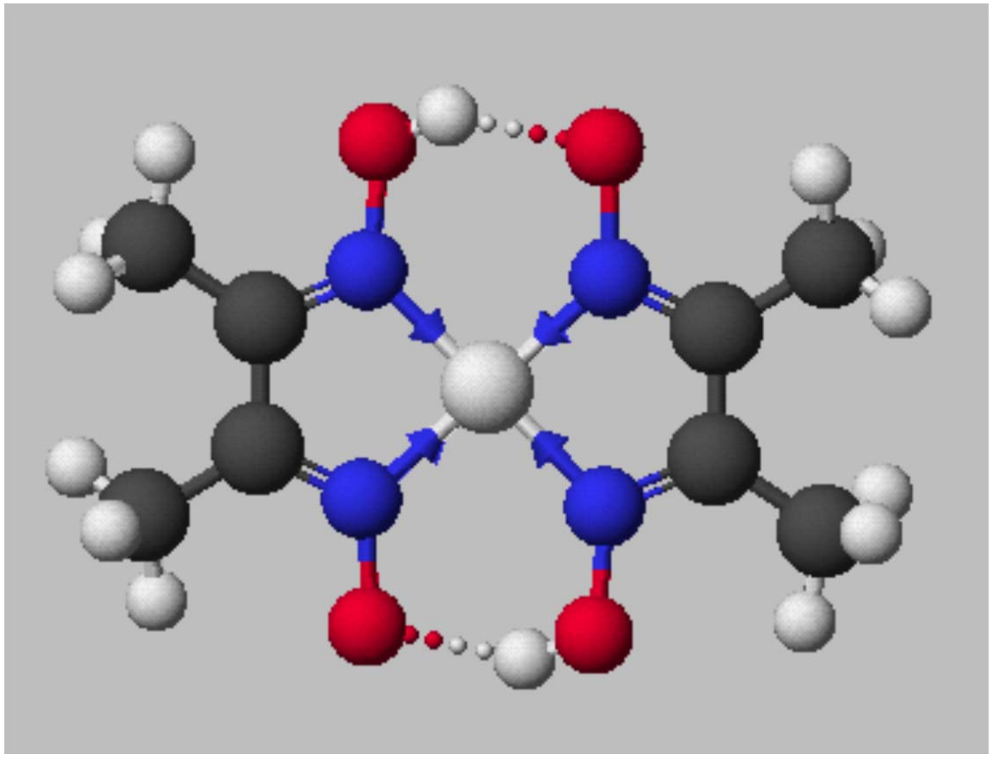


The Lewis Acid-Base Chemistry of Nickel(II)

Lewis Acids & Bases

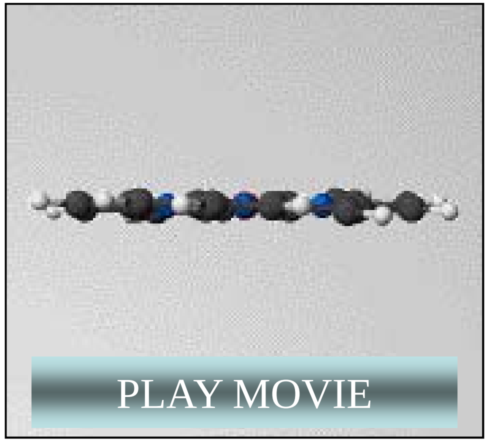
$[Ni(H_2O)_6]^{2+}$ + 6 NH_3 → $[Ni(NH_3)_6]^{2+}$

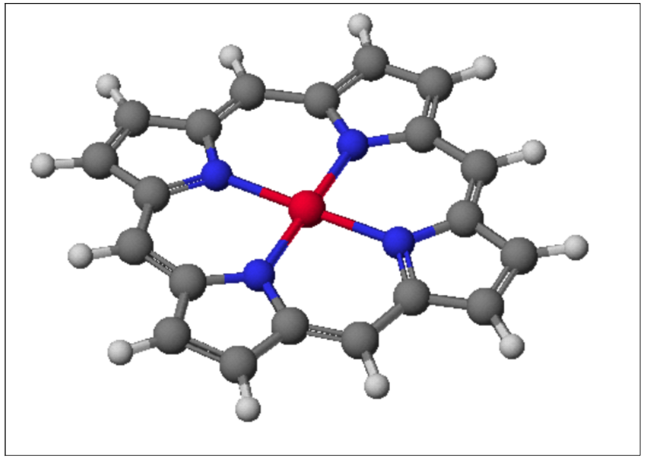
+ DMG



DMG = dimethylglyoxime, a standard reagent to detect nickel(II)

Lewis Acid-Base Interactions in Biology





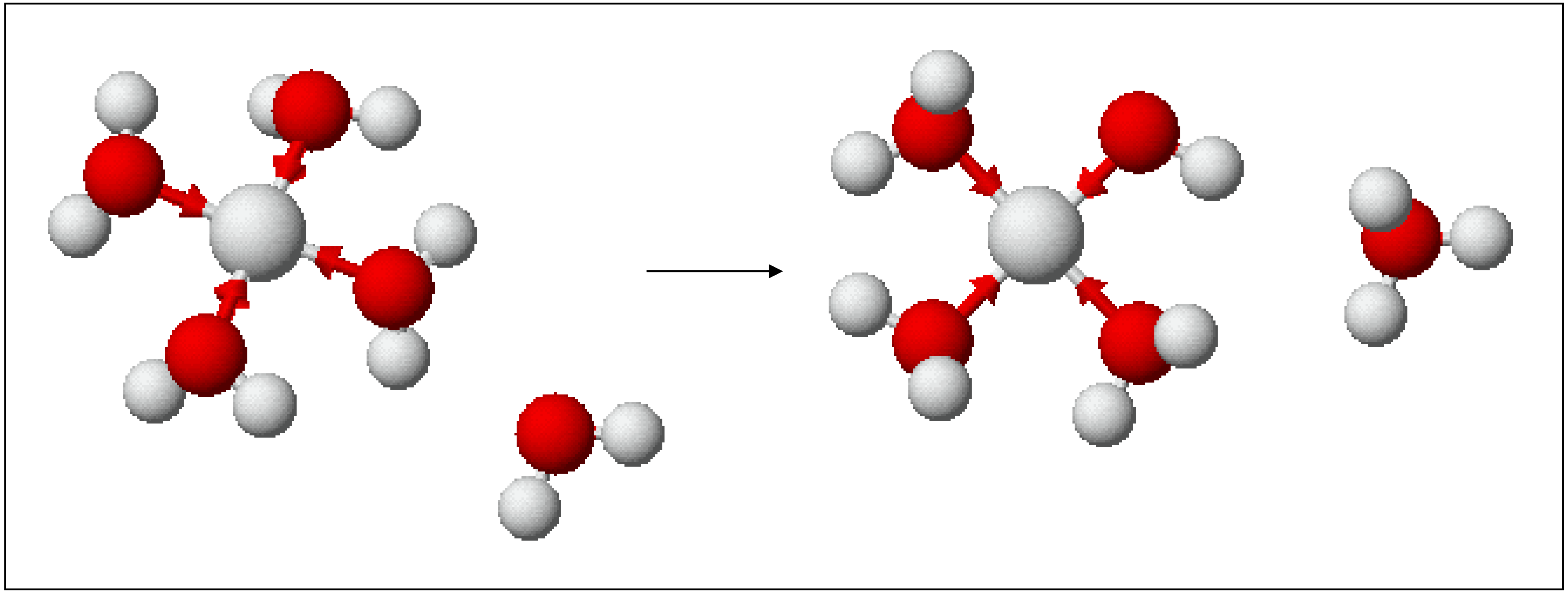
Heme group

- The heme group in hemoglobin can interact with O_2 and CO.
- The Fe ion in hemoglobin is a Lewis acid
- O_2 and CO can act as Lewis bases

Lewis Acids & Bases

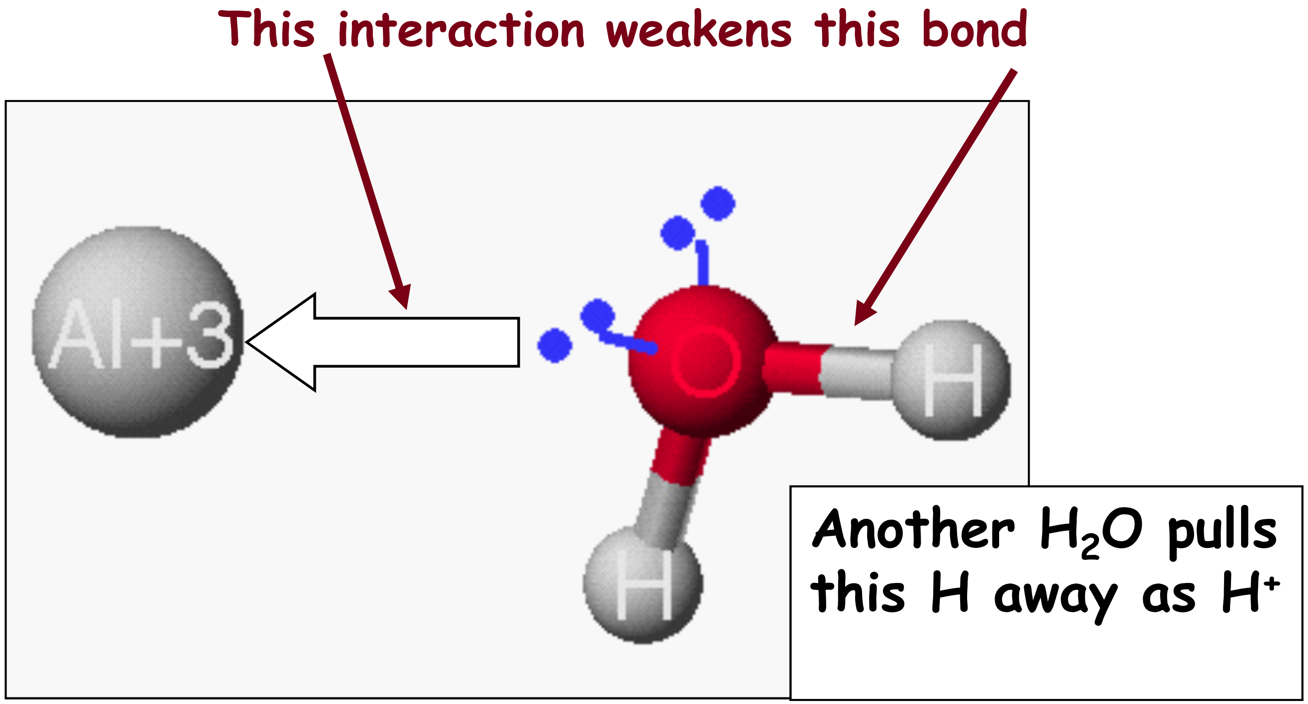
Many complex ions containing water undergo HYDROLYSIS to give acidic solutions.

$[Cu(H_2O)_4]^{2+} + H_2O \rightarrow [Cu(H_2O)_3(OH)]^{+} + H_3O^{+}$

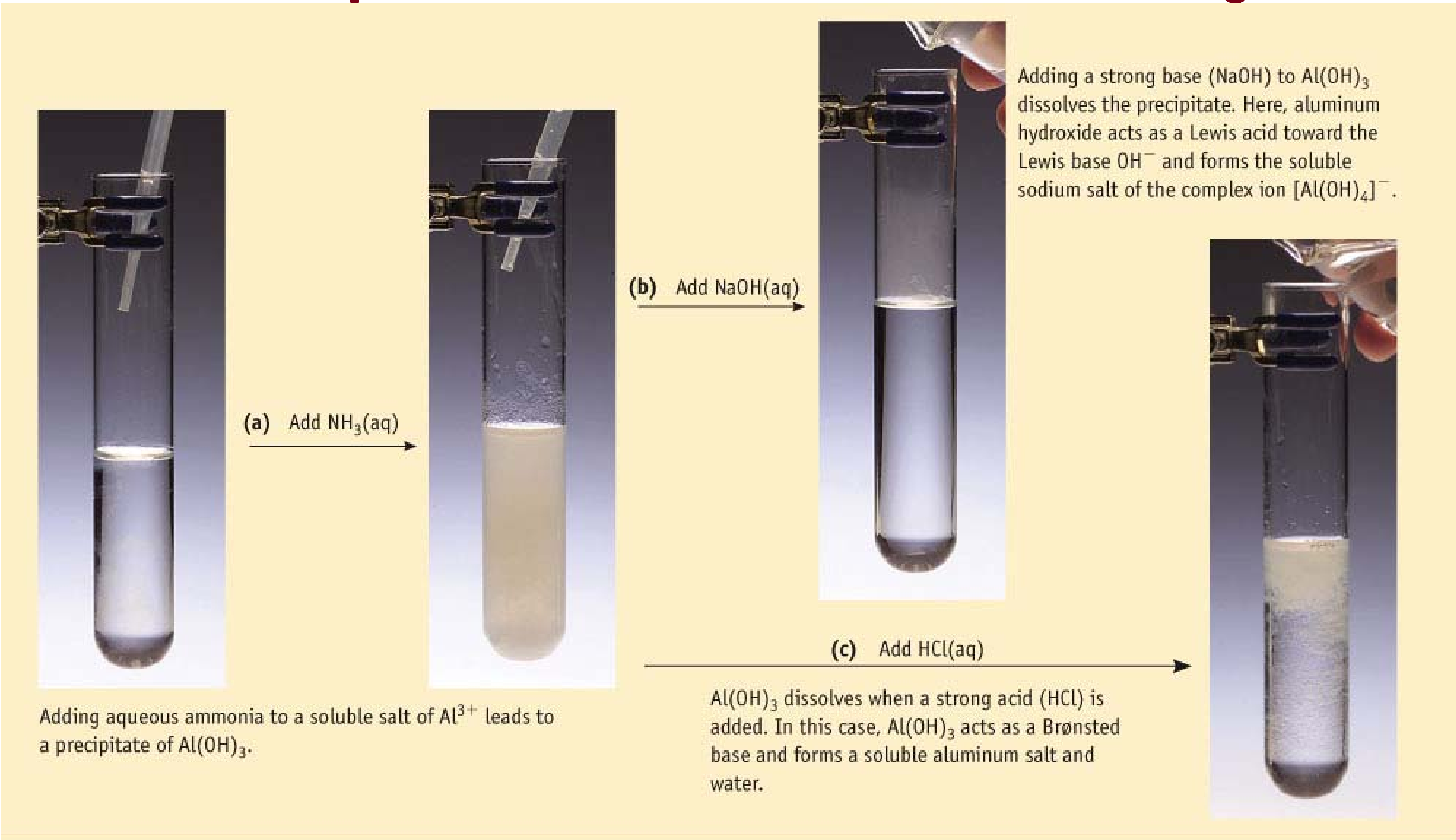


Lewis Acids & Bases

This explains why water solutions of Fe^{3+}, Al^{3+}, Cu^{2+}, Pb^{2+}, etc. are acidic.



Amphoterism of $Al(OH)_3$



Lewis Acids & Bases

This explains AMPHOTERIC nature of some metal hydroxides.

$Al(OH)_3(s) + 3\ H_3O^+ \rightarrow Al^{3+} + 6\ H_2O$

Here $Al(OH)_3$ is a Brønsted base.

$Al(OH)_3(s) + OH^- \rightarrow Al(OH)_4^-$

Here $Al(OH)_3$ is a Lewis acid.