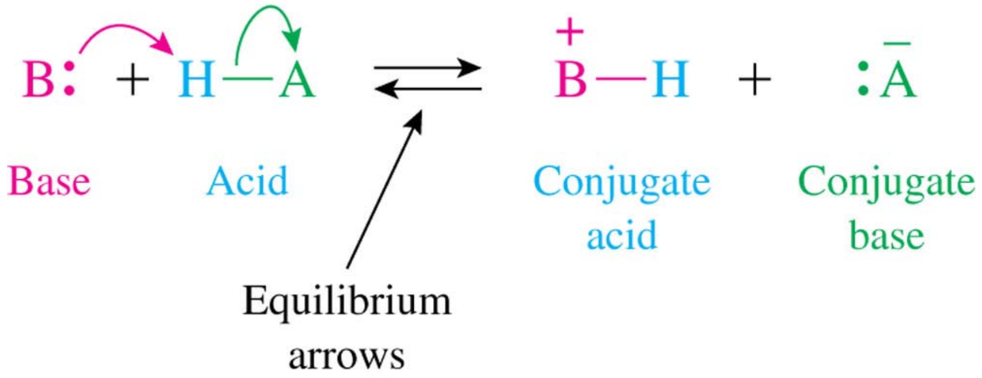
Chapter 4. The Acid-Base Reaction

- What to master
  - Writing Equations for Acid-Base Reactions
  - Identifying Lewis Acids and Bases
  - Understanding the Acid-Base Equilibrium
  - Understanding the Factors of Acidity and Basicity
  - Predicting the Strengths of Acids and Bases Based on the Structure
  - Comparing the Acidity of Protons in a Compound

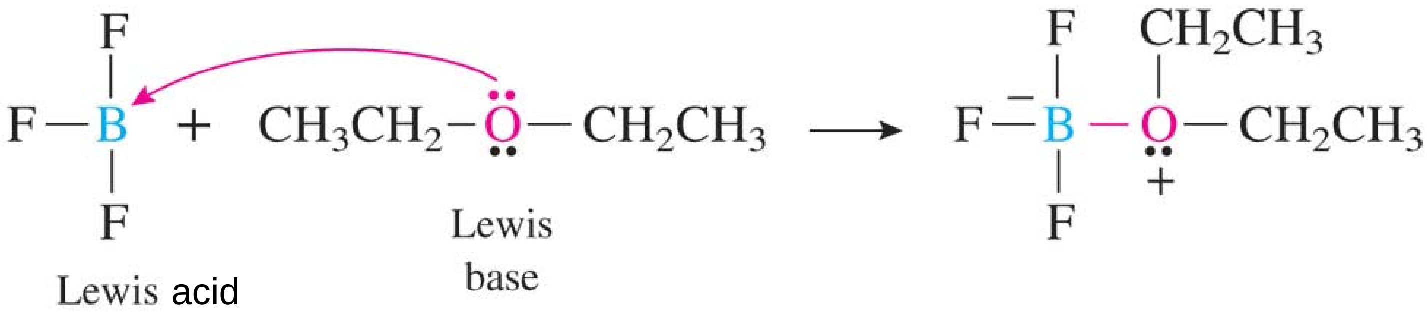
Chapter 4. The Acid-Base Reaction

- Brönsted-Lowry definition: proton (H^+); 105
  - acid - proton donor, base - proton acceptor
    - any H-A: a potential acid; H-X, H-OR, H-NR_2, H-CR_3
    - base: unshared e^- pair (B: or B^-); RNH_2 (amphoteric), RNH^-
    - *practice*: 104 Problem 4.1, 105 Problems 4.2 & 4.3



❖ The Acid-Base Reaction (continued)

- Lewis definition: electron pair; 📖 106
  - acid - e^- acceptor, base - e^- donor:
    - all Brönsted-Lowry bases are Lewis bases
  - *practice*: 📖 106 Problem 4.5



The Acid-Base Equilibrium

$$\text{H–A} + H_2O \underset{}{\overset{K_{(HA)}}{\rightleftharpoons}} A^- + H_3O^+$$

$K_{(HA)} = [A^-][H_3O^+] / [HA][H_2O]$; $[H_2O] \cong$ constant

$[H_2O]K_{(HA)} = K_{a(HA)} = [A^-][H_3O^+] / [HA]$; $K_{a(HOAc)} = 1.8 \times 10^{-5}$

- Acidity constants: K_a (= $K[H_2O]$), 📖 107
  - the strength of an acid: pK_a = −log K_a, 📖 131 Table 4.3
    - pKa↑ acidity↓ conjugate base↑: 📖 108 Problems 4.7 & 4.8

Equilibrium of the Acid-Base Reaction

$$B{:} + H{-}A \overset{K}{\rightleftharpoons} B{-}H + A{:}$$

K = [A:][BH] / [HA][B:] = [A:]/[HA] x [BH]/[B:] = [A:][H_3O^+]/[HA] x [BH]/[B:][H_3O^+] = $K_{a(HA)}$ / $K_{a(HB)}$ = 10exp(-p$K_{a(HA)}$ + p$K_{a(HB)}$)

K > 1, when HA is stronger than HB (p$K_{a(HA)}$ < p$K_{a(HB)}$)

- equilibrium to the product: $\Delta G = - RT \ln K < 0$, 📖 111 Fig. 4.3

H-Br + H_2O ⇌ Br^- + H_3O^+ K=1.8 x 10^7 = 10^9 / 55 or $10^{(9-1.74)}$

- 📖 109 Figure 4.2 (📖 129-30 Table 4.2) & aq. NH_3 vs NH_4OH

H_2O + H−A ⇌ H_3O^+ + A: $K_{a(HA)}$ = [A:][H_3O^+] / [HA]

B−H + H_2O ⇌ B: + H_3O^+ $K_{a(HB)}$ = [B:][H_3O^+] / [HB]

Rate of the Acid-Base Reaction

- Requirements for the reaction: effective collisions
  - feasibility: thermodynamics ≡ equilibrium; ΔG
  - probability: kinetics ≡ rate
    - orientation: stereoelectronic effect; 📖 112 top
    - energy: activation energy ($\Delta G^{\ddagger}$); 📖 112 Fig. 4.4
      - – free energy vs. reaction progress diagram

$$\text{H-Br} + H_2O \rightleftharpoons Br^- + H_3O^+ \quad \Delta G << 0$$

  - *practice*: $HOAc + H_2O \rightleftharpoons AcO^- + H_3O^+$; 📖 113 Practice 4.4

Factors on the Acidity (I)

- Effect of atoms bonded to H (H-A): stability of **A^-**
  - the more stable A^-, the stronger acid HA
    - electronegativity: 114 bottom; $H\text{-}CH_3 < H\text{-}NH_2 < H\text{-}OH < H\text{-}F$
    - size: diffusibility, 115 middle; $HF < HCl < HBr < HI$, $H_2O < H_2S$
    - *practice*: 115 Problems 4.13, 4.14 & 116 Problem 4.15

Factors on the Acidity (II)

- Inductive effect: interaction between nearby dipoles
  - the more & the closer the e^--withdrawing groups, the stronger
    - $ClCH_2CO_2H$ (2.86) vs. CH_3CO_2H (4.76): 📖 116 Figure 4.4
      - – destabilizing & stabilizing interactions: 📖 117 Figure 4.5
    - inductive groups: electron-withdrawing & electron-donating
      - – 📖 117 bottom & 📖 118 Table 4.1
    - *practice*: 📖 122, Problem 4.16

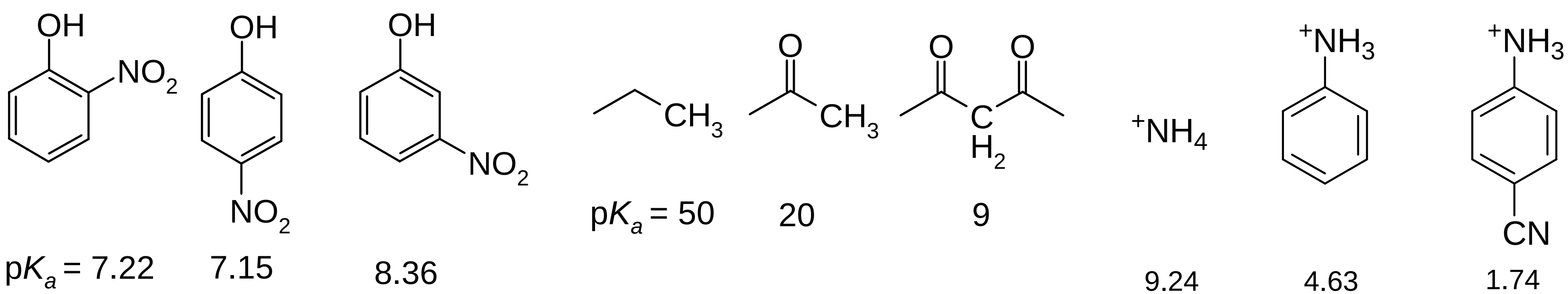
Factors on the Acidity (III)

- Hydrogen bonding: destabilizing the conjugate base
  - decreasing the e^--withdrawing ability of the carbonyl group: weaker acid, 📖 119 Fig. 4.7

- Hybridization: the more ***s***, the more electronegative
  - the more stable conjugate base: stronger acid; 📖 120 top

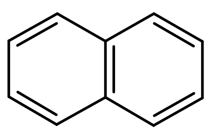
Factors on the Acidity (IV)

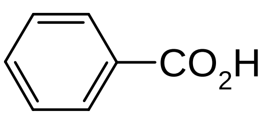
- Resonance: stabilizing the conjugate base
  - delocalization of the anion: stronger acid (+ inductive effect)
    - CH_3CH_2OH (16) vs CH_3CO_2H (4.76): 122 mid & Figure 4.9
    - $PhCH_2OH$ (16), PhOH (10), *p*-NO_2-PhOH (7.15): 123-4
  - *practice*: 127 Problems 4.19 & 4.20



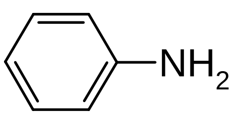
Acids & Bases

- Tables: 129-31 Table 4.2, 4.3 & 4.4
  - *practice*: 128 Problem 4.21
- Reaction solvents: the leveling effect
  - strongest base ≤ the conjugate base of the solvent: aprotic solvents (ethers), 134 top
  - acids ≤ the conjugate acidity of the solvent: 134 middle
    - super acids: stronger than 100% H_2SO_4; 135 top
- Separation & isolation of a mixture of acids & bases
  - *practice*:

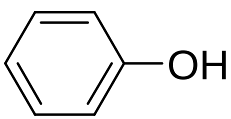

naphthalene



benzoic acid



aniline



phenol

공부하는 방법

"그저 익숙하도록 읽는 것뿐이다. 글을 읽는 사람이, 비록 글의 뜻은 알았으나, 만약 익숙하지 못하면 읽자마자 곧 잊어버리게 되어, 마음에 간직할 수 없을 것은 틀림없다.

이미 읽고 난 뒤에, 또 거기에 자세하고 익숙해질 공부를 더한 뒤라야 비로소 마음에 간직할 수 있으며, 또 흐뭇한 맛도 있을 것이다." - 퇴계 이황 (금장태 著)