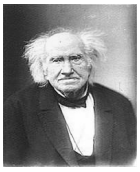
A long time ago….

- What is organic chemistry?
  - 1700s differences between living matter and minerals
  - Organic molecules difficult to isolate
  - Torbern Bergman (1770) – compounds of living organisms
  - Compounds have "vital force"
    - Can't be prepared or manipulated

Vital force theory – refuted

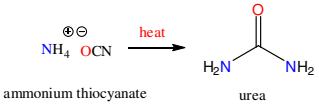
- Vital force theory didn't last very long
  - 1816 Michael Chevreul (discovered margarine)
  - Animal fat with NaOH made Soap and Glycerin



1886

Organic from inorganic compounds

- Preparation of Urea
  - 1828 Friedrich Wöhler prepared urea



ammonium thiocyanate

urea

1850

Why do atoms form bonds?

- The answer to this question
  - All atoms have energy
  - By forming bonds, this lowers the energy
  - Energy of compound is less than energy of atoms

Bond breaking absorbs energy

Bond making releases energy

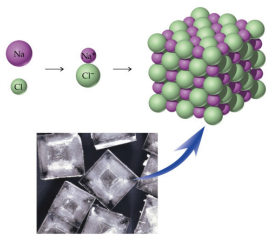
Notes on making ions.

- Notes
  - Easier to ionize ($\Delta H_{\text{ionization energy}}$ is small) elements to form **cations** for elements on left side of periodic table.
  - Easier to ionize ($\Delta H_{\text{electron affinity}} < 0$) to form anions for elements to right of periodic table.

Ionic bonds

- Example:

$$\mathbf{Na}_{(s)} + \mathbf{Cl}_{2\,(g)} \longrightarrow \mathbf{NaCl}_{(s)}$$



Na lose electron + 496 kJ

Cl gain electron -350 kJ

A violent reaction!

??? How come ???

Ionic compounds notes

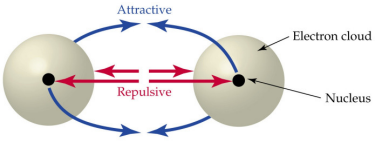
- Electrostatic attractions - cations and anions.
  - Metal transfer electron to nonmental
    Metal (cation) and nonmetal (anion)

Property of ionic solids

- High melting solids (eg NaCl mp 801°C)

Covalent bond

First look at a simple model of two H-H atoms forming a molecule



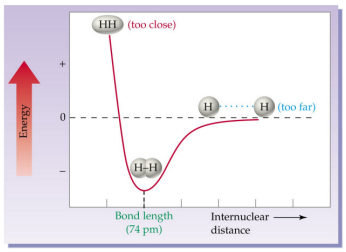
Repulsive forces 1. negative electrons
2. positive nuclei

Attractive forces 1. negative electrons with positive nuclei

What holds the two atoms together to form a molecule?

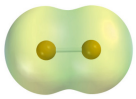
The bond length

- This is the optimum distance between the atomic nuclei.

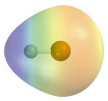


The covalent bond – sharing of electrons

1. **Nonpolar covalent**: equal sharing of electrons

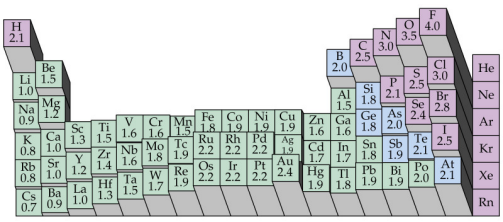
Cl:Cl 

2. **Polar covalent**: unequal sharing of electrons

$\delta^+H—Cl^{\delta-}$ 

Electronegativity

Electronegativity between atoms in a bond gives a good measure of bond polarity



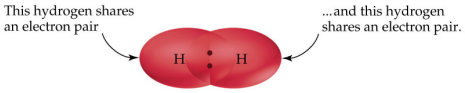
Bond polarity prediction (rough)

- Nonpolar covalent bonds
  - Same or similar electronegativities
- Polar covalent bonds
  - Electronegativity differs by less than 2 units
- **Ionic bonds**
  - Electronegativity differs by more than 2 units

Bonding theories

1. Electron dot structures (Lewis structures)
   - VSEPR (molecular geometry)
2. Valence bond theory
   - Hybridization of orbitals
3. Molecular orbital theory

1. Electron dot structure

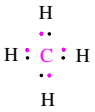


Special stability of Nobel gas electron configuration

- Ne $1s^2 2s^2 2p^6$ valence shell has 8 electrons (octet).
- Ar $1s^2 2s^2 2p^6 3s^2 3p^6$
  - -Group 1 – lose one electron
  - -Group 2 – loses two electrons
  - -Group 17 – gains one electron
  - -Group 16 – gains two electrons

Electron dot structures

Also known as **Lewis structures**



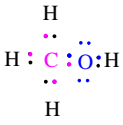
C electronic configuration: $1s^2 2s^2 2p^2$

Valence electrons are used in bonding

Carbon fulfill its requirement for 8 electrons

8 electrons = Octet

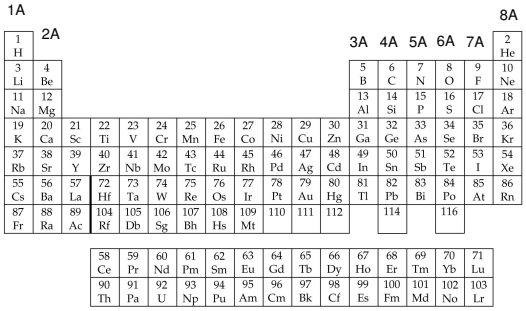
Electron dot structure of methanol



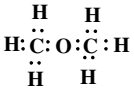
	Electron configuration
Carbon purple dots	$1s^2 2s^2 2p^2$
Oxygen blue dots	$1s^2 2s^2 2p^4$
Hydrogen black dots	$1s^1$

Goal is to attain Noble gas electron configuration

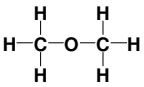
Periodic table: Old classification



Line bond structure



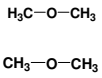
Electron dot structure
(Lewis structure)



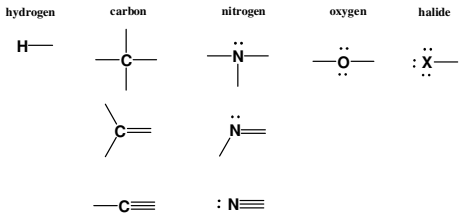
Line structure
(aka Kekulé structure)

CH_3OCH_3

Condensed structure



Electron dot distribution



Drawing Lewis structures

- Draw the Lewis structure for NCl_3

Steps: (note first atom listed is central atom)

1) Determine the number of valence electrons
2) Connect atoms
3) Complete octet on terminal atoms
4) Complete octet for central atom

Note: Lewis structures do not give the geometry of the structure

Examples

1) SF_2
2) $ClO_4^{\ominus}$
3) $POCl_3$

Formal Charge

- Several possible Lewis structures
  - Obey octet rule
- Formal charge definition: is the charge on an atom in a molecule if all atoms are given the same electronegativity
- This is electron "book keeping" of valence electrons
  - Find how many electrons does an atom "own"
  - Find how many are shared
  - Find how many are not shared

Formal charge = (VE – NBE – BE/2)

Resonance structures

- More than one possible Lewis structure

$NO_3^{\ominus}$

$NCS^{\ominus}$

Which structure is the **major** contributor?

Exceptions to the octet rule

1. Less than an octet

   BX_3 X = F, Cl, Br, I

   These molecules are very good Lewis bases

2. More than an octet

   PCl_5, SF_6, SiF_6^{2-} (central atom is large)

2. VSEPR Theory

- Gives the molecular geometry
  - Electron domain is region where electrons are most likely to be found)
    - Bonding electrons (single or multiple)
    - Non bonding electrons

How many electron domains are present in the following:

1. CH_4
2. $HC{\equiv}CH$
3. NH_3
4. BrF_5

Highlighted in red

Principle of electron domain

- Also called charged electron clouds
  - Negative charges that repel each other
  - Maximize distance away from each other
  - Minimize repulsions
  - Electron domain geometry (5 types)
  - Molecular geometry (actual shape of the molecule)
- Theory predicts shape of molecules, but doesn't explain the bonding between atoms in molecules.

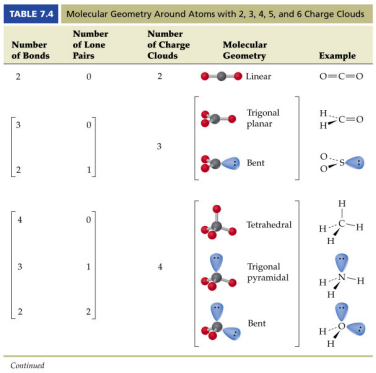


TABLE 7.4 Molecular Geometry Around Atoms with 2, 3, 4, 5, and 6 Charge Clouds

Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry	Example
2	0	2	Linear	O=C=O
3	0	3	Trigonal planar	H–C(=O)–H
2	1		Bent	O–S–O
4	0	4	Tetrahedral	CH4
3	1		Trigonal pyramidal	NH3
2	2		Bent	H2O

Continued

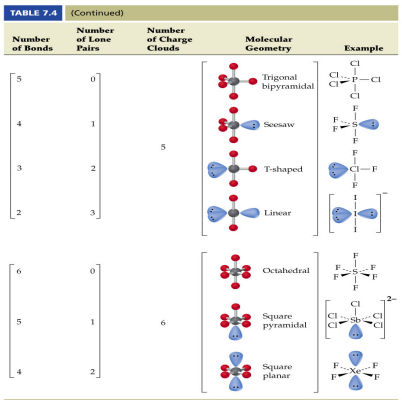
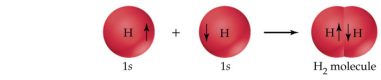


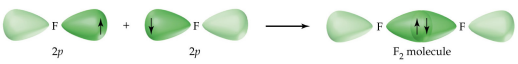
TABLE 7.4 (Continued)

Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry	Example
5	0	5	Trigonal bipyramidal	PCl5
4	1		Sawsaw	SF4
3	2		T-shaped	ClF3
2	3		Linear	I_3^-
6	0	6	Octahedral	SF6
5	1		Square pyramidal	$SbCl_5^{2-}$
4	2		Square planar	XeF4

3. Valence bond theory

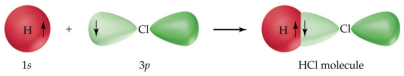
- This is an extension of Lewis's bonding theory.
  - Valence atomic orbitals are involved in bonding





What about Helium?

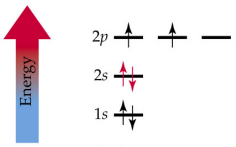
Other atomic orbital overlap



What about CH_4?

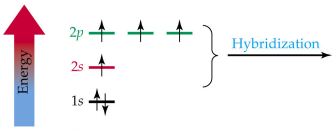
Hybridization of orbitals

- This is a bonding theory.
- How can atomic orbitals become hybridized?



Carbon:
ground-state electron
configuration

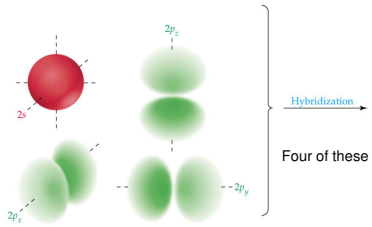
Hybridization



Carbon:
excited-state electron
configuration

The result - **to make four orbitals equal in size and energy**

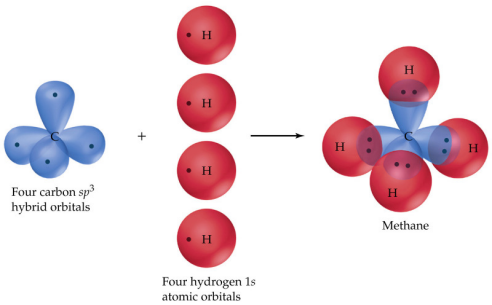
Alternative view



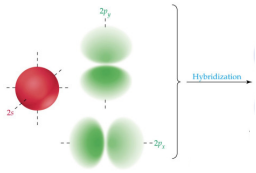
Four of these

Non bondir

Methane orbitals

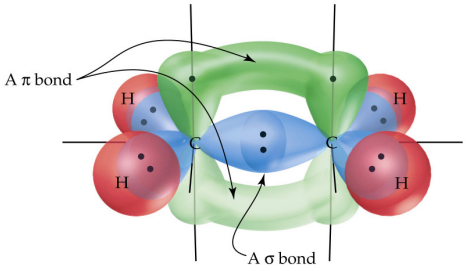


Hybridization sp^2

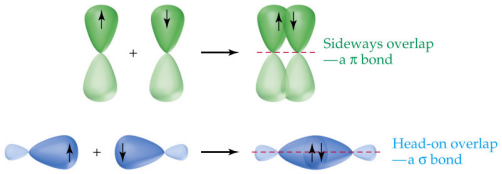


Three of these are formed

Bonding in ethylene



The overlap summary



Net result from hybridization

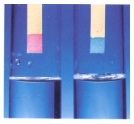
- Bond angles can be predicted
  - sp^3 hybridization: 109.5°
    - Typical of Carbon with four single bonds
  - sp^2 hybridization: 120°
    - Typical for presence of one double bond
  - sp hybridization: 180°
    - Typical for presence of one triple bond

Hill, Baum, and Scott-Ennis, "Chemistry of Life", page 224

Some properties of acids

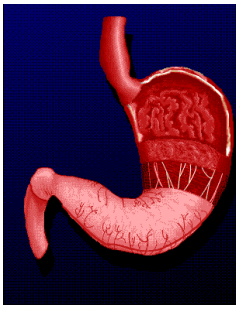
WHMIS Label

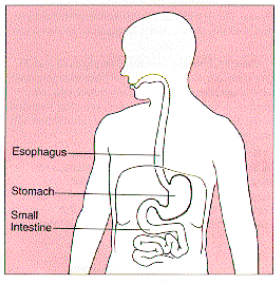
Acid



Base

Acid in your belly

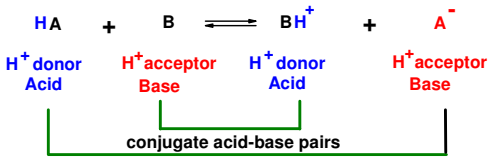




Bronsted-Lowry definitions

- Acid – donates $H^{\oplus}$ (protons)
- Base – accepts $H^{\oplus}$ (protons)
- Water is amphiprotic

Bronsted Lowry – Acid-Base



Strong acids give weak conjugate bases

Strong acids

- 100% ionize in water

HCl, HBr, HI, HNO_3, H_2SO_4, and $HClO_4$

$$HCl + H_2O \longrightarrow H_3O^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$$

Acid base

$$HCl_{(aq)} \longrightarrow H^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$$

Strong bases

- Most strong bases contain (hydroxide ion)
  - Strong bases are soluble in water

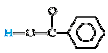
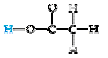
NaOH, KOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$

$$Ca(OH)_{2\,(s)} + H_2O \longrightarrow Ca^{2+}_{(aq)} + 2OH^{\ominus}_{(aq)}$$

Other strong bases: **$NaOCH_3$, $KOCH_3$, NaOR, KOR**

Examples of weak acids

SOME WEAK ACIDS IN WATER AT 25°C*

Acid	Molecular Formula	Structural Formula	Conjugate Base	Ka
Hydrofluoric	HF	H—F	F^-	6.8×10^{-4}
Nitrous	HNO_2	H—O—N=O	NO_2^-	4.5×10^{-4}
Benzoic	$HC_7H_5O_2$		$C_7H_5O_2^-$	6.5×10^{-5}
Acetic	$HC_2H_3O_2$		$C_2H_3O_2^-$	1.8×10^{-5}
Hypochlorous	HClO	H—O—Cl	ClO^-	3.0×10^{-8}
Hydrocyanic	HCN	H—C≡N	CN^-	4.9×10^{-10}
Phenol	HOC_6H_5		$C_6H_5O^-$	1.3×10^{-10}

* The proton that ionizes is shown in blue.

The meaning of Ka

$$HB\,(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$pK_a = -\log_{10} K_a$$

Periodic trends (binary acids)

- Binary acids (H-E), where E = element

Across a period

CH_4 < NH_3 < H_2O < HF

($H\text{-}CH_3$) ($H\text{-}NH_2$) H-OH H-F

What causes this trend?

Periodic trends

Down a Group

F	H-F
Cl	H-Cl
Br	H-Br
I	H-I

stronger acids at bottom

Based on **strength of bond**

Organic acids

- Derivatives of water HO–H pKa = 15.7

Alcohols:

$CH_3O\text{–}H$ Methanol **pKa = 15.2**

$CH_3CH_2O\text{–}H$ Ethanol **pKa = 16**

$(H_3C)_2CH\text{–}O\text{–}H$ Isopropanol **pKa = 17**

$(H_3C)_3C\text{–}O\text{–}H$ *tert*-butanoll **pKa = 18**

Organic acids

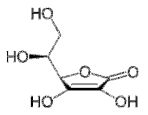
$CH_3CH_2O\text{–}H$ ethanol **pKa = 16**

$CF_3CH_2O\text{–}H$ 2,2,2-Trifluroethanol **pKa = 11.3**

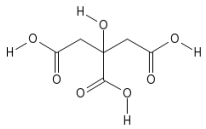
H_3CCO_2H Acetic acid **pKa = 4.7**

F_3CCO_2H Trifluoroacetic acid **pKa = 0.50**

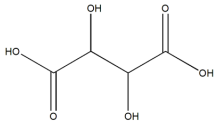
Organic acids



Ascorbic acid



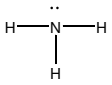
Citric acid

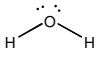


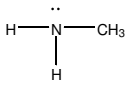
Tartaric acid

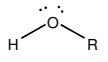
Recognizing bases

- Neutral bases
  - Has lone pair of electrons
  - Normally an Oxygen atom or Nitrogen atom



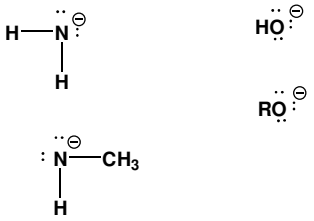






Recognizing bases

- Negatively charged molecules



K_b

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

•The base dissociation constant, *Kb*, is defined as

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Weaker the acid gives **stronger the conjugate base**

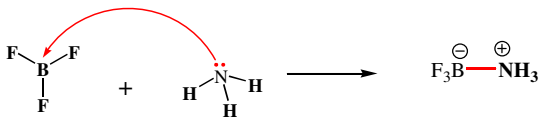
SOME WEAK BASES AND THEIR AQUEOUS SOLUTION EQUILIBRIA

Base	Lewis Structure	Conjugate Acid	Equilibrium Reaction	K_b
Ammonia (NH_3)		NH_4^+	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Hydroxylamine (H_2NOH)		H_3NOH^+	$H_2NOH + H_2O \rightleftharpoons H_3NOH^+ + OH^-$	1.1×10^{-8}
Methylamine (NH_2CH_3)		$NH_3CH_3^+$	$NH_2CH_3 + H_2O \rightleftharpoons NH_3CH_3^+ + OH^-$	4.4×10^{-4}
Hydrosulfide ion (HS^-)		H_2S	$HS^- + H_2O \rightleftharpoons H_2S + OH^-$	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	1.8×10^{-4}
Hypochlorite ion (ClO^-)		HClO	$ClO^- + H_2O \rightleftharpoons HClO + OH^-$	3.3×10^{-7}

The Lewis Definition of acids and bases

- Lewis acid – substance that accepts a pair of e-
  - Hydronium ion ($H^{\oplus}_{(aq)}$) found in compounds
  - Compounds: $ZnCl_2$, $TiCl_4$, $FeCl_3$, $FeBr_3$)
  - Metal cations ($Li^{\oplus}$, $Na^{\oplus}$, $Mg^{2\oplus}$)
- Lewis base – substance that donates a pair of e-
  - Compounds containing lone pairs to donate.
    - Contain N or O or S
- Amphiprotic– can act as acid or base

Curved arrows to show electron flow



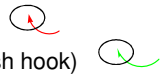
Boron trifluoride
Acid

Ammonia
base

Adduct - salt

More about curved arrows

- Full arrow head
- Half arrow head (fish hook)



- Arrow *starts* at electron rich (nucleophile) to *point* at e- poor (electrophile)

Other examples

- Show on blackboard
  - HCl and Ethanol
  - H_2SO_4 and CH_3COOH
  - H_2SO_4 and acid chloride