1. Lewis Structures (review) – why do atoms bond to other atoms?
   1. Starting from a formula: add up valence electrons for all atoms when neutral
   2. add or subtract electrons to account for charge
   3. # bonds = (Σfull shell count - Σvalence electrons)/2
      1. full shell (2 for first row, 8 for second row)
      2. difference between full shell and valence electrons = number of electron needed to make full shell = therefore atoms must share to fill up the shell
      3. if every atom had a full shell there would be no need to make bonds
      4. H3O+: (8(O) + 2(H) + 2(H) +2(H) – [6(O) + 1(H) + 1(H) + 1(H) -1(+)]/2 = 3 bonds
   4. Steps to draw structure
      1. Draw single bonds between atoms (could be more than one isomer)
      2. fill in lone pairs to make octets
      3. move lone pairs as needed to multiple bonds to (a) make octets (carbonyl?) (b) minimize charge separation
   5. # bonds per atom (typical neutral) <http://www.chem.qmul.ac.uk/iupac/AtWt/table.html>
      1. one (H, F, Cl, Br, I)
      2. two (O, S)
      3. three to four (N, P)
      4. four (C, Si)
   6. # lone pairs per atom (typical neutral)
      1. one (N, P)
      2. two (O, S)
      3. three (F, Cl, Br, I)
   7. atom formal charge =

neutral atomic valence -(lone pair electrons + 1/2 covalent electrons)

* 1. total charge on molecule = sum of formal charges
  2. Try CH4N+. practice: SO3-2, SO4-2, O3, CH2P(CH3)3, N3-, CNO-, HCN
  3. Hints: optimize octets and bonds, minimize charge separation, negative charge on most electronegative atom, positive charge on least electronegative atoms

1. Acid-Base Chemistry
   1. Lewis acid - accepts pair of electrons - electrophile - empty or potentially empty orbital
   2. Lewis base - electron pair donor – nucleophile
   3. difference between base and nucleophile
      1. nucleophile refers to reactivity toward carbon electrophiles
      2. reactivity toward protic acid and carbon electrophiles are not always parallel
   4. Bronsted acid - proton donor
   5. Bronsted base - proton acceptor - electron pair donor
   6. Why is Bronsted acid-base chemistry so important?
      1. many reactions are acid or base catalyzed (water addition to carbonyl)
      2. predict organic reactivity: many (all) organics are acids and bases
      3. extent of formation of intermediates can be determined from pKa
      4. strong acid has weak conjugate base
         1. easy to remove proton
         2. conjugate base does not want to share electrons
      5. weak acid has strong conjugate base
         1. hard to remove proton
         2. conjugate base wants to share electrons
      6. conjugate acid of strong base and weak base?
2. pKa is a measure of acid strength (in water)
   1.  
   2.   H20 ~ constant if HA is dilute
   3. Ka defined as ability to protonate water*, based on results in water*
   4. Ka dependent on relative stability of HA and A-
      1. bond energy of HA
      2. electronegativity of A
      3. difference in solvation of HA and A-
      4. delocalization of electrons on HA and A-
   5. Ambiguity in text: pKa of butylamine?
   6. strongest acid in water is hydronium and strongest base is hydroxide
3. Understanding acid and base strengths
   1. Changing the structure of acid also changes structure of conjugate base
   2. Must rationalize change in energy of both acid and conjugate base



* 1. pKa reflects tendency for HA to lose a proton
  2. also reflects tendency for A- to gain a proton.
  3. HA2 has the lower pKa and is the stronger acid
  4. A2- must be the weaker base because the conjugate acid is the stronger acid
  5. No need to learn or have separate measurements for base strength
  6. Strength of base is determined from conjugate acid pKa

1. calculate equilibria from pKa’s
   * 1.  
     2. **pKeq = pKa = pKa1 - pKa2**
     3. strong acid + strong base → weaker base + weaker acid
2. structure effects on pKas: list of acids, see Handbook of Biochemistry
   1. electronegativity: CH4 (48) NH3 (38) H2O (16) HF (5)



* 1. charge/field: NH3 (38) vs. NH4+ (9) CH3CO2H (5) vs. CF3CO2H (0)
     1. NH3 → H+ + NH2- vs. NH4+ → H+ + NH3
     2. CH3CO2- vs. CF3CO2-: effect greatest in products (show diagrams)
     3. Induction/field effects over distance







* 1. delocalization: CH3CO2H (5) vs. CH3CH2OH (16)
  2. hybridization: HC≡CH (25) H2C=CH2 (44) CH3CH3 (50) cyclopropane ?



* 1. bond energy/spatial overall HI (-10) HBr (-8) HCl (-7) HF (5)
  2. solvation:
     1. CH3OH v *t*-BuOH in solution and gas-phase, unique properties of water?
     2. Ethanoic versus methanoic: bigger solvation difference for ethanoic/ethanoate, enthalpy change is similar, both anions strongly solvated, methyl inhibits solvation much more than H in acids



* 1. **see list of pKa's on last page**
  2. Why is phenol a weaker acid than ethanoic acid? Plus 2 oxygens





* 1. Delocalization – direct charge transfer





* 1. field effect?



* 1. Which is the stronger base



* 1. Explain the trend in first three pKa’s

 

* 1. A) What is hybridization of N in pyrrole? B) Compare lone pair with pyridine. Is pyrrole more basic or acidic than pyridine?
  2. self test: explain the following acidity trends



1. acid/base catalysis
   1. adding or removing a proton dramatically changes the electron density (charge)
   2. intermediate much more reactive (raises the energy, closer to TS)
   3. specific acid catalysis: SA
      1. rate dependent directly on pH: [H3O+]
      2. independent of which acid or base used to adjust pH
      3. Addition of proton is rapid and reversible
      4. precedes rate determining step, rate expression looks like?
      5. Why does catalyst increase the rate? Fix methyl



* 1. general acid catalysis: GA
     1. rate of GA catalysis dependent directly on [HA], independent of pH
     2. proton transfer is in rate determining step (subsequent steps are fast)
  2. compare specific acid and general acid catalysis





* + 1. kH+ > kHA, why? ???
    2. often RateH+ = kH+[H+][ketone][Nu] < RateHA = kHA[HA][ketone][Nu], why?
    3. RateH+ = kH+[H+]< RateHA = kHA[HA]
    4.  adjust p[H+] = pKHA then [A-] = [HA]
    5. Example, pKHA = 9 = pH? What is [HA] if 0.2 M HA added [HA] = [A-] = 0.1 M
    6. = Suppose kH+ = 103, and kHA = 10-2.
       1. kH+[H+] = 103 x 10-9 = 10-6
       2. kHA[HA] = 10-2 x 0.1 = 10-3
  1. specific base catalysis, SB
     1. rate dependent directly on pH: [OH-]
     2. independent of which acid or base used to adjust pH
     3. Removal of proton is rapid and reversible
     4. precedes rate determining step



* 1. general base catalysis: GB
     1. rate of GBC dependent directly on [B-], independent of pH
     2. GBC occurs in rate determining step (subsequent step are fast)
     3. often specific and general base catalysis compete



* 1. GA and GB catalysis occurs in rate determining step, not an equilibrium reaction
  2. hydrogen bond is formed prior to proton transfer

1. proton transfer is diffusion controlled if pKa is < 2 for transfer between heteroatoms (N, O, S)
   1. rarely applies to carbon carbon
   2. lmost always slower than diffusion control because of poor hydrogen bond and (stabilizing) electronic reorganization occurs after transfer

