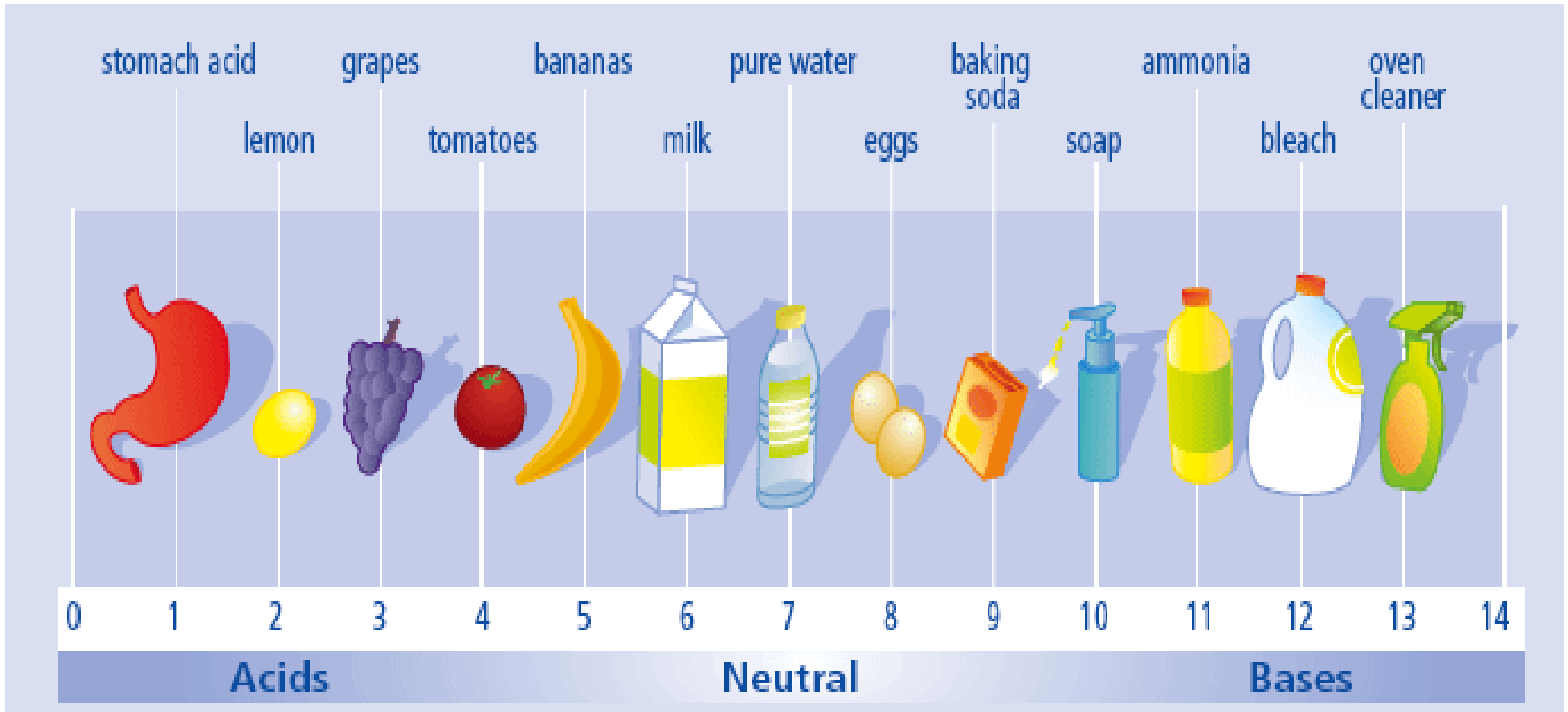# Acids and Bases Overview
Chemistry 362

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 properties

stomach acid · lemon · grapes · tomatoes · bananas · milk · pure water · eggs · baking soda · soap · ammonia · bleach · oven cleaner

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

Acids **Neutral** **Bases**

Focused on water and protons and hydroxide ions:

Protic Acids: compounds that ionize to add to H^+ ion concentration of Water.

Bases: compounds that increase OH^- concentration of water.

Svante August Arrhenius

1859 – 1927

Arrhenius' concept based on water

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.

A Neutralization Reaction

Acid + Base $\rightarrow$ Salt + Water

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

pH, pOH and other pBeasts

In general, $pX = -\log_{10}(X)$

$pH = -\log[H^+]$ $\qquad$ $pOH = -\log[OH^-]$ $\qquad$ $pK = -\log K$

In pure water, $pH = pOH = 7$

In acidic solution, $pH < 7$; $pOH > 7$

In basic solutions, $pH > 7$, $pOH < 7$

Since $pH + pOH = 14$, either value is sufficient to describe both $[H^+]$ and $[OH^-]$

Johannes Nicolaus Brønsted

1879 – 1947

Thomas Martin Lowry

1874 – 1936

Brønsted-Lowry Approach to Acids and Bases: Extends Arrhenius and Introduces Conjugate Acid/Base Pairs

Brønsted and Lowry, 1923:

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

"fuzzy term"

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^-

Conjugate Acid–Base Pairs Arranged by Strength

Acid name	Acid formula	Base formula	Base name
Strong acid			**Very weak base**
hydroiodic acid	HI	I^-	iodide ion
perchloric acid	$HClO_4$	ClO_4^-	perchlorate ion
hydrobromic acid	HBr	Br^-	bromide ion
hydrochloric acid	HCl	Cl^-	chloride ion
sulfuric acid	H_2SO_4	HSO_4^-	hydrogen sulfate ion
chloric acid	$HClO_3$	ClO_3^-	chlorate ion
nitric acid	HNO_3	NO_3^-	nitrate ion
hydronium ion	H_3O^+	H_2O	*water*
hydrogen sulfate ion	HSO_4^-	SO_4^{2-}	sulfate ion
hydrofluoric acid	HF	F^-	fluoride ion
nitrous acid	HNO_2	NO_2^-	nitrite ion
acetic acid	CH_3COOH	$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3	HCO_3^-	hydrogen carbonate ion
hydrosulfuric acid	H_2S	HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+	NH_3	ammonia
hydrocyanic acid	HCN	CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-	CO_3^{2-}	carbonate ion
methylammonium ion	$CH_3NH_3^+$	CH_3NH_2	methylamine
water	H_2O	OH^-	*hydroxide ion*
ammonia	NH_3	NH_2^-	amide ion
hydrogen	H_2	H^-	hydride ion
methane	CH_4	CH_3^-	methide ion
hydroxide ion	OH^-	O^{2-}	oxide ion
Very weak acid			**Strong base**

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. But practically, very difficult for many element-hydrogen bonds to be cleaved by loss of proton.**

$pK_a = -log10\ K_a$ from equilibrium:

$$HB\ +\ H_2O\ =\ H_3O^+\ +\ B^-\ (H_2O)_x$$
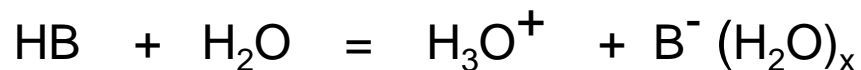
Table 8.3 From Jolly, "Modern Inorganic Chemistry" **Aqueous** pK values of the binary hydrides of the nonmetals at 22 deg C.

CH_4 ~ 44	NH_3 39	H_2O 15.74	HF 3.15
SiH_4 ~ 35	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

What does it take to rip a proton away from a base? Analyze Thermodynamics for Proton Gain Reaction Cycle; Proton Affinity Should Inversely Relate to Acid Strength

$H^+(g) + A^-(g)$

$\Delta_{eg}H^{\ominus}(A)$

$H^+(g) + A(g) + e^-(g)$

$I(H)$

$\Delta_{pg}H^{\ominus}(A^-)$

$H(g) + A(g)$

$B(H-A)$

$HA(g)$
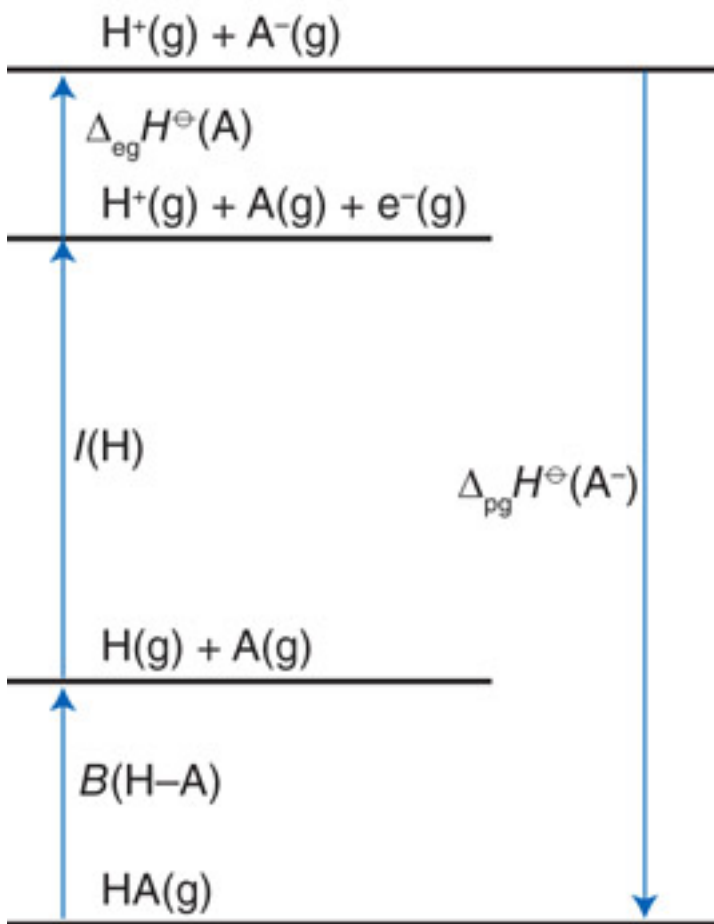
Helpful for increased acidity:

➢ A weak H-A bond

➢ Strong electron affinity energy of A

➢ Sum of the left side = proton affinity

F
i

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

$$EtOH + Me_2N^- \ Li^+ \rightarrow EtO^- \ Li^+ + Me_2NH$$

Acid1 + Base2 → Base1 + Acid2

$$EtOH + H_2SO_4 \rightarrow EtOH_2^+ + HSO_4^-$$

Base1 + Acid2 → Acid1 + Base2

➢ 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.

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

$$SbF_5 + BrF_3 \rightleftharpoons BrF_2^+ + SbF_6^-$$
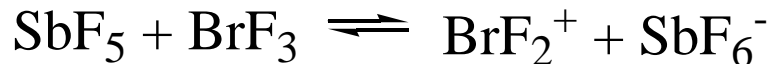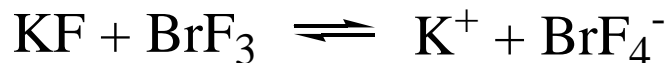
An acid-base reaction in water is the reaction between H^+ and OH^-; an acid-base reaction in BrF_3 is the reaction between BrF_2^+ and BrF_4^-.

Mikhail Ilyich Usanovich

1894 – 1981

Usanovich concept

Base – any material that forms salts with acids through neutralization, gives up anions, combines with cations, or gives up electrons.

Acid – any material that forms salts with bases through neutralization, gives up cations, combines with anions, or accepts electrons.

Lux-Flood concept may be applied to non-aqueous, non-protic systems

Base – an oxide donor.

Acid – an oxide acceptor.

$$Na_2O + CO_2 \rightarrow Na_2CO_3$$

$$ZnO + S_2O_7^{2-} \rightarrow Zn^{2+} + 2SO_4^{2-}$$

Hermann Lux

1904 – 1999

Håkon Flood

1905 – 2001

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, CO_2, and N_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

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

Alkali metal and alkaline earth oxides are basic (dissolve in acid).
Or, they react directly with acidic oxides:
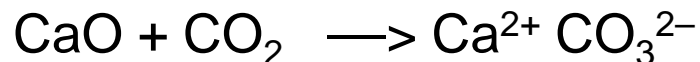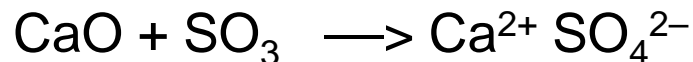
$$CaO + SO_3 \longrightarrow Ca^{2+} SO_4^{2-}$$

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

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

$$SO_3 \; + \; H_2O \; \longrightarrow \; H_2SO_4$$

$$CO_2 \; + \; H_2O \; \longrightarrow \; H_2CO_3$$

$$SO_2 \; + \; H_2O \; \longrightarrow \; H_2SO_3$$

$\left.\right\}$ $\xrightarrow{\;H_2O\;}$ Ionization into protons and anions
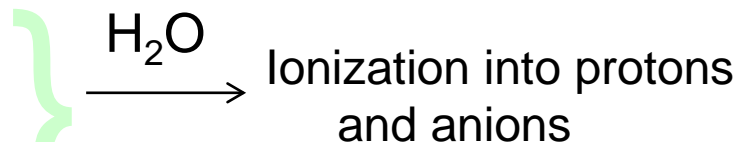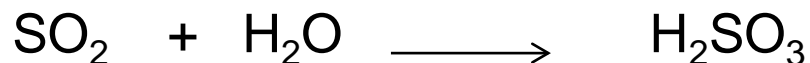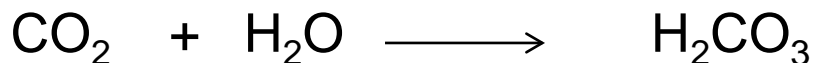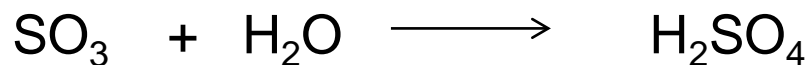
Note: The element-oxygen (E–O) bond is not broken on dissolution.
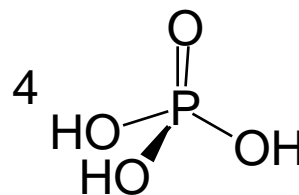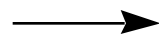
either
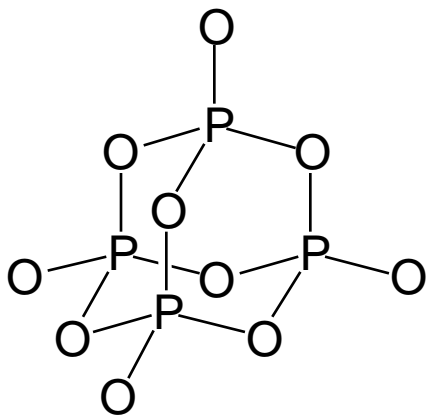 an E – O – E group is hydrolyzed by water;
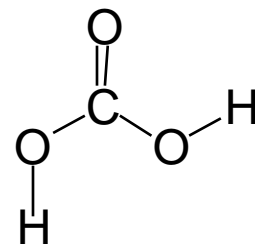**or**
  water is added across the E=O double bond.

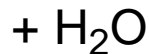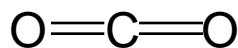# Examples of Acidic Oxides, or Acid Anhydrides, reactions with water give "oxy-acids"
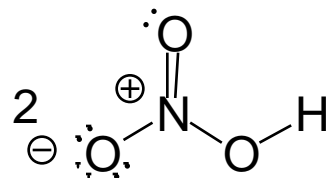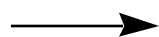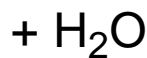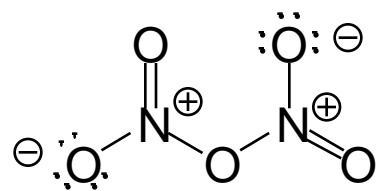
Acidic Oxides (Non-metal Oxides or Acid Anhydrides)

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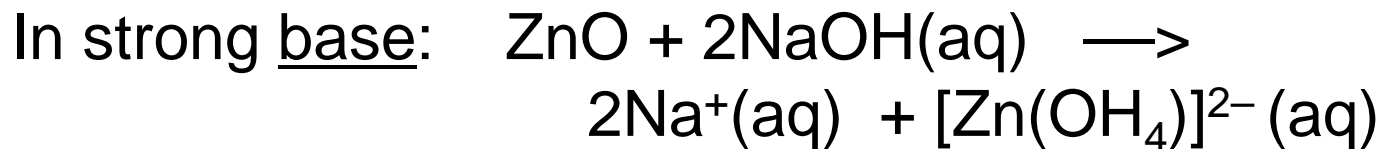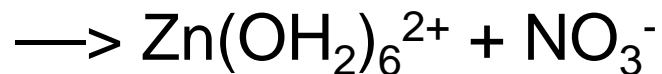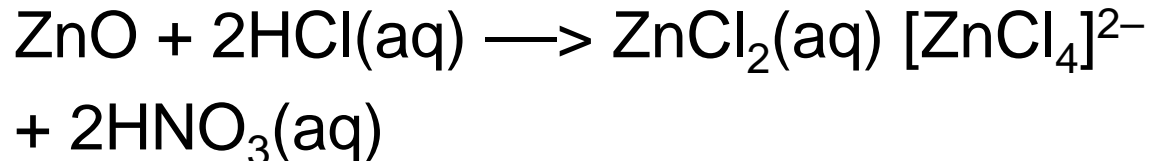
eg. $As_2O_3 + 2NaOH(aq) \longrightarrow 2NaH_2As\ O_3$

(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 <u>acids</u>:

$ZnO + 2HCl(aq) \longrightarrow ZnCl_2(aq) \, [ZnCl_4]^{2-}$

$+ \, 2HNO_3(aq)$

$\longrightarrow Zn(OH_2)_6^{2+} + NO_3^{-}$

In strong <u>base</u>: $ZnO + 2NaOH(aq) \longrightarrow$

$2Na^+(aq) \; + [Zn(OH_4)]^{2-} \, (aq)$

Transition Metal Oxides Acidity or Basicity Depends on Oxidation Number (State)
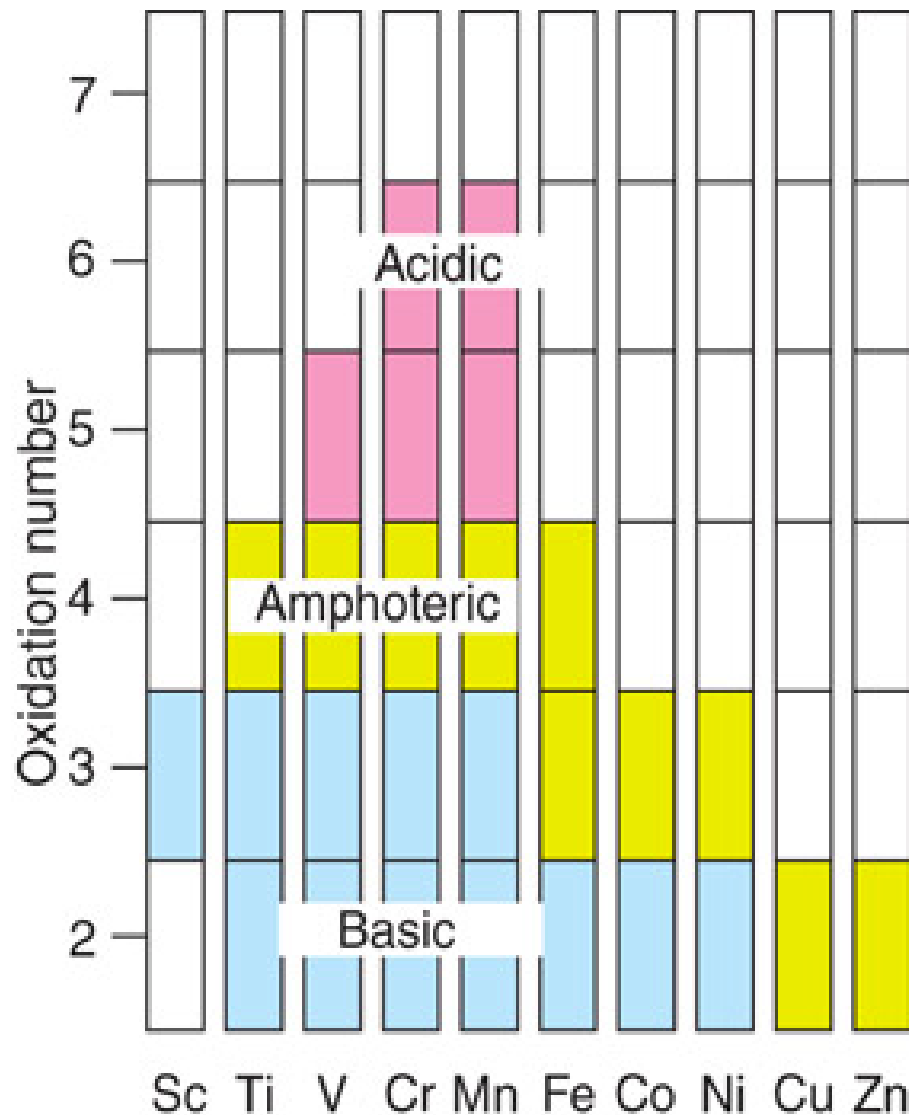
MnO is basic;
MnO_2 is amphoteric
MnO_3 is acidic

Figure 4.6 Shriver, et al.

Gilbert Newton Lewis

1875 – 1946

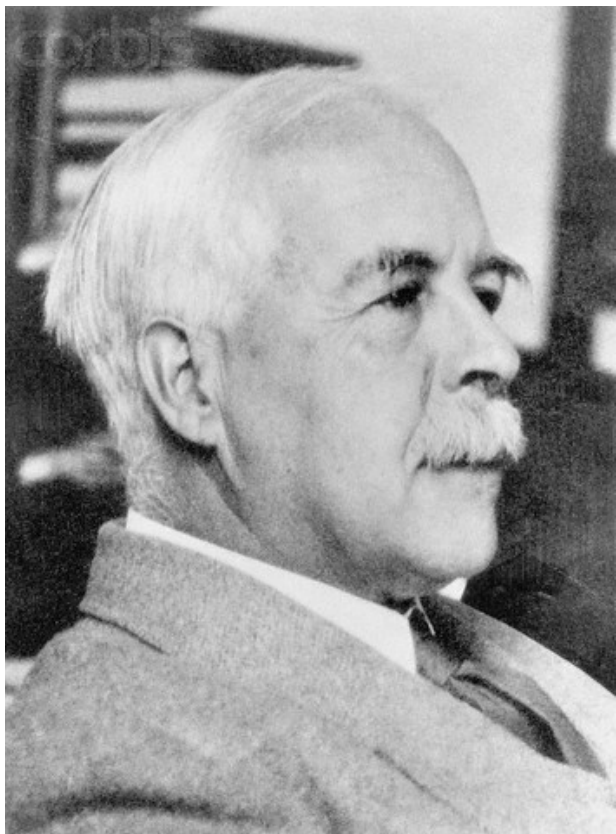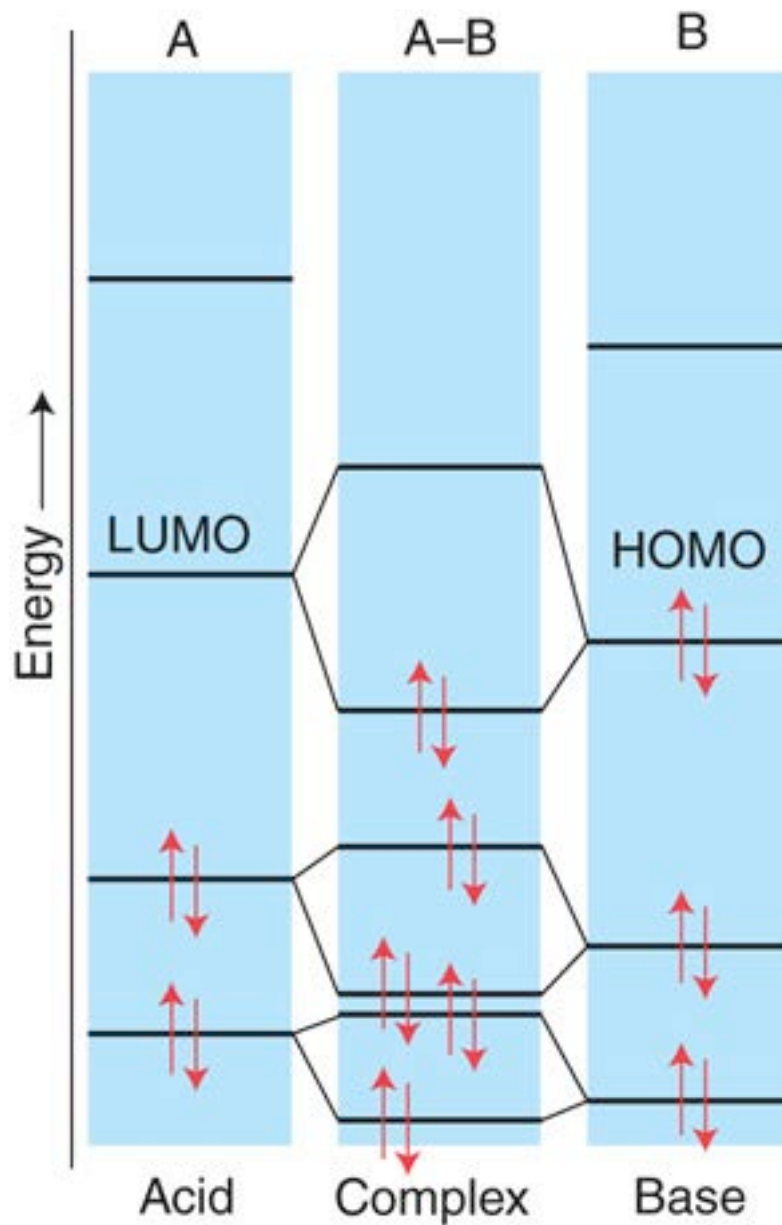# Lewis Concept

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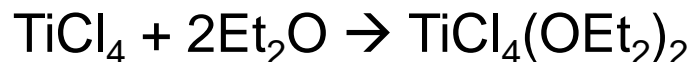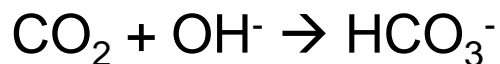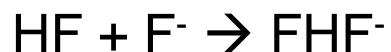
A more general view also classifies compounds that can generate a species with an empty orbital as Lewis acids. Then we can include **B_2H_6, Al_2Cl_6, HCl** etc.

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.

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

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

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

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

$$TiCl_4 + 2Et_2O \rightarrow TiCl_4(OEt_2)_2$$
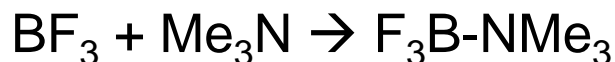
In fact, any chemical compound can be mentally disassembled into Lewis acids and bases:

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

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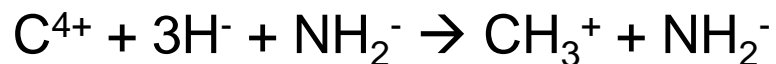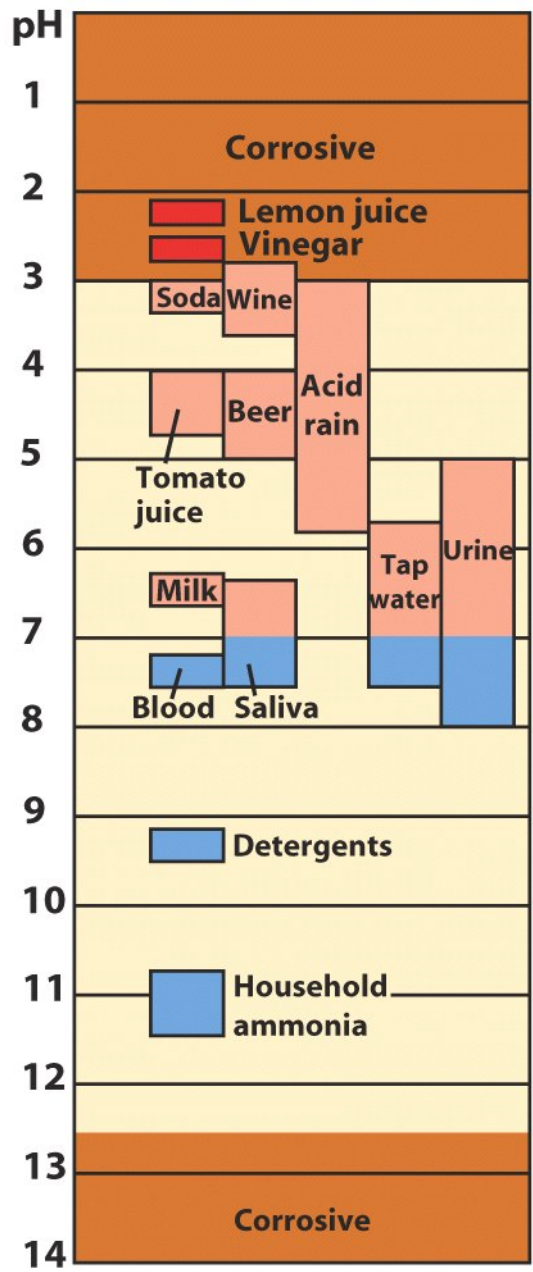
Acidity constants

Acidity constants define the "strength" of an acid or its propensity to dissociate (which is a propensity to donate proton to the solvent)

For dilute solutions of acid HA,

$K_a = [H^+][A^-] / [HA]$

$pK_a = -logK_a$

K_a is a constant at a given T for a given solvent; it is an intrinsic property of a compound

Acidity Constants at 25°C*

Acid	K_a	pK_a
trichloroacetic acid, CCl_3COOH	3.0×10^{-1}	0.52
benzene sulfonic acid, $C_6H_5SO_3H$	2.0×10^{-1}	0.70
iodic acid, HIO_3	1.7×10^{-1}	0.77
sulfurous acid, H_2SO_3	1.5×10^{-2}	1.81
chlorous acid, $HClO_2$	1.0×10^{-2}	2.00
phosphoric acid, H_3PO_4	7.6×10^{-3}	2.12
chloroacetic acid, $CH_2ClCOOH$	1.4×10^{-3}	2.85
lactic acid, $CH_3CH(OH)COOH$	8.4×10^{-4}	3.08
nitrous acid, HNO_2	4.3×10^{-4}	3.37
hydrofluoric acid, HF	3.5×10^{-4}	3.45

*The values for K_a listed here have been calculated from pK_a values with more significant figures than shown so as to minimize rounding errors. Values for polyprotic acids—those capable of donating more than one proton—refer to the first deprotonation.
†The proton transfer equilibrium is $B(OH)_3(aq) + 2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + B(OH)_4^-(aq)$.

Acidity Constants at 25°C[*]

Acid	K_a	pK_a
formic acid, HCOOH	1.8×10^{-4}	3.75
benzoic acid, C_6H_5COOH	6.5×10^{-5}	4.19
acetic acid, CH_3COOH	1.8×10^{-5}	4.75
carbonic acid, H_2CO_3	4.3×10^{-7}	6.37
hypochlorous acid, HClO	3.0×10^{-8}	7.53
hypobromous acid, HBrO	2.0×10^{-9}	8.69
boric acid, $B(OH)_3$[†]	7.2×10^{-10}	9.14
hydrocyanic acid, HCN	4.9×10^{-10}	9.31
phenol, C_6H_5OH	1.3×10^{-10}	9.89
hypoiodous acid, HIO	2.3×10^{-11}	10.64

[*]The values for K_a listed here have been calculated from pK_a values with more significant figures than shown so as to minimize rounding errors. Values for polyprotic acids—those capable of donating more than one proton—refer to the first deprotonation.
[†]The proton transfer equilibrium is $B(OH)_3(aq) + 2 H_2O(l) \rightleftharpoons H_3O^+(aq) + B(OH)_4^-(aq)$.

Basicity constants

Basicity constants define the "strength" of a base or its propensity to dissociate or accept protons (e.g., from water)

For dilute aqueous solutions of base B,

$K_b = [HB^+][OH^-] / [B]$

$pK_b = -logK_b$

K_b is a constant at a given T for a given solvent; it is an intrinsic property of a compound

Basicity Constants at 25°C*

Base	K_b	pK_b
urea, $CO(NH_2)_2$	1.3×10^{-14}	13.90
aniline, $C_6H_5NH_2$	4.3×10^{-10}	9.37
pyridine, C_5H_5N	1.8×10^{-9}	8.75
hydroxylamine, NH_2OH	1.1×10^{-8}	7.97
nicotine, $C_{10}H_{14}N_2$	1.0×10^{-6}	5.98
morphine, $C_{17}H_{19}O_3N$	1.6×10^{-6}	5.79
hydrazine, NH_2NH_2	1.7×10^{-6}	5.77

*The values for K_b listed here have been calculated from pK_b values with more significant figures than shown so as to minimize rounding
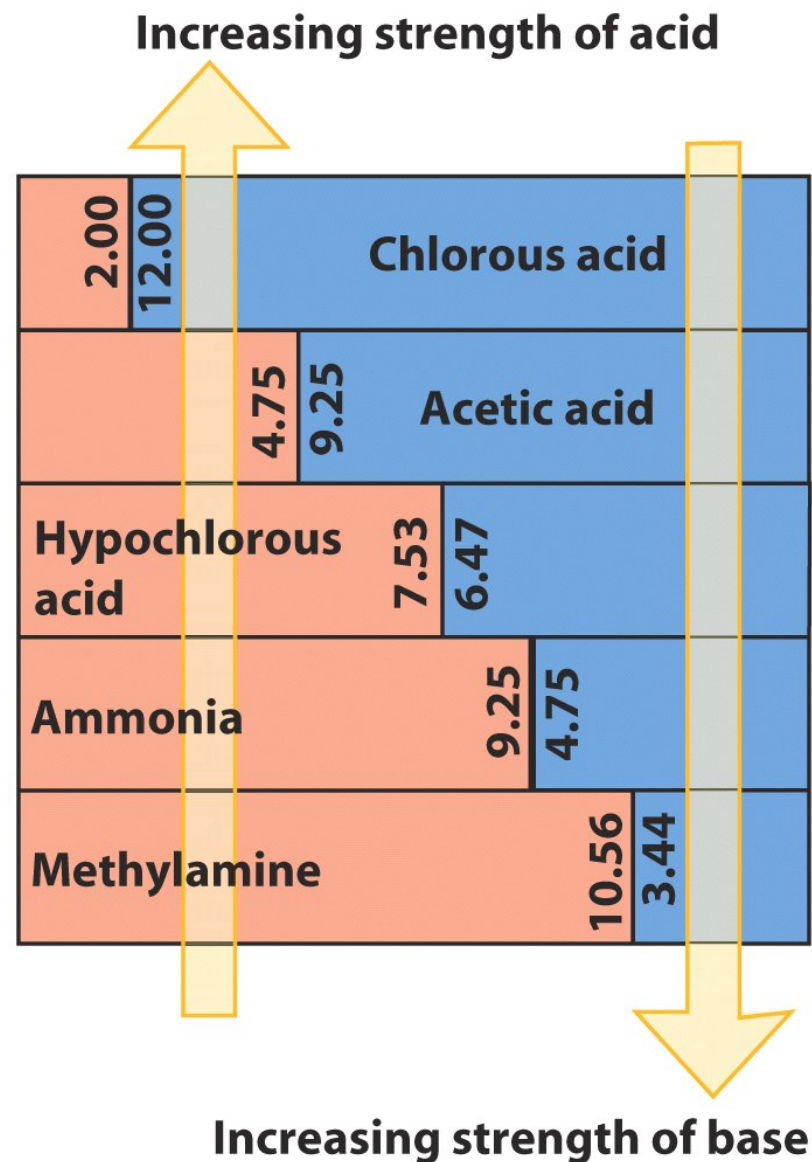
Conjugate acid-base pairs

The stronger the acid, the weaker its conjugate base

The weaker the acid, the stronger its conjugate base

$$K_a \times K_b = K_w$$

The pK_a value defines both acidity of the acid and the basicity of the conjugate base

Conjugate Acid–Base Pairs Arranged by Strength

Acid name	Acid formula	Base formula	Base name
Strong acid			**Very weak base**
hydroiodic acid	HI	I^-	iodide ion
perchloric acid	$HClO_4$	ClO_4^-	perchlorate ion
hydrobromic acid	HBr	Br^-	bromide ion
hydrochloric acid	HCl	Cl^-	chloride ion
sulfuric acid	H_2SO_4	HSO_4^-	hydrogen sulfate ion
chloric acid	$HClO_3$	ClO_3^-	chlorate ion
nitric acid	HNO_3	NO_3^-	nitrate ion
hydronium ion	H_3O^+	H_2O	*water*
hydrogen sulfate ion	HSO_4^-	SO_4^{2-}	sulfate ion
hydrofluoric acid	HF	F^-	fluoride ion
nitrous acid	HNO_2	NO_2^-	nitrite ion
acetic acid	CH_3COOH	$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3	HCO_3^-	hydrogen carbonate ion
hydrosulfuric acid	H_2S	HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+	NH_3	ammonia
hydrocyanic acid	HCN	CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-	CO_3^{2-}	carbonate ion
methylammonium ion	$CH_3NH_3^+$	CH_3NH_2	methylamine
water	H_2O	OH^-	*hydroxide ion*
ammonia	NH_3	NH_2^-	amide ion
hydrogen	H_2	H^-	hydride ion
methane	CH_4	CH_3^-	methide ion
hydroxide ion	OH^-	O^{2-}	oxide ion
Very weak acid			**Strong base**

Acidity and structure

Let us look at how the structure affects acidity of HA.

1) Which element is the hydrogen bound to?

The acidity increases from left to right in the periodic table and from up to down (for main group elements). This is not the same trend as for electronegativities!

Thus $HF > H_2O > NH_3 > CH_4$,

but $HI > HBr > HCl > HF$, or $H_2Te > H_2Se > H_2S > H_2O$

For otherwise analogous compounds, the one with the heaviest element bound to H is the more acidic one. E.g., CH_3SH is more acidic than CH_3OH, PH_3 is more acidic than NH_3 etc.

2) Substituents on the atom that is directly bound to H in HA that stabilize the anion A^- increase the acidity of HA. Generally, these are electron withdrawing substituents, however, both inductive and resonance effects must be taken into account.

Proton exchange in water

Water undergoes rapid autodissociation or autoprotolysis:

$$2H_2O \rightleftharpoons H_3O^+ + OH$$
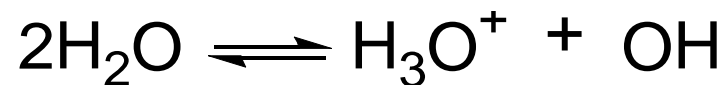
The equilibrium constant at 25 ºC for this process is

$K_w = 1.0 \times 10^{-14}$