Polar Covalent Bonds:
Acids and Bases

Topics

Part 1:

Polarity, Electronegativity and Dipole Moments

Polarity Applied

Formal Charges

Resonance (Rules and Forms)

Part 2:

Bronsted-Lowry Acids & Bases

Acid Base Strength

Predicting Acid Base Reactions from pKa Values

Organic Acids and Bases

Lewis Acids and Bases

Non-covalent interactions between molecules

Pauling Electronegativity Values

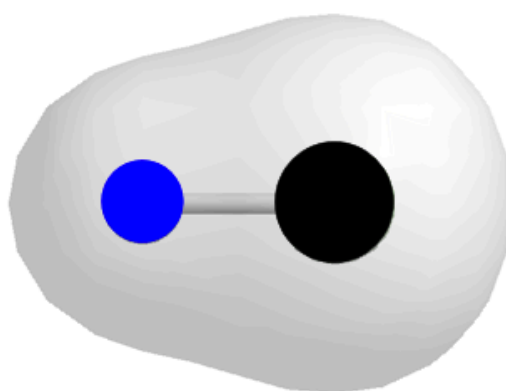| 1 H 2.20																	
3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98	
11 Na 0.93	12 Mg 1.31											13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16	
19 K 0.82	20 Ca 1.00	21 Sc 1.36	22 Ti 1.54	23 V 1.63	24 Cr 1.66	25 Mn 1.55	26 Fe 1.83	27 Co 1.88	28 Ni 1.91	29 Cu 1.90	30 Zn 1.65	31 Ga 1.81	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96
37 Rb 0.82	38 Sr 0.95	39 Y 1.22	40 Zr 1.33	41 Nb 1.6	42 Mo 2.16	43 Tc 1.9	44 Ru 2.2	45 Rh 2.28	46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66
55 Cs 0.79	56 Ba 0.89	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 2.36	75 Re 1.9	76 Os 2.2	77 Ir 2.20	78 Pt 2.28	79 Au 2.54	80 Hg 2.00	81 Ti 1.62	82 Pb 2.33	83 Bi 2.02	84 Po 2.0	85 At 2.2
87 Fr 0.7	88 Ra 0.9															

- Scale made of arbitrary units
- Metals = weakly attract electrons
- Non-metals, metalloids, halogens = strongly attract electrons
- Noble gasses do not attract electrons
- Bond difference of electronegativity (Δ EN) for reactions mechanisms
- Molecular sum of electronegativity (dipole moment) for reaction solvents and extractions

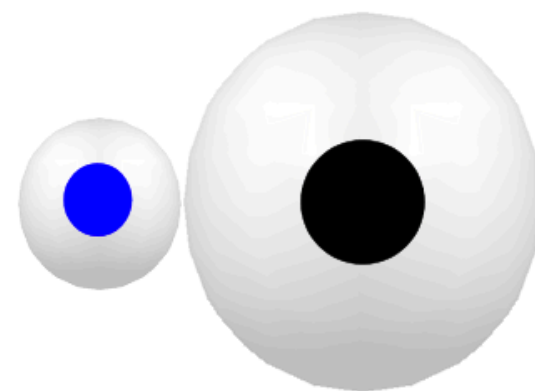# Polar Covalent Bonds - Electronegativity
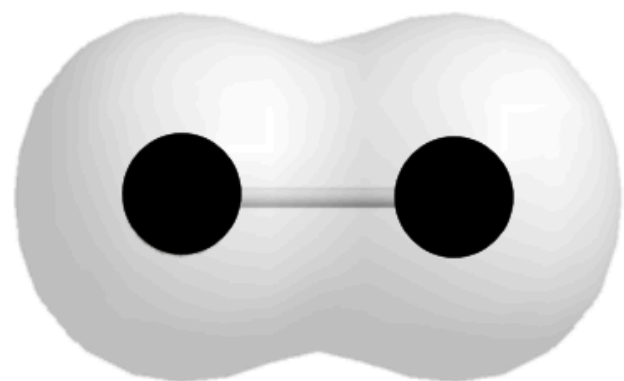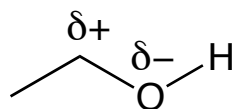

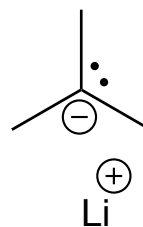| Nonpolar Covalent Bond	Polar Covalent Bond	Ionic Bond
ΔEN 0-0.4	ΔEN 0.4-2.0	ΔEN > 2.0

Most organic compounds

ethanol

t-butyllithium

$\Delta EN = 3.5 - 2.5 = 1.0$ $\Delta EN = 2.5 - 1.0 = 1.5$

Polar Covalent Bonds

- Individual bonds are polarized
- Molecules as a whole act as vector sum of
  - All individual bond polarities
  - Lone pair contributors

  When vector sum of all +ve and –ve charges do not perfectly align, there's a dipole moment

- Dipole moment = net molecular polarity

Dipole Moments of Some Common Compounds and Organic Solvents

Dipole moment (μ) = Q x r

Q = charge magnitude at either end of molecular dipole
r = distance between the charges
1 Debeye (D) = 3.336 x 10^{-30} Coulomb x meter

Physical properties influenced:

- boiling point, melting point
- solubility (e.g "like dissolves like")

Compound	Dipole Moment (D)
NaCl*	9.0
CH_3Cl	1.87
H_2O	1.85
NH_3	1.47
CO_2	0
CCl_4	0

* Measured in the gas phase.

Compound	μ (debye)
CCl_4	0.00
Ethanol	1.73
Thiophene	0.51
t-Butanol	1.67
Ethyl ether	1.30
Benzene	0.00
Chlorobenzene	1.58
Fluorobenzene	1.35
Phenol	1.55
Aniline	1.56
Toluene	0.43
Anisole	1.25
Diphenylamine	1.08
Water	1.82

Electronegative atoms with lone pairs

- Oxygen, Nitrogen, Halogens
- Lone pairs extend into space away from +ve nuclei
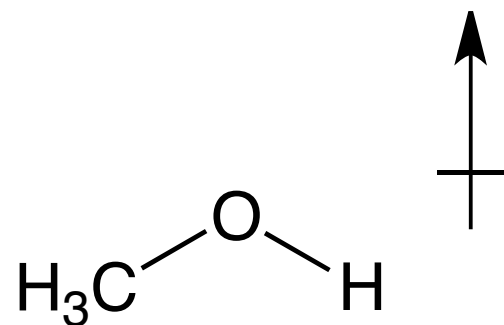- Causes charge separation
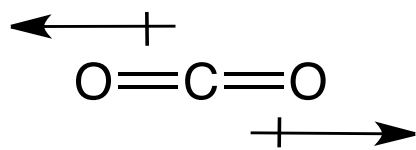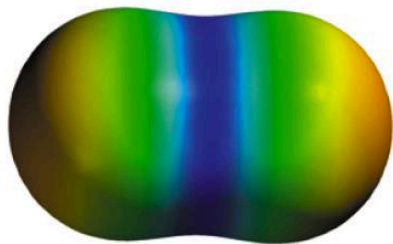- ***Large contribution to μ***

Asymmetric Bond Polarities Add
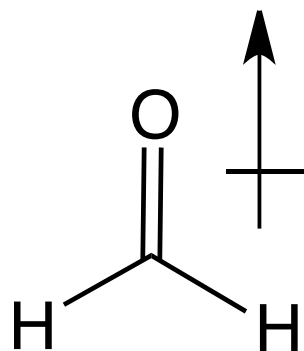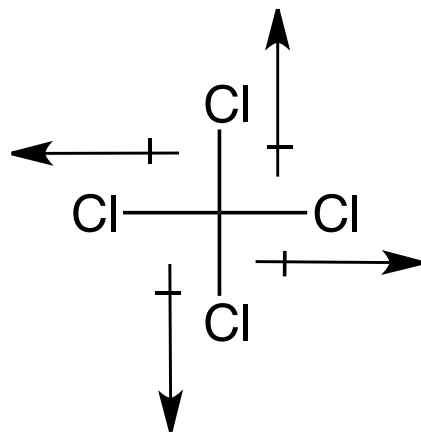

Formaldehyde
= 2.33 D
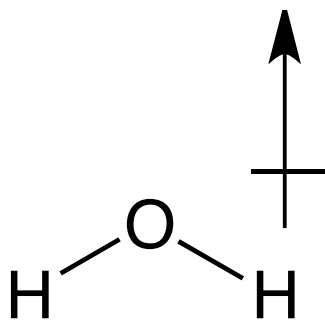
Water
= 1.85 D
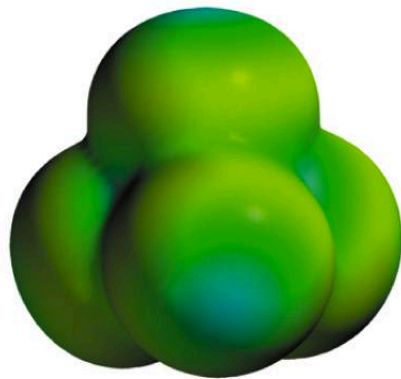
Methanol
= 1.70 D

Symmetrical bond polarities cancel

O=C=O

Carbon dioxide
= 0 D

Cl—C—Cl with Cl above and Cl below

Carbon tetrachloride
= 0 D
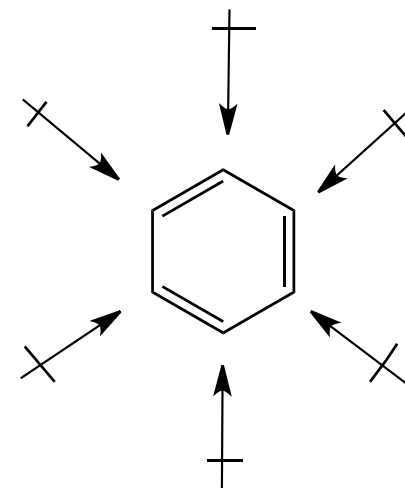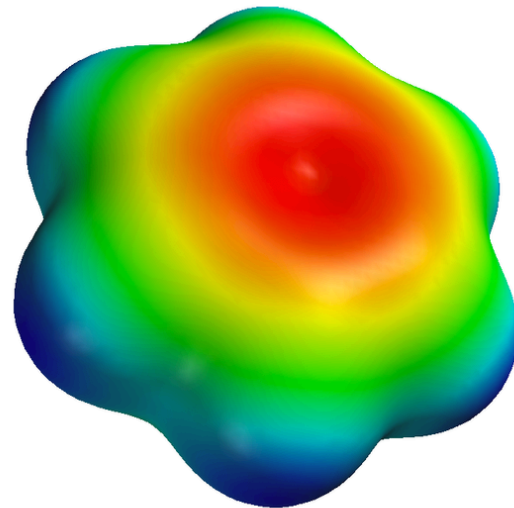
Benzene
= 0 D

Inductive effects

- Induction = shifting e-s in a sigma (σ) bond in response to electronegativity of neighboring atoms

- Metals (Group I, II and transition elements) inductively *donate* electrons

- Non-metals (N, O, halogens) inductively *withdraw* electrons

Polarity Applied in the Kitchen

- Chemical extractions "like dissolves like"
- Reaction "work-up" for product purification
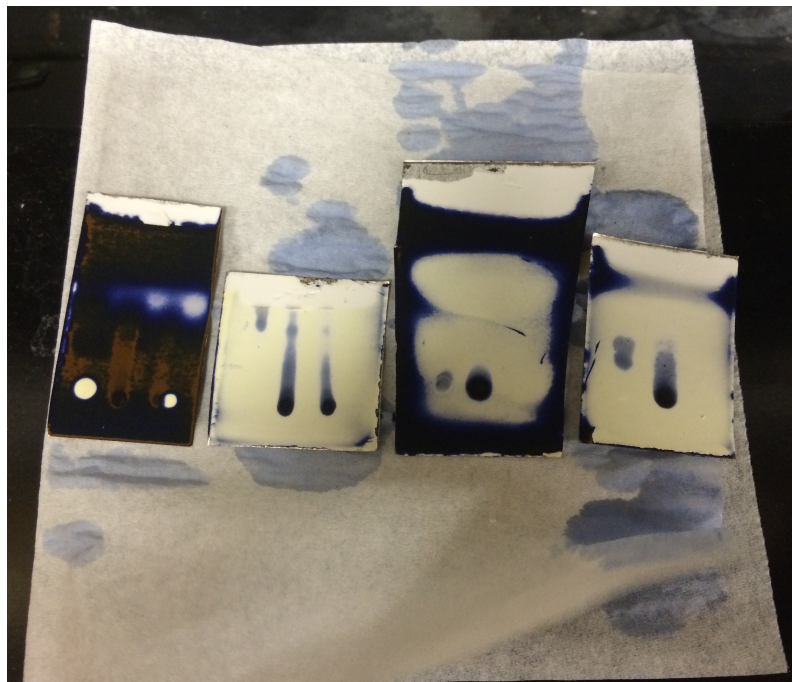

"Drip" extraction
(hot water)

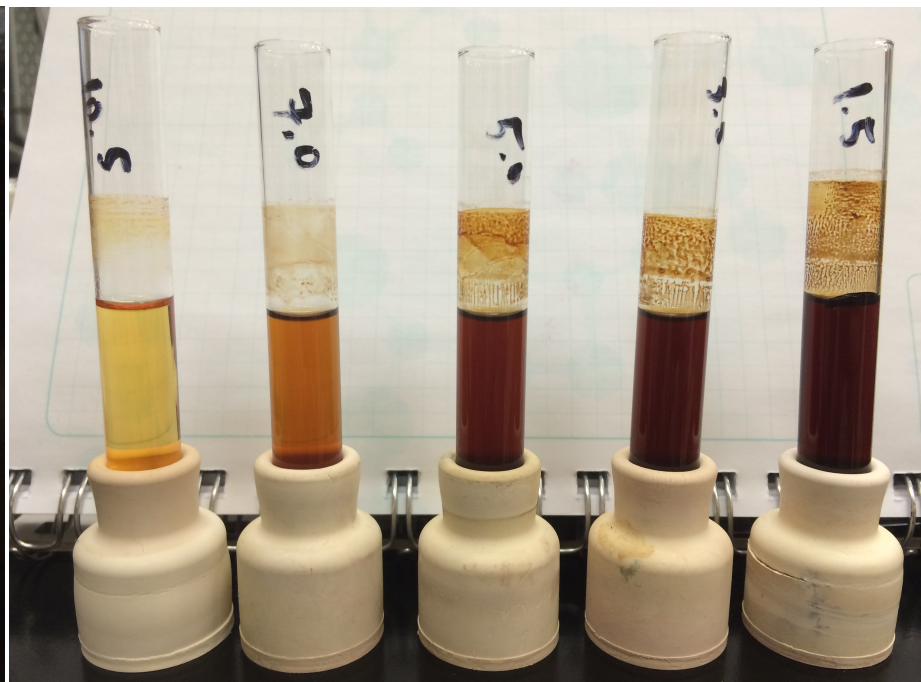"Espresso" extraction
(steam = pressure)

"Siphon funnel" extraction
(perfect temp, vacuum filtration)

# Polarity Applied in the Lab: Chromatography and pH dependent extractions

Thin Layer Chromatography (TLC) of vanillin and "vanillin amine" crude reaction mixtures using (L -> R) 100% EtOAc; 1: 1 EtOAc: toluene, 100% hexane, 1: 1 hexane: EtOAc

pH dependent extractions of depolymerized lignin (a polyphenol) showing increasing concentration (as visable light absorbance) with lower pH values

Polarity Applied on the Computer: Electrostatic potential maps of ionic liquids
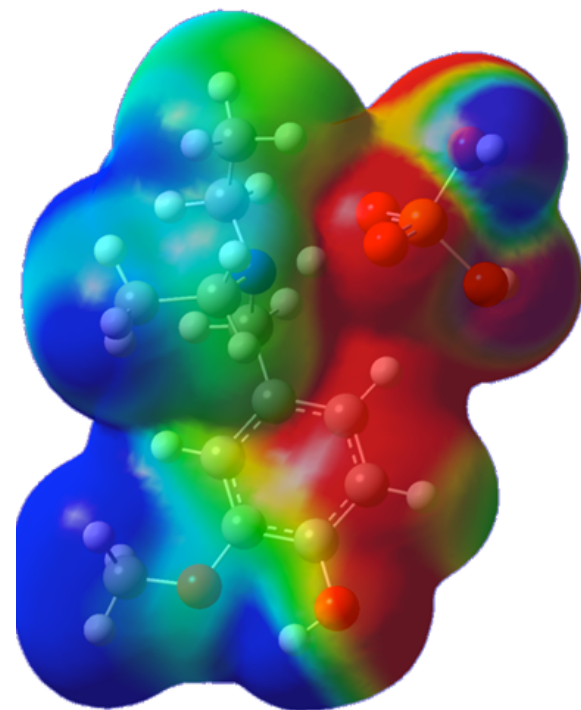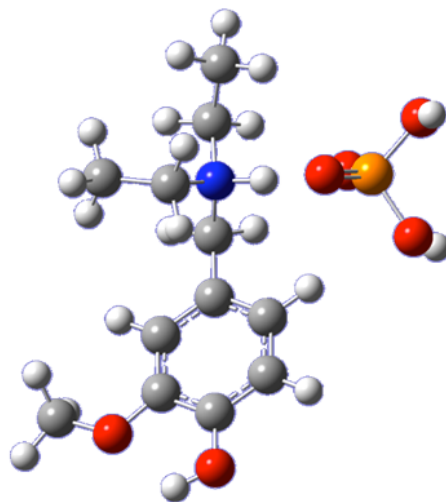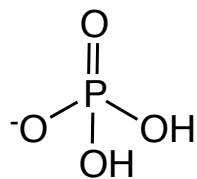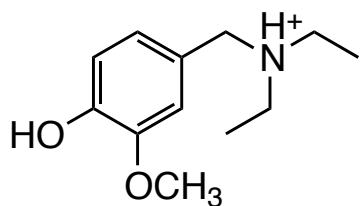
C (grey), H (white), N (blue), O (red), P (orange)

Red = High electron density (-)
Blue = Low electron density (+)

- Used to visualize charge distribution using electrostatic potential energy
- Electrostatic potential energy = K $[(q_1 * q_2) / r]$
  where K = Coulomb's constant, q = charge and r = radius
- Allow prediction of molecular interaction and reaction potential for portions of complex molecules
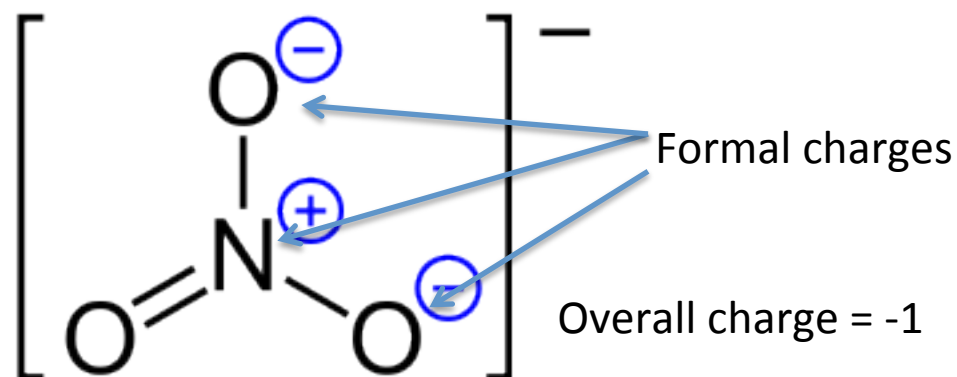
Formal Charge

"Electronic book-keeping"
Calculated for individual atoms in a molecule

valance e-s in free atom
- (# bonding electrons/ 2)
<u>- # of non-bonding electrons</u>
Formal Charge

Formal charges

Overall charge = 0

Ozone

Formal charges

Overall charge = -1
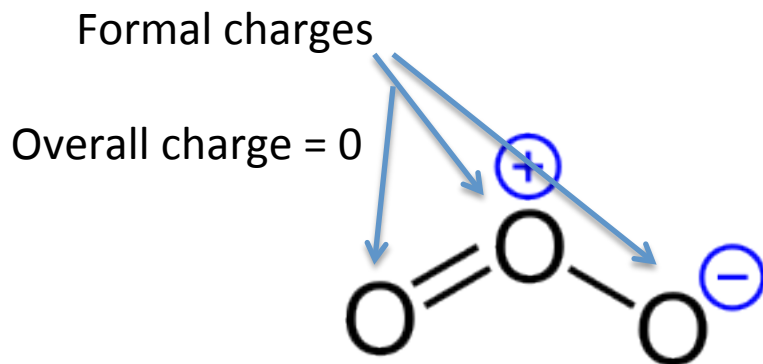
Nitrate

Formal Charge Practice Problems

- Draw the following compounds and calculate the formal of all atoms then calculate the net charge of the entire molecule:

    1. carbon dioxide

    2. carbon monoxide

    3. propyl nitrile

    4. butyldiazenide

Resonance Structures: Resonance Forms and Hybrids

"The state attributed to certain molecules of having a structure that cannot adequately be represented by a single structural formula - but is rather a composite of two or more structures of different energies/stabilities."

- *Resonance form*: individual Kekulé structures
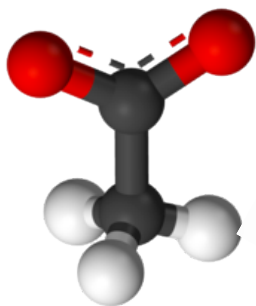- *Resonance hybrid*: the actual molecular structure

The molecules have single, unchanging structures; they do not switch back and forth between resonance forms

- a.k.a "When there's more than one way to draw the same molecule"
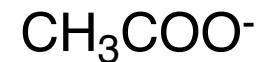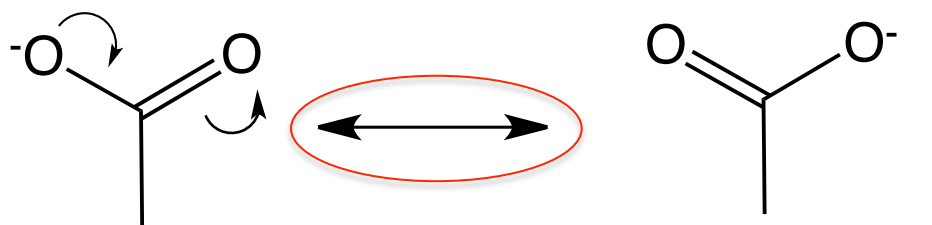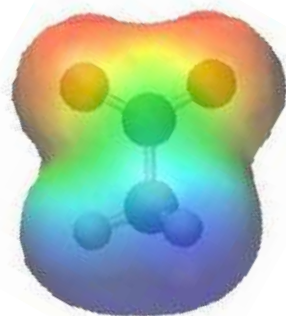
Resonance forms of the acetate anion are experimentally equivalent

O   ⊖   O

127 pm   127 pm

CH₃COO⁻
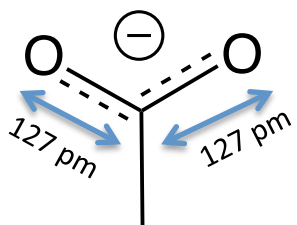
Resonance *hybrid*

Resonance hybrid models
ball and stick (L) and electrostatic (R)

⁻O   O

CH₃COO⁻

O   O⁻

CH₃COO⁻

Individual resonance forms
* note double headed arrow is different than two equilibrium arrows

- Acetate C-O bond length measured at 127 pm which is halfway between a single C-O bond (120 pm) and double C=O bond (135pm)
- Confirmed by electrostatic model
- π and non-bonding electrons move, not atoms
- Overall 3D shape remains the same

Why Draw Resonance Forms

- Resonance hybrids can not be used to clearly illustrate reaction mechanisms

- If the individual structures did exist, the most thermodynamically stable structures would comprise more of the hybrid

- The structure of the product is influenced by which resonance form reacts

When to Draw Resonance Forms?

1. *Molecules with resonance always involve at least one double bond*

2. *Resonance forms differ only in the placement of their π or nonbonding electron(s):*

   - A curved arrow always represents the movement of electrons, not the movement of atoms

Double headed arrow = 2 electron movement

Single headed arrow = 1 electron movement (radical)

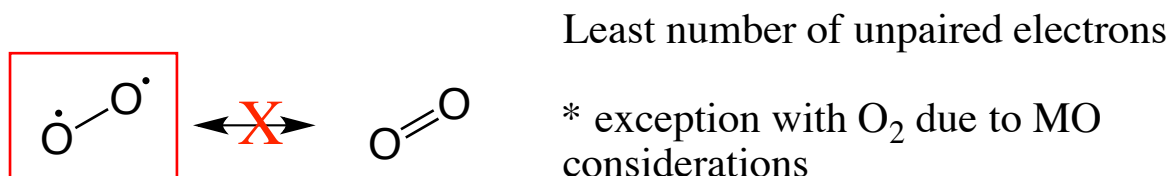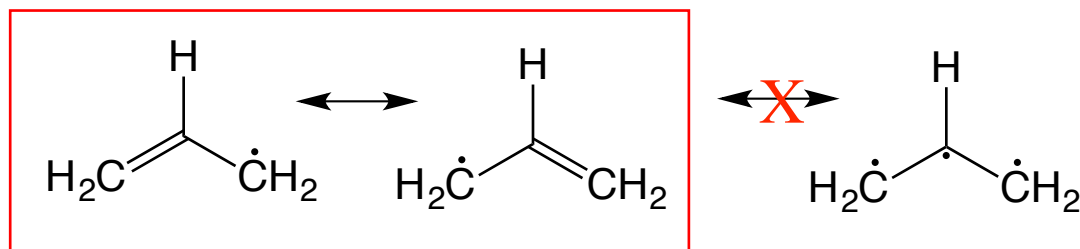3. *More resonance forms the better.* Because more negative charge can *delocalize* over more positive nuclei
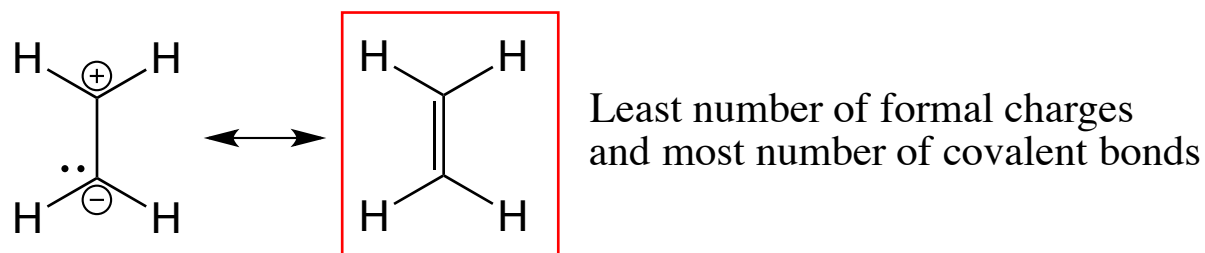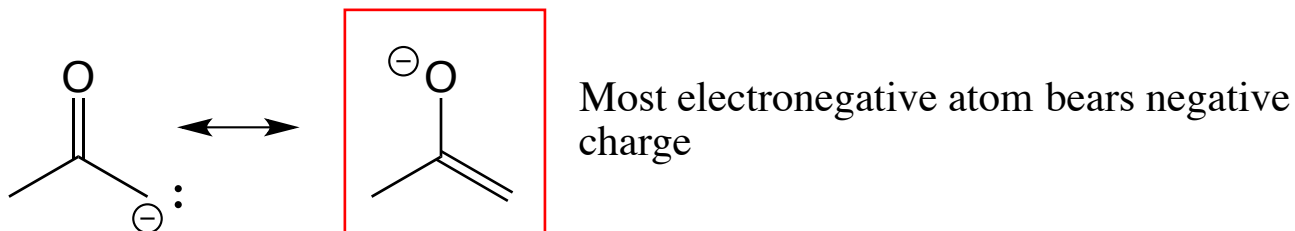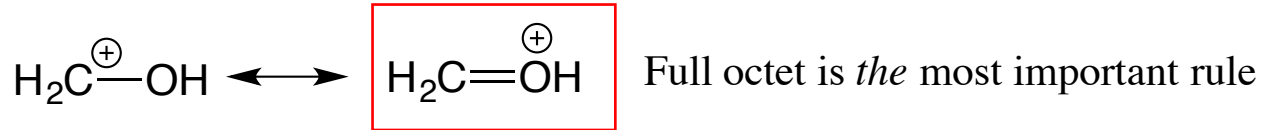
How to Draw Resonance Forms

The most important resonance form has the maximum number of atoms with full octets

If a resonance form must have a formal charge(s), the resonance form should accommodate the charge(s) appropriately. Otherwise minimize formal charge(s).

Maximize the number of covalent bonds

Minimize the number of unpaired electrons

$H_2C^{\oplus}-OH \longleftrightarrow \boxed{H_2C=\overset{\oplus}{O}H}$ Full octet is *the* most important rule

 Most electronegative atom bears negative charge

 Least number of formal charges and most number of covalent bonds

Least number of unpaired electrons

* exception with O_2 due to MO considerations

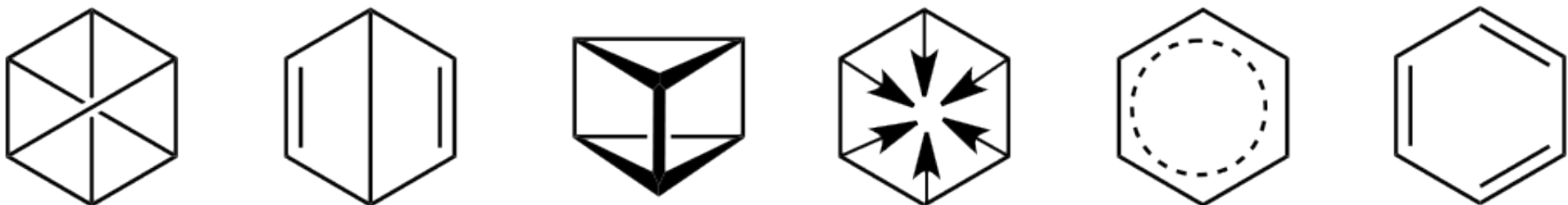# 1906: Benzene used to make *Café Sanka* (decaffeinated coffee)
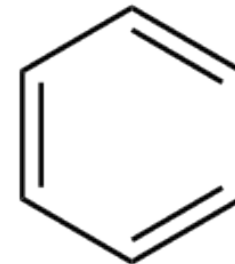
Benzene – a proven carcinogen
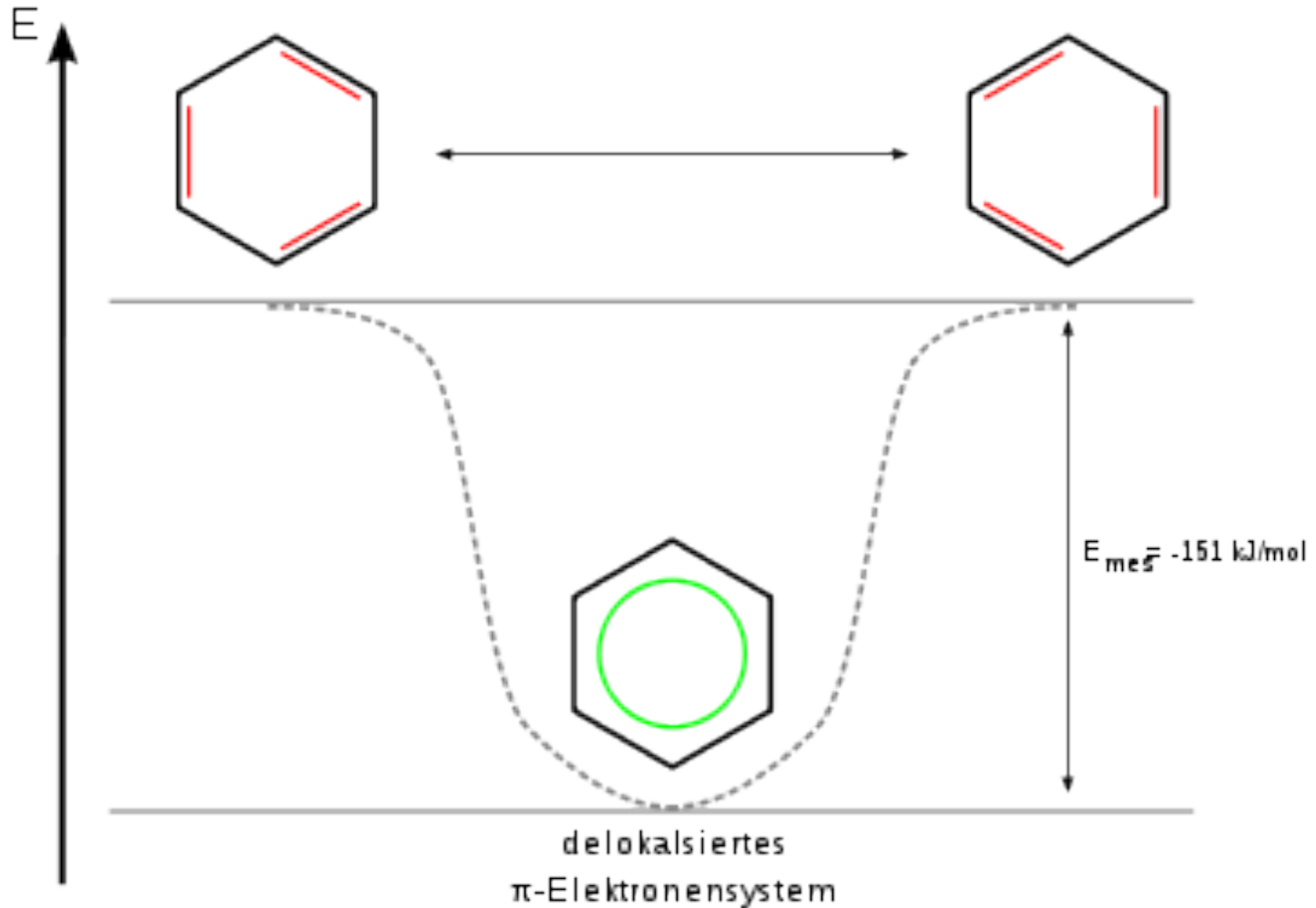
Benzene (1867-today)

Again, experimentally measured bond length represents the average of a single and a double bond

Cyclohexane C-C bond = 147 pm
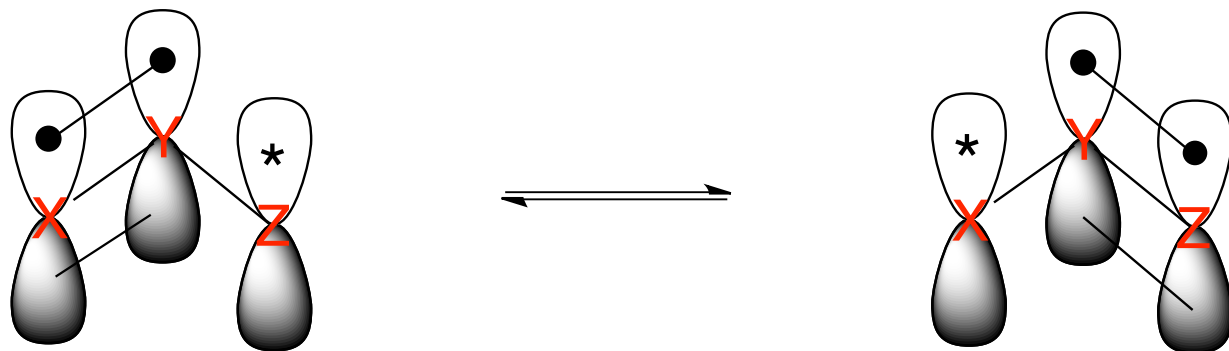Cyclohexene C=C bond = 135 pm

Benzene C--C bond = 140 pm

Resonance stability

$E_{mes} = -151$ kJ/mol

delokalsiertes
π-Elektronensystem

Drawing resonance structures

- Any 3 atom grouping with a p-orbital on each atom has 2 resonance forms

X, Y or Z = C, N, O, P, S or other atoms

- Asterisk (*) indicates the p-orbital is **either** vacant, contains a single e- (radical) **or** an e- pair (lone pair)

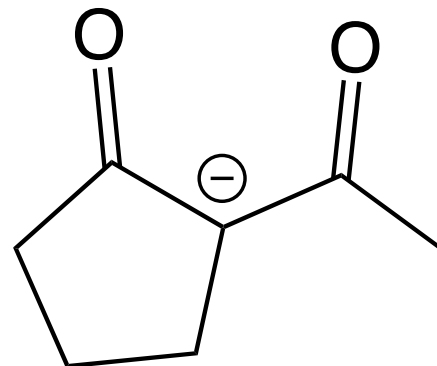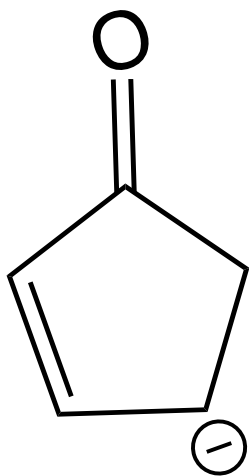- Exchange the position of the multiple bond and the * from one end of the molecule to the other
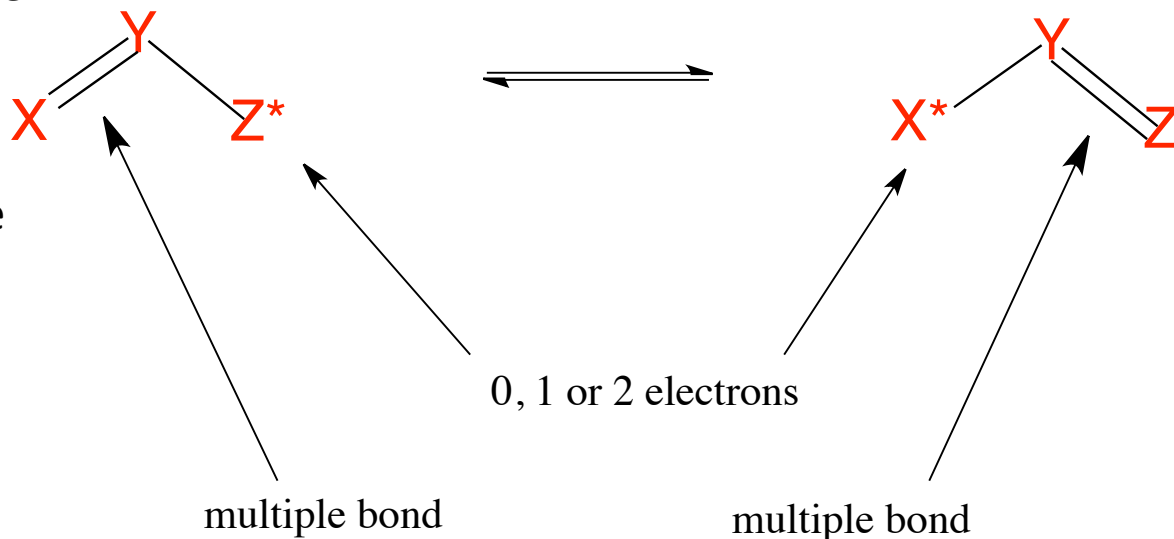
Some examples:

2,4 – pentanedione anion
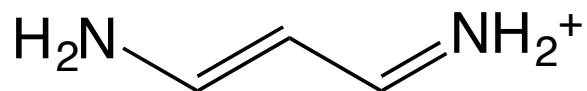Carbonate anion
Pentadienyl radical

0, 1 or 2 electrons

multiple bond

multiple bond
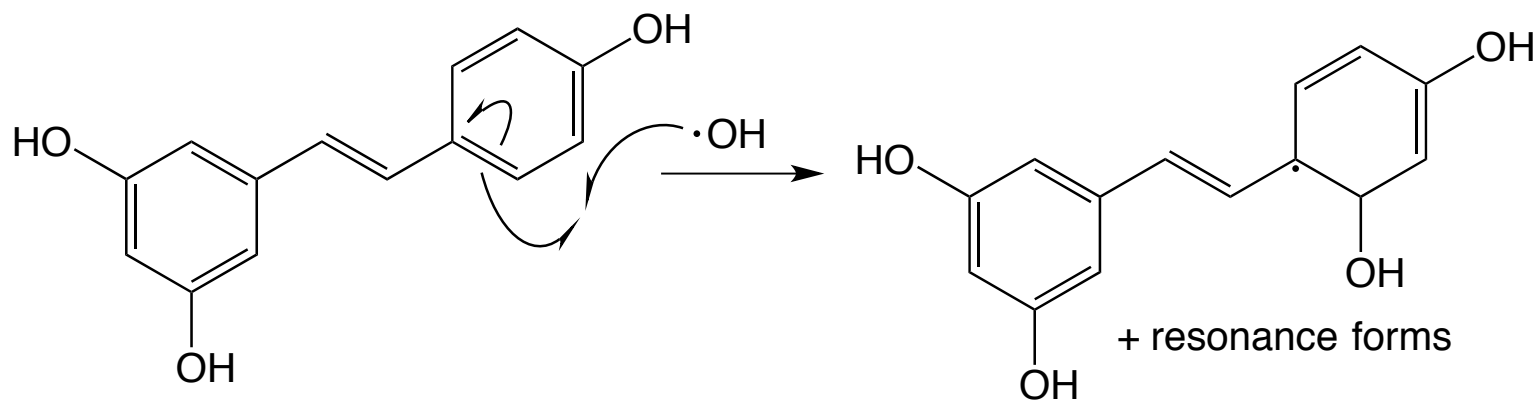
Practice Problems: Draw all resonance forms of the following compounds
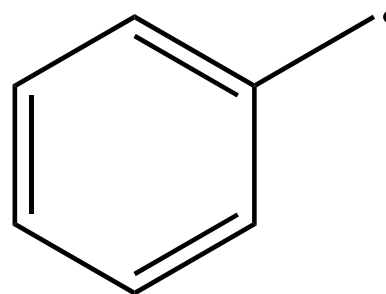
Antioxidant activity of resveratrol: an example of multiple resonance forms that "quenches" free radicals


resveratrol

hydroxy resveratrol radical

+ resonance forms

Coffee Antioxidants

- Chlorogenic acids (CGAs)

- 12% of dry weight of green (unroasted) beans

- Large Range 20-675 mg per cup

- Concentration dependent on extraction technique

- Decaffeinated coffee can have equal or more CGAs per cup

- These compounds are also the reason for the colors of both coffee and red wine

http://www.rsc.org/chemistryworld/Issues/2011/May/ChemistryInEveryCup.asp
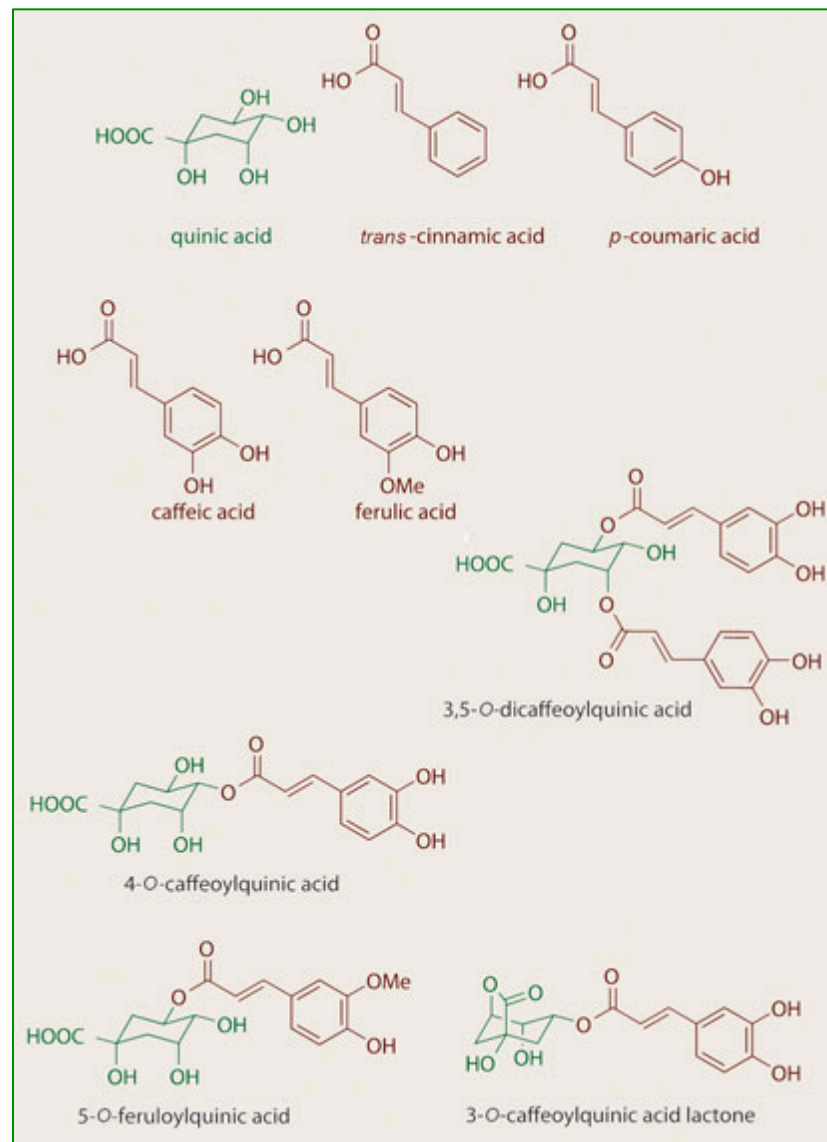
Part 2: Acids and Bases

Organic compound acidity (pKa) and basicity determines:
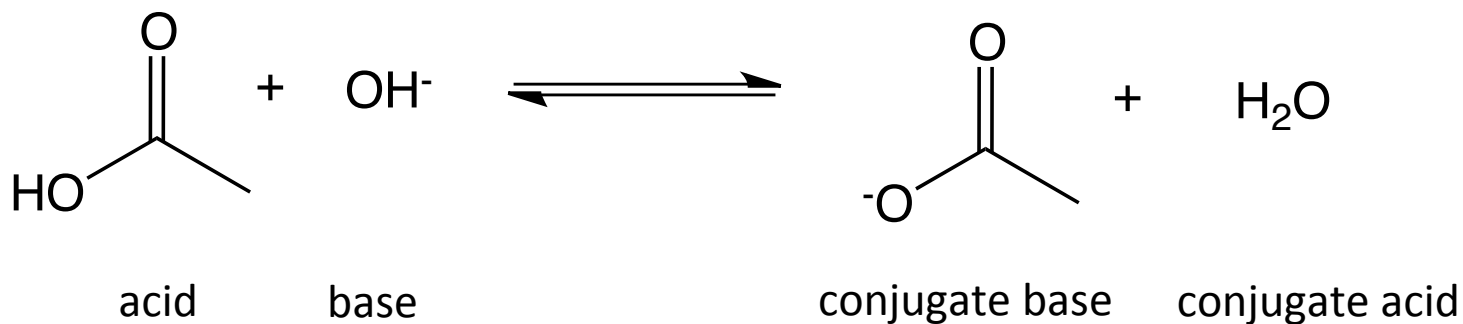
- reactivity
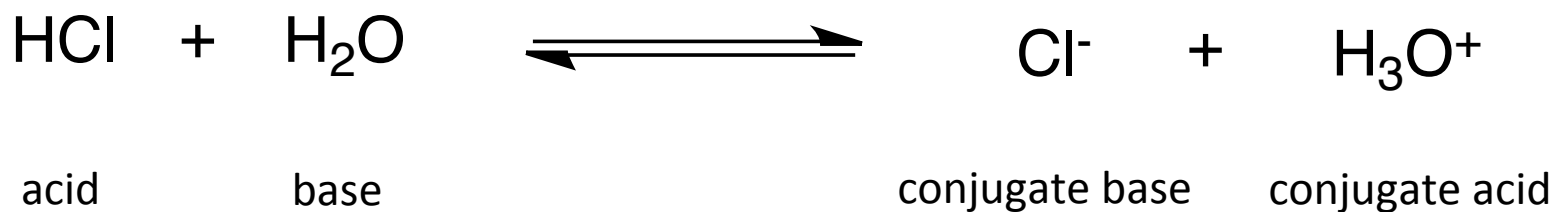- solubility

Under appropriate pH conditions

Brønsted Acids and Bases

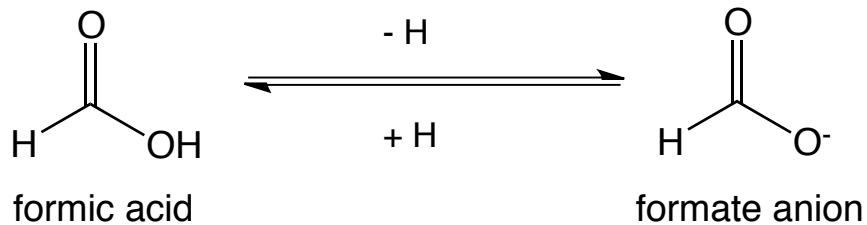- Acids = Donate H^+ (hydrogen ion, aka proton)
- Bases = Accept H^+

Nomenclature
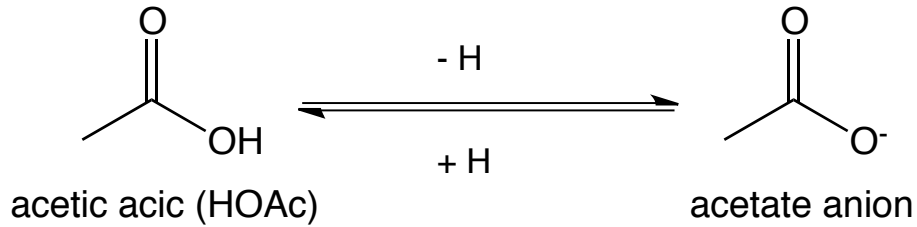- Acids and conjugate acids (both donate H^+)
- Bases and conjugate bases (both accept H^+)
  - "An acid is an acid, and a base is a base"

Acid base chemistry

$$HCl \; + \; H_2O \; \rightleftharpoons \; Cl^- \; + \; H_3O^+$$

acid   base   conjugate base   conjugate acid

acid   base   conjugate base   conjugate acid

Legal Examples

acetic acic (HOAc) ⇌ (- H / + H) acetate anion
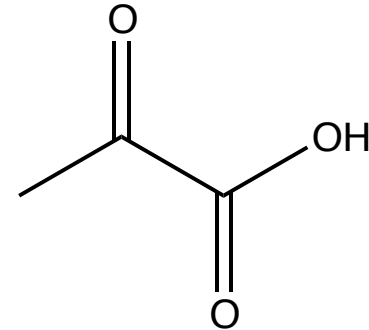
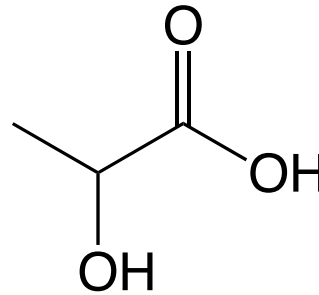formic acid ⇌ (- H / + H) formate anion

Legal examples cntd
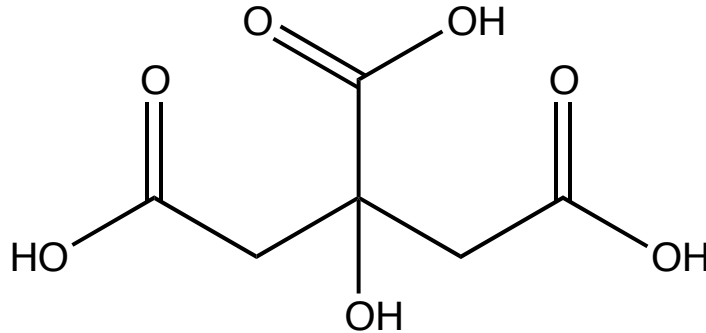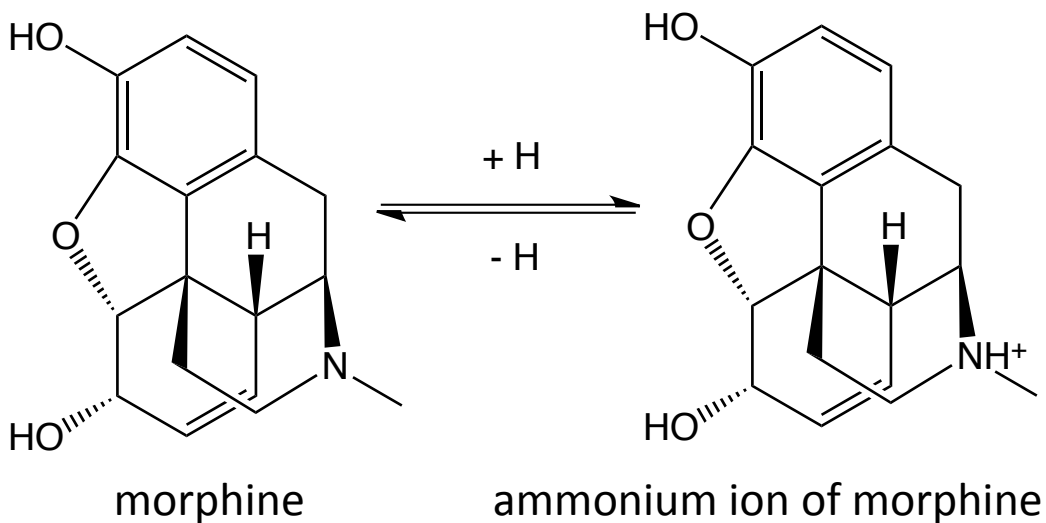
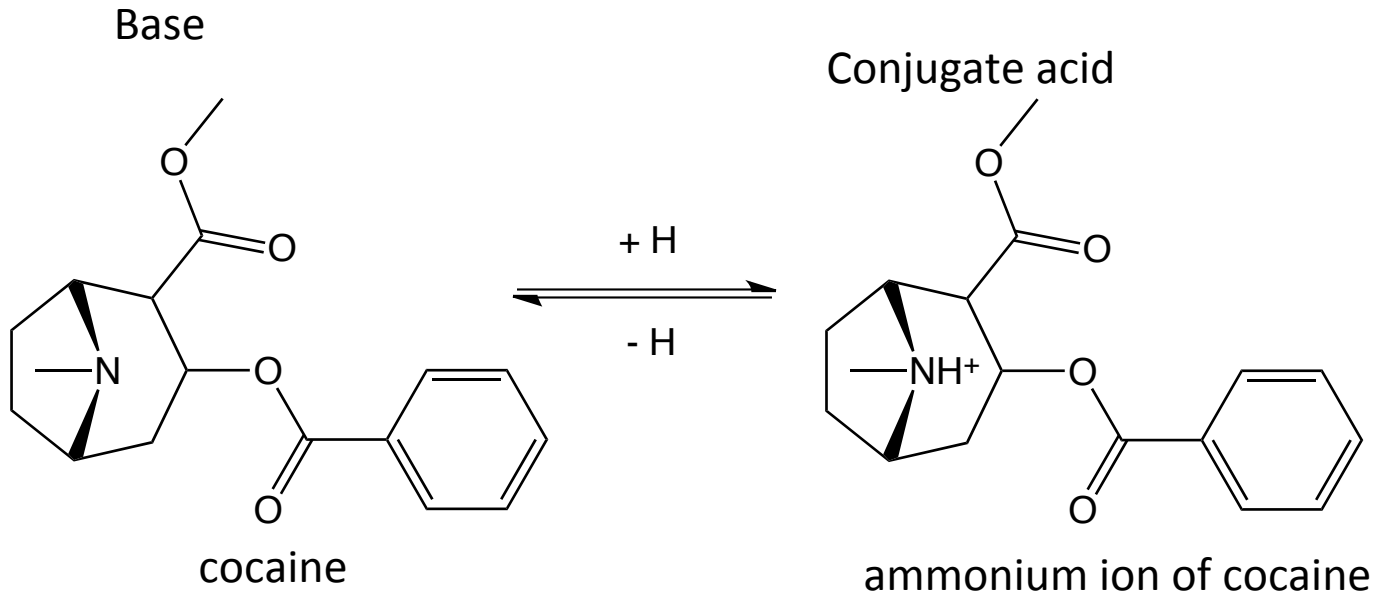2-hydroxypropane-1,2,3-tricarboxylic acid
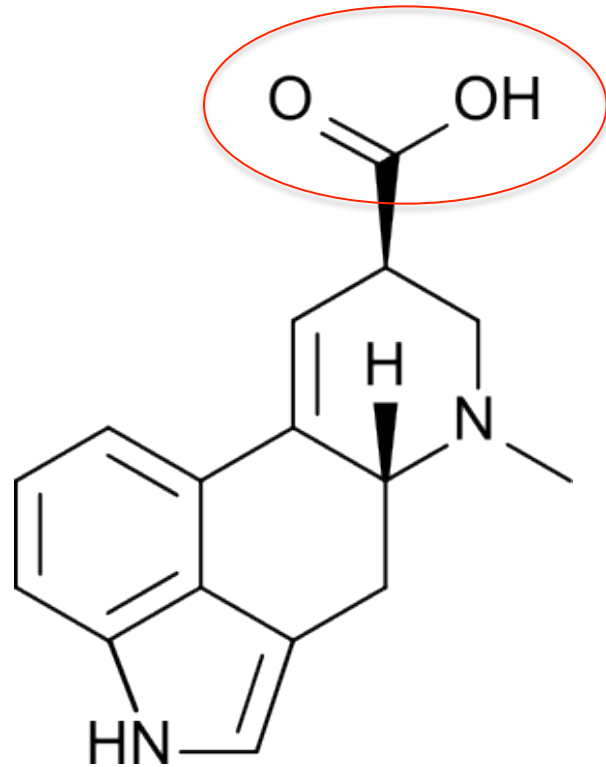
"citric acid"

2-oxopropanoic acid

"pyvuvic acid"

lactic acid

Illegal Examples

Base

Conjugate acid

cocaine

ammonium ion of cocaine

+ H

- H

morphine

ammonium ion of morphine

+ H

- H

Illegal examples cntd

D-lysergic acid
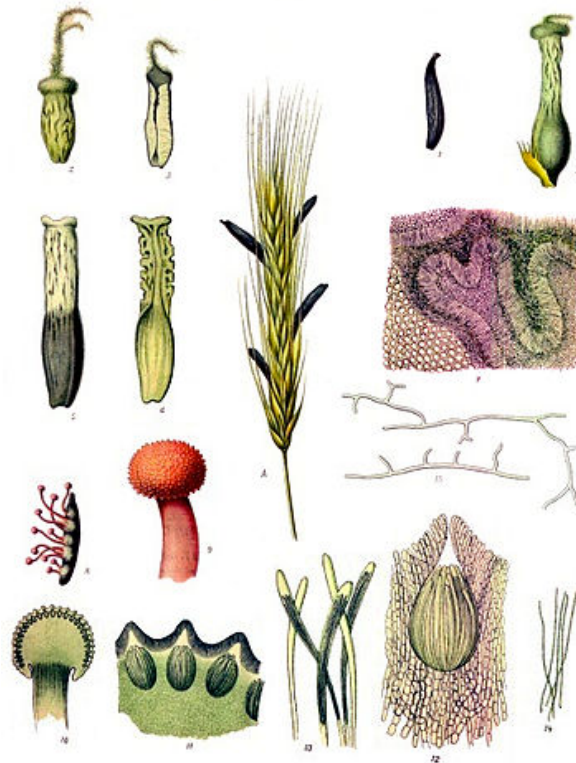
Ergot fungus
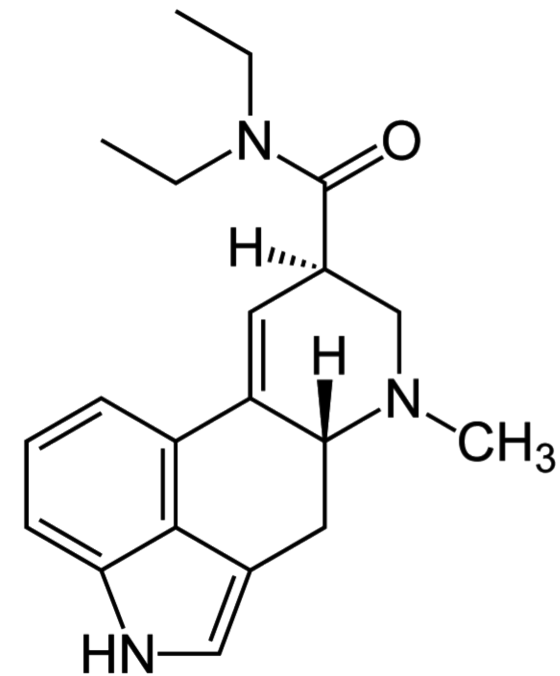
Lysergic acid diethylamide
(LSD)

pKa
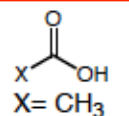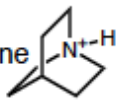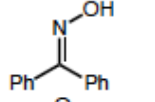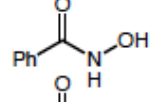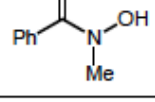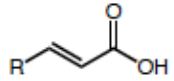
- The measure of the strength (or weakness) of an acid

- "The pH at which 50 mole % of your molecule is ionized"

- Large range (-16 to 60)

- ***Lower the pKa = stronger the acid***

- pKa values differ depending on solvent (e.g. pKa of acetic acid in water is 4.73, in DMSO it's 12.3)

$$Ka = \frac{[A\text{-}][H\text{+}]}{[HA]}$$ $$pKa = -log_{10}\ Ka$$

Henderson-Hasselbalch equation: $pH = pKa + log_{10}\ \frac{[A\text{-}]}{[HA]}$

pKa of some common compounds

INORGANIC ACIDS

Substrate	pKa H_2O	(DMSO)
H_2O	15.7	(32)
H_3O^+	-1.7	
H_2S	7.00	
HBr	-9.00	(0.9)
HCl	-8.0	(1.8)
HF	3.17	(15)
HOCl	7.5	
$HClO_4$	-10	
HCN	9.4	(12.9)
HN_3	4.72	(7.9)
HSCN	4.00	
H_2SO_3	1.9, 7.21	
H_2SO_4	-3.0, 1.99	
H_3PO_4	2.12, 7.21, 12.32	
HNO_3	-1.3	
HNO_2	3.29	
H_2CrO_4	-0.98, 6.50	
CH_3SO_3H	-2.6	(1.6)
CF_3SO_3H	-14	(0.3)
NH_4Cl	9.24	
$B(OH)_3$	9.23	
HOOH	11.6	

CARBOXYLIC ACIDS

Substrate	pKa H_2O	(DMSO)
X= CH_3	4.76	(12.3)
CH_2NO_2	1.68	
CH_2F	2.66	
CH_2Cl	2.86	
CH_2Br	2.86	
CH_2I	3.12	
$CHCl_2$	1.29	
CCl_3	0.65	
CF_3	-0.25	
H	3.77	
HO	3.6, 10.3	
C_6H_5	4.2	(11.1)
$o\text{-}O_2NC_6H_4$	2.17	
$m\text{-}O_2NC_6H_4$	2.45	
$p\text{-}O_2NC_6H_4$	3.44	
$o\text{-}ClC_6H_4$	2.94	
$m\text{-}ClC_6H_4$	3.83	
$p\text{-}ClC_6H_4$	3.99	
$o\text{-}(CH_3)_3N^+C_6H_4$	1.37	
$p\text{-}(CH_3)_3N^+C_6H_4$	3.43	
$p\text{-}OMeC_6H_4$	4.47	
R= H	4.25	
trans-CO_2H	3.02, 4.38	
cis-CO_2H	1.92, 6.23	

ALCOHOLS

Substrate	pKa H_2O	(DMSO)
HOH	15.7	(31.2)
MeOH	15.5	(27.9)
i-PrOH	16.5	(29.3)
t-BuOH	17.0	(29.4)
c-hex$_3$COH	24.0	
CF_3CH_2OH	12.5	(23.5)
$(CF_3)_2CHOH$	9.3	(18.2)
C_6H_5OH	9.95	(18.0)
$m\text{-}O_2NC_6H_4OH$	8.4	
$p\text{-}O_2NC_6H_4OH$	7.1	(10.8)
$p\text{-}OMeC_6H_4OH$	10.2	(19.1)
2-napthol		(17.1)

OXIMES & HYDROXAMIC ACIDS

Substrate	pKa H_2O	(DMSO)
	11.3	(20.1)
	8.88	(13.7) (NH)
		(18.5)

PEROXIDES

Substrate	pKa H_2O	(DMSO)
MeOOH	11.5	
CH_3CO_3H	8.2	

PROTONATED NITROGEN

Substrate	pKa H_2O	(DMSO)
N^+H_4	9.2	(10.5)
EtN^+H_3	10.6	
$i\text{-}Pr_2N^+H_2$	11.05	
Et_3N^+H	10.75	(9.00)
PhN^+H_3	4.6	(3.6)
$PhN^+(Me)_2H$	5.20	(2.50)
$Ph_2N^+H_2$	0.78	
2-napthal-N^+H_3	4.16	
$H_2NN^+H_3$	8.12	
HON^+H_3	5.96	
Quinuclidine	11.0	(9.80)
Morpholine	8.36	

AMINES

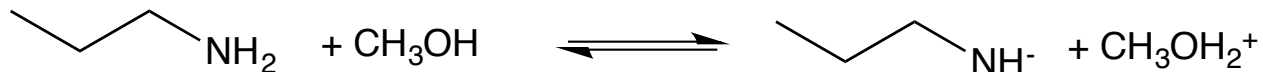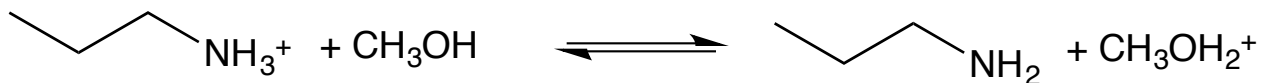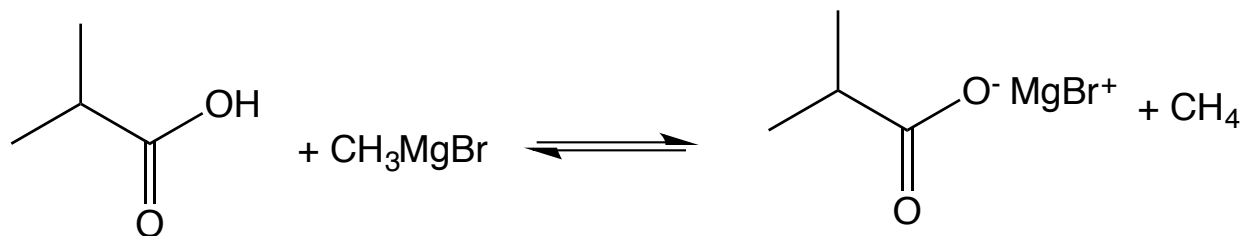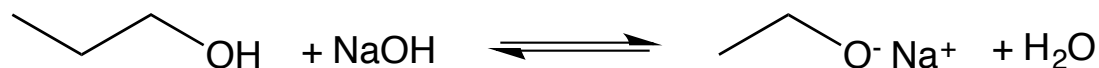| Substrate	pKa H_2O	(DMSO)
HN_3	4.7	(7.9)
NH_3	38	(41)
$i\text{-}Pr_2NH$		(36 THF)
TMS_2NH	26(THF)	(30)
$PhNH_2$	(30.6)	

Predicting Acid / Base reactions from pKa

- The proton (H^+) will always go from from stronger acid to the stronger base

- An acid will donate a proton to the conjugate base of a weaker acid

- The conjugate base of a weaker acid will remove a proton from a stronger acid

- The product conjugate acid in an acid-base reaction must be weaker and less reactive than the starting acid

- The product conjugate base must be weaker and less reactive than the starting base

pKa of the conjugate acid product must be higher than pKa of the starting acid
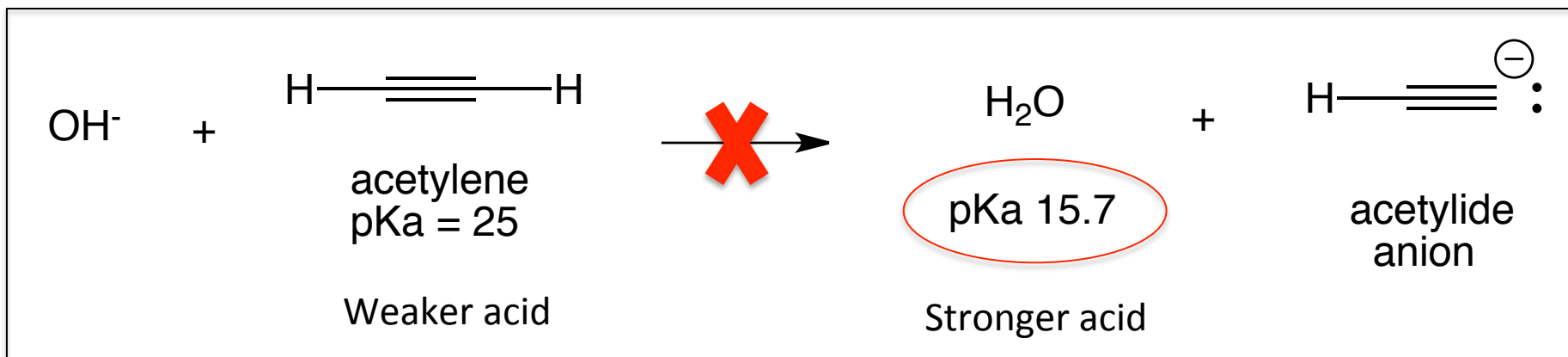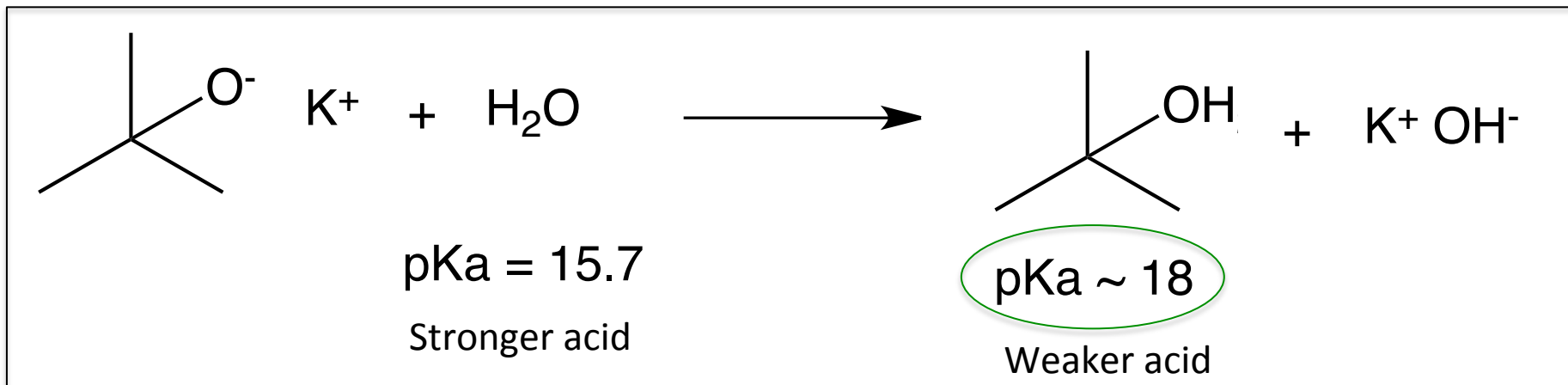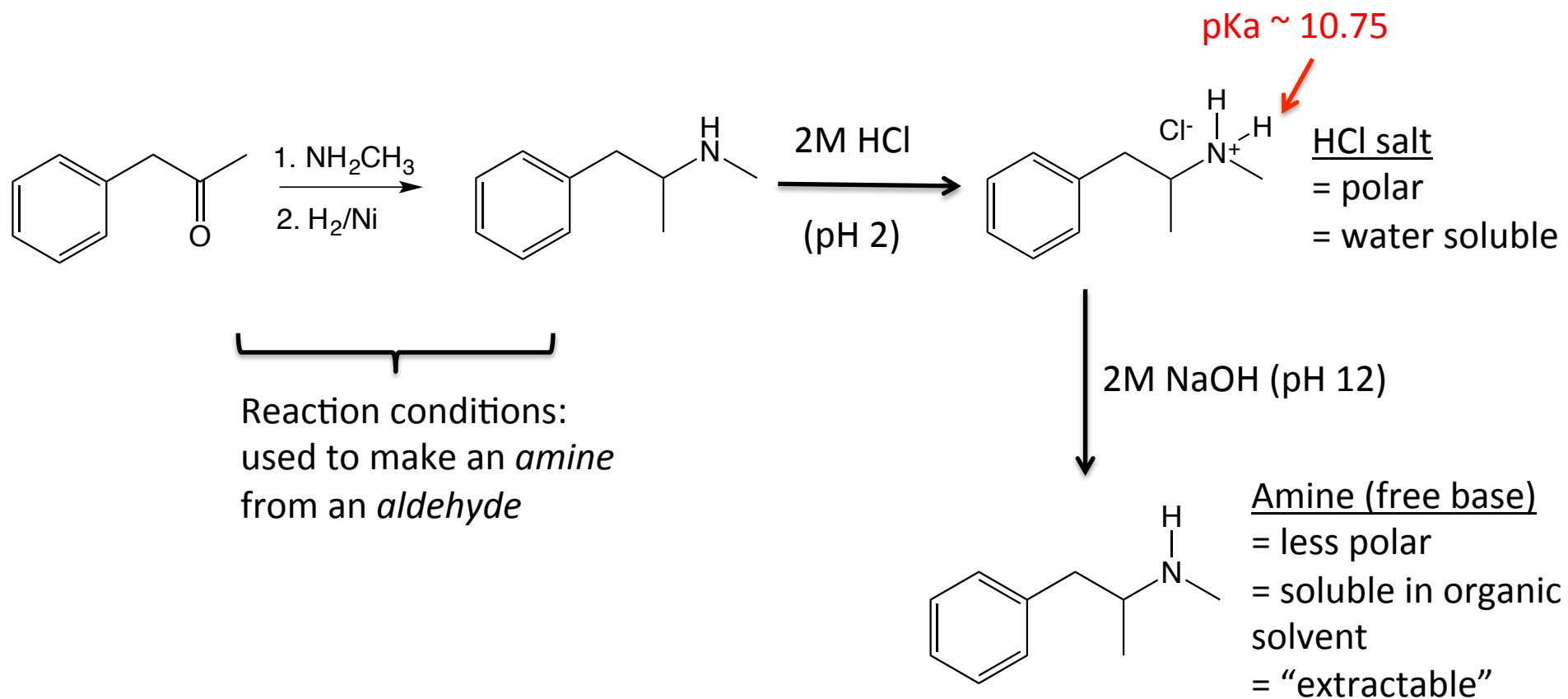

Rule of thumb – reaction goes to 99% completion when pKa of the conjugate acid (product) is 3 orders of magnitude greater than that of the starting acid
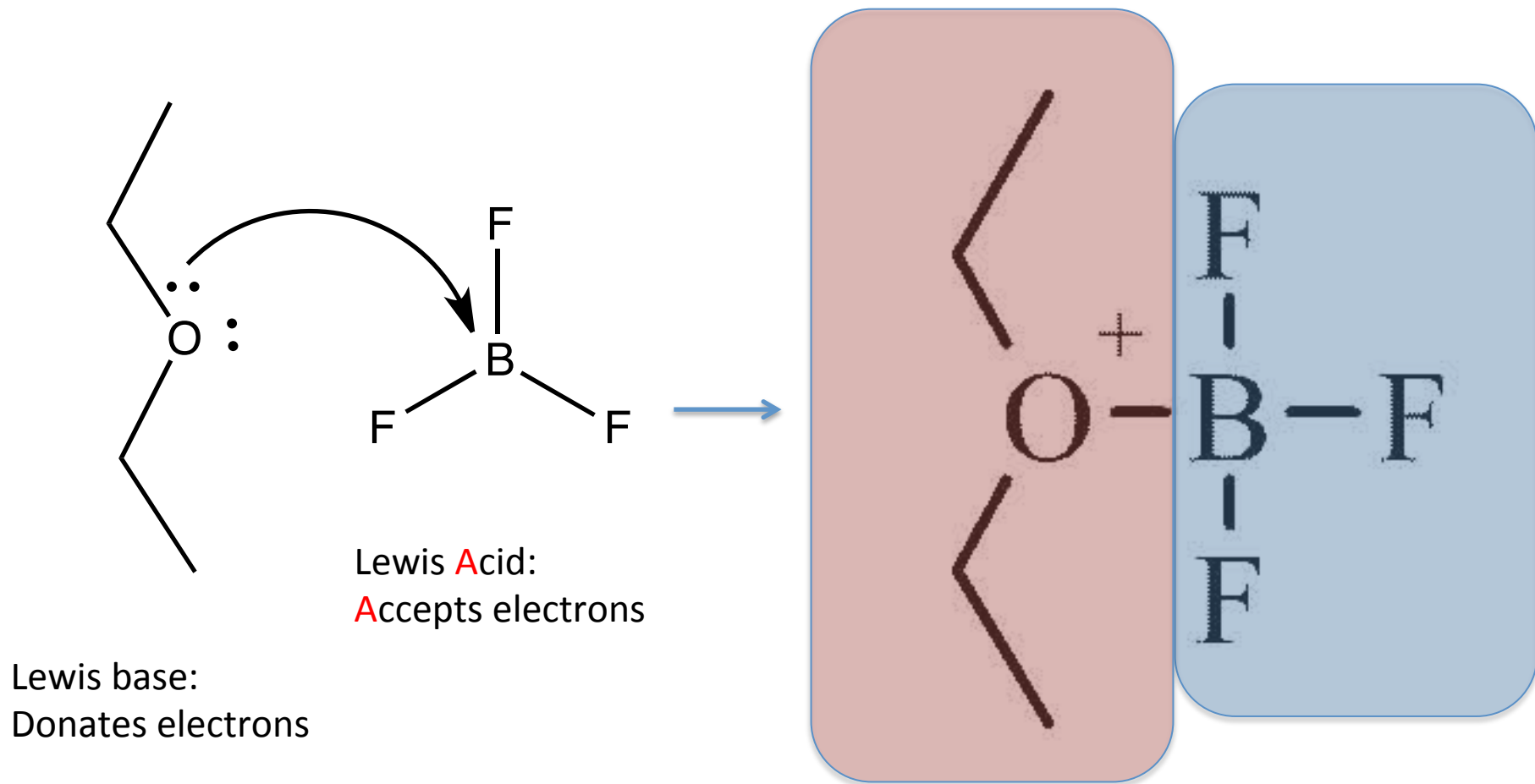
Practice problems: Will the following reactions proceed?

$CH_3CH_2CH_2OH$ + NaOH $\rightleftharpoons$ $CH_3CH_2O^- Na^+$ + H_2O

$(CH_3)_2CHCOOH$ + CH_3MgBr $\rightleftharpoons$ $(CH_3)_2CHCOO^- MgBr^+$ + CH_4

$CH_3CH_2CH_2NH_3^+$ + CH_3OH $\rightleftharpoons$ $CH_3CH_2CH_2NH_2$ + $CH_3OH_2^+$

$CH_3CH_2CH_2NH_2$ + CH_3OH $\rightleftharpoons$ $CH_3CH_2CH_2NH^-$ + $CH_3OH_2^+$

$CH_3CH_2CH_2NH_2$ + CH_3OH $\rightleftharpoons$ $CH_3CH_2CH_2NH_3^+$ + CH_3OH^-

Using pKa for product isolation: synthesis of methamphetamine

pKa ~ 10.75

1. NH$_2$CH$_3$

2. H$_2$/Ni

2M HCl

(pH 2)

Cl$^-$

HCl salt
= polar
= water soluble

Reaction conditions:
used to make an *amine*
from an *aldehyde*

2M NaOH (pH 12)

Amine (free base)
= less polar
= soluble in organic solvent
= "extractable"

Lewis bases and Lewis acids

Lewis Acid:
Accepts electrons

Lewis base:
Donates electrons

Electrons always flow in the direction of the arrow

Lewis Acids = Electron Acceptors

- Have vacant low energy (S) orbitals
(e.g. H^+, Li^+, Mg^+ cations)

- Have polar bonds to hydrogen so they can donate H^+
(e.g. carboxylic acids, phenols, alcohols)

- Some are also Brønsted acids
(e.g. H_2O, HCl, HBr, HNO_3, H_2SO_4)

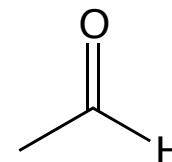- Some are metal compounds
(e.g. $AlCl_3$, $TiCl_4$, $FeCl_3$, $ZnCl_2$)
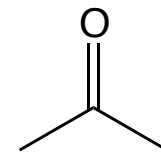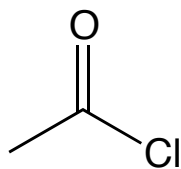
Lewis Bases = Electron Donors
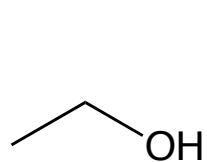
Lone pairs:
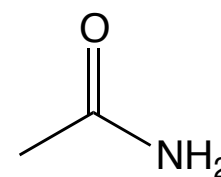**(e.g. N, O, P, S)**

alcohol
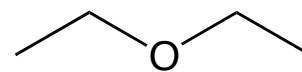
ether

aldehyde
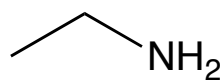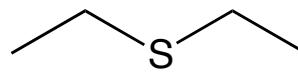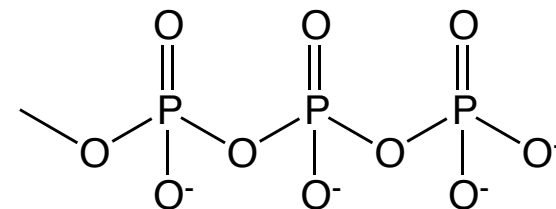
ketone

acid chloride
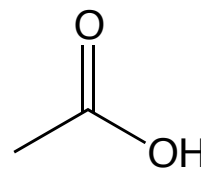
carboxylic acid
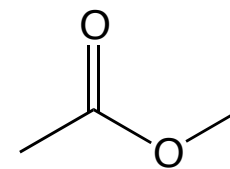
ester

amide

amine

sulfide

organotriphosphate ion

Other notes on organic acids/bases

- Anions are stabilized by placing charge on most electronegative atom and through resonance (e.g. alcohols, carboxylic acids, ketones)
- In biological systems (pH 7.3) carboxylates prevail, amino acids are "zwitterionic"
- Organic bases typically contain nitrogen, but strong enough acids can protonate oxygen
- To react completely with NaOH (> 99.9%) an acid must have a pKa at least 3 units smaller than the pKa of water (15.7) (So, ~ 12.7 or less)
- More delocalization of charge (e.g. acetate, phenylamine) makes a weaker base because the electrons are spread over a larger area and have less access to acquire the proton (H+)
- Alcohols and carboxylic acids can donate and accept H^+

Acetic acid as a base (and where)

- Protonation at the carbonyl is resonance stabilized
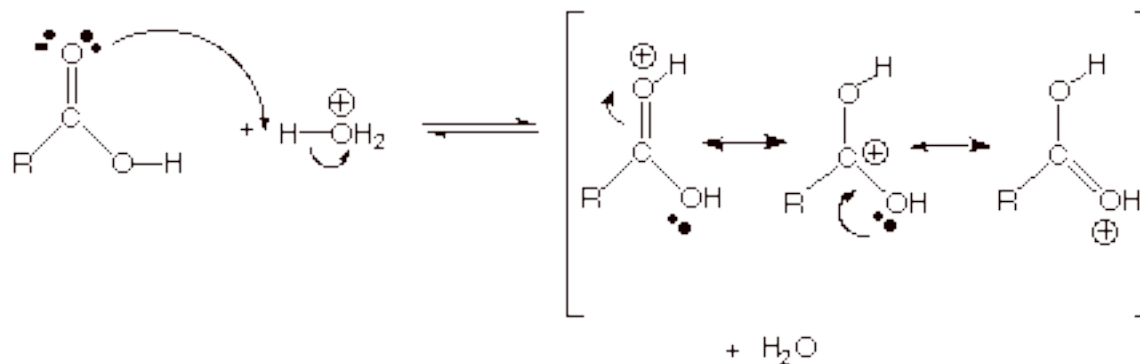
- Protonation at the OH does not occur
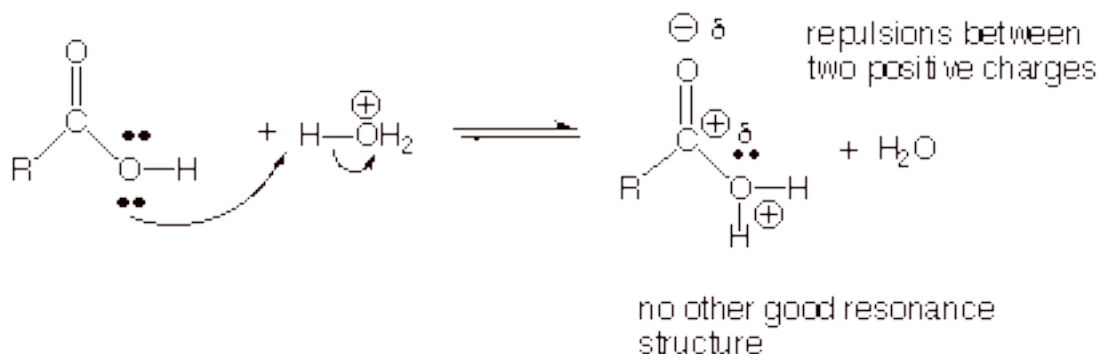
Intermolecular forces

- Attract molecules to other molecules
- Non-covalent interactions
- Additive (i.e. molecules can have multiple types of intermolecular forces acting simultaneously)
- Generally much weaker than intramolecular forces (i.e.covalent and ionic bonds)

London Dispersion Forces

- Weakest intermolecular forces
- Result from instantaneous dipole
- "Polarizability" allows these dipoles and is a result of how well electrons can move around orbitals
    - increases as orbital size increases
- a.k.a Van Der Waals Forces
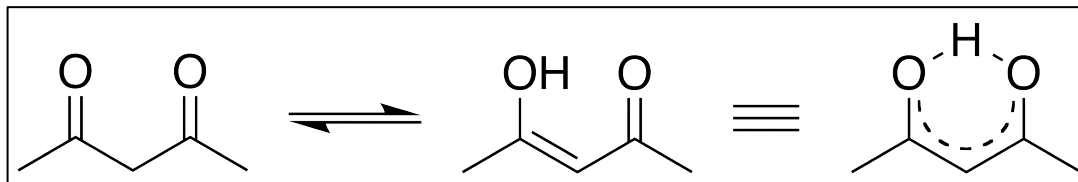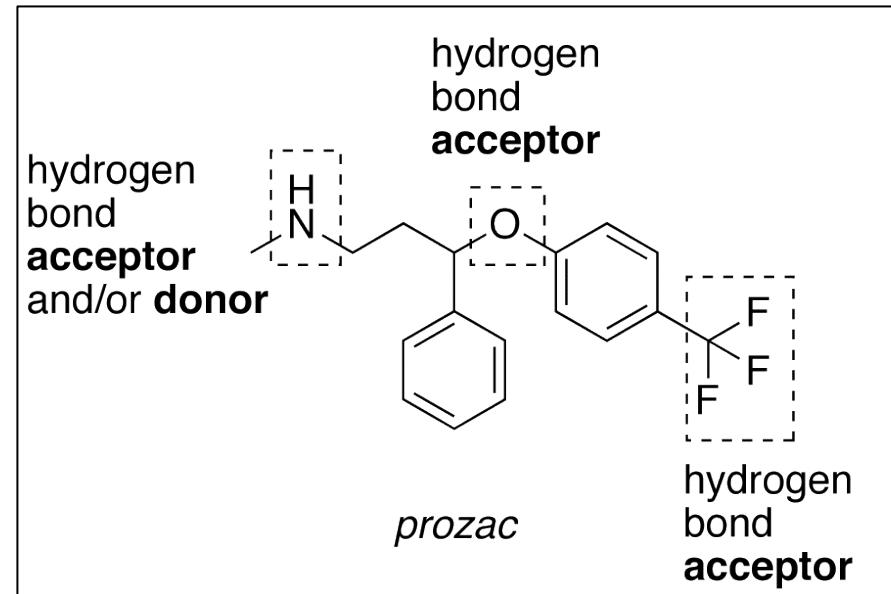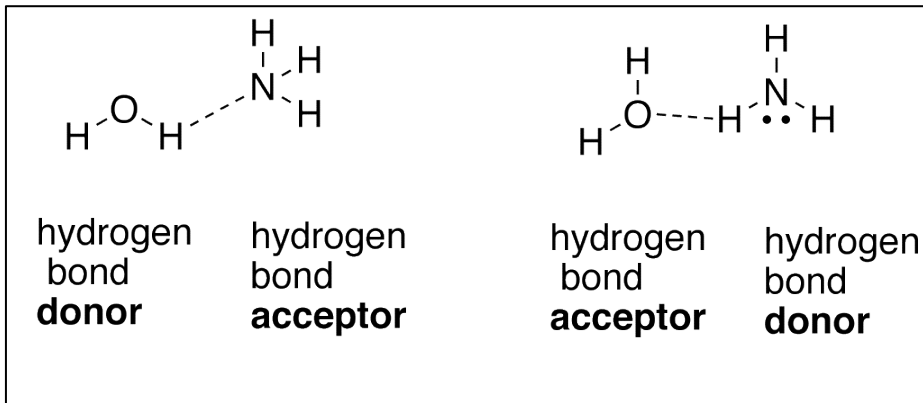- Can occur in molecules with zero dipole moment (i.e. octane, below)
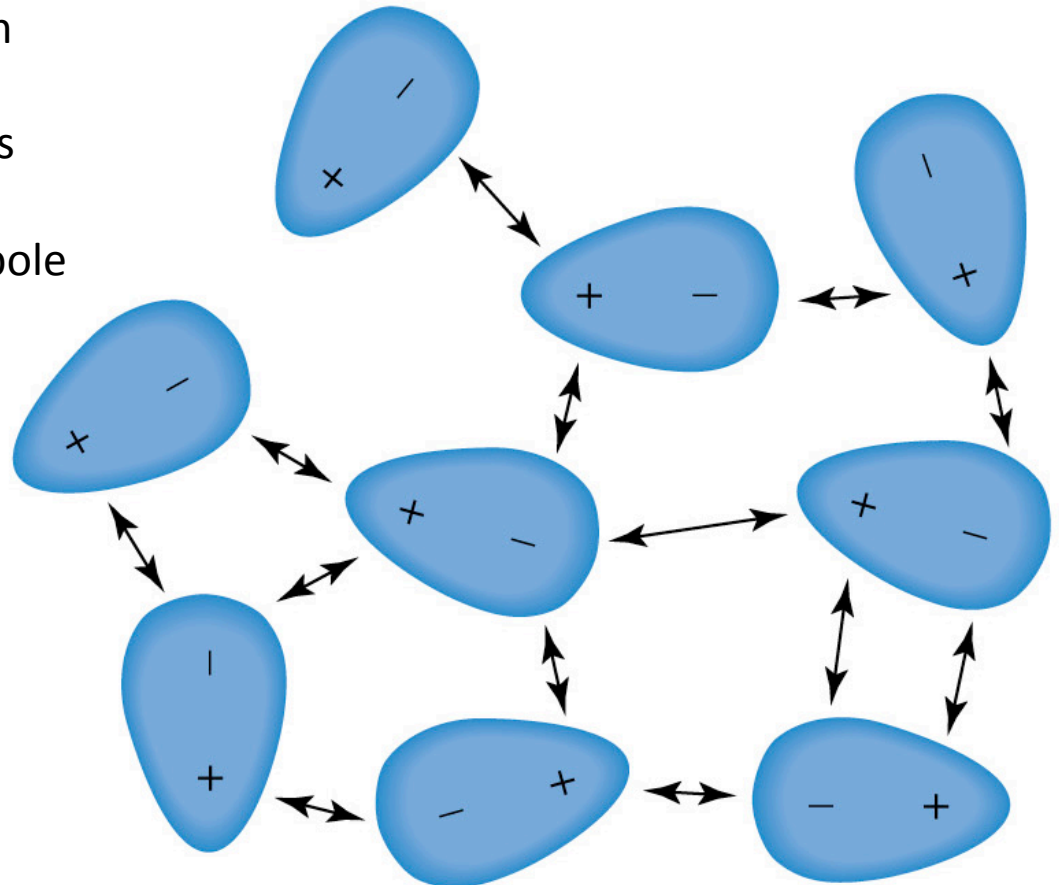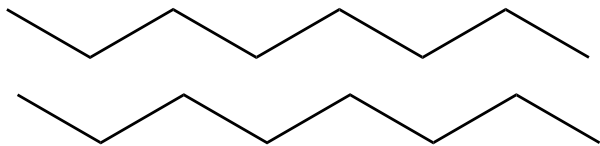
Dipole Dipole Interaction

- Stronger than London forces
- Result from interacting dipoles among
molecules with permanent dipole moments
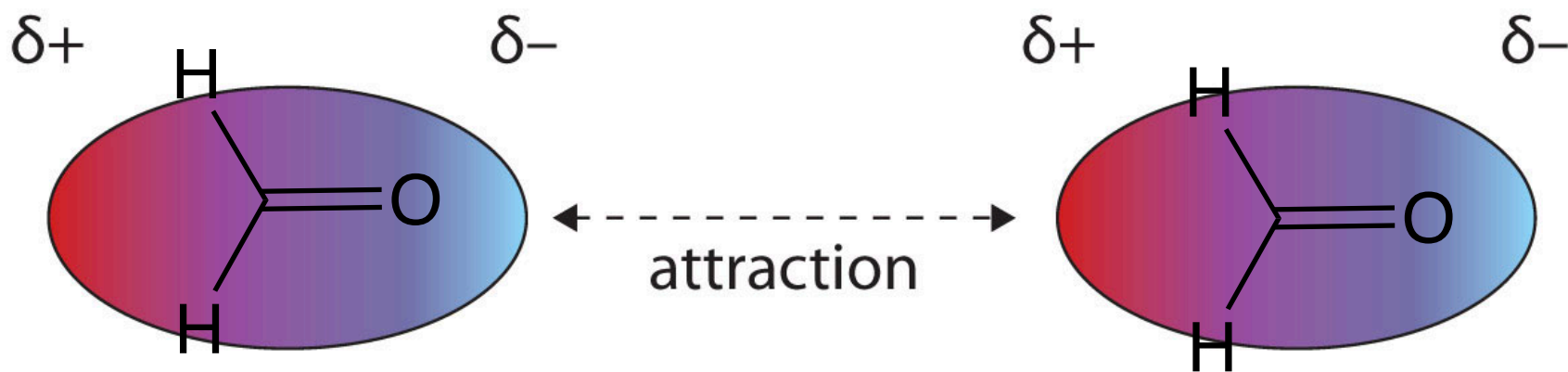
Hydrogen Bonding

- Strongest intermolecular force (5-30 kJ/mol)
- "H-bonds are made on the FON"
- Can be both inter- and intramolecular
- Occur in numerous biomolecules (i.e. water, DNA, protein/enzymes, etc)

hydrogen bond **donor**   hydrogen bond **acceptor**   hydrogen bond **acceptor**   hydrogen bond **donor**

hydrogen bond **acceptor**

hydrogen bond **acceptor** and/or **donor**

hydrogen bond **acceptor**

prozac

Intramolecular H-bonding stabilizes the keto-enol tautomer

Forces of Attraction

Interaction	Example	Energy
ion- ion	Na^+ Cl^-	400 - 4000 kJ
Covalent Bonds	H - H	150-1100 kJ
ion-dipole (I-D)	Na^+ HCl	40-600 kJ
dipole - dipole (D-D)	HCl HCl	5-25 kJ
dipole - induce dipole (D-ID)	HCl O_2	2-10 kJ
London Dispersion (LD)	N_2 N_2	0.05 - 40 kJ

Homework Problems

- In chapter – 2, 3, 5, 6, 7, 9, 10, 11, 12, 13, 14,15, 17, 18, 19

- End of chapter – 33, 34, 53, 54, 56, 57

- Mrs. Meer's 'Even More Resonance' problems

a-j   http://www.csebcc.org/CHM_31/resonance_practice.pdf