I. Review
• strong or weak acid:
  microscopic considerations → weak H-A bonds
  macroscopic considerations → equilibrium is shifted to the right,
    magnitude of K, nature of conjugate base
• characterization by [H+] or pH – note the significant decimal places

| [H+] | 10^-7 | 9 · 10^-8 | 8 · 10^-8 | 7.943 · 10^-8 | dilute by 10 times |
| pH  | 7.000 | 7.046 | 7.097 | 7.100 | increase by ~0.05 |

II. Consider the solution of HA
• equilibria present: acid dissociation and water autoionization
• species present: HA, A^-, H_3O^+, OH^- (add water to acid)
  initial concentrations: [HA]_0 0 0
  change: acid dissociation
    water autoionization
  in equilibrium [HA]_0-x x x+y y

• species present: HA, A^-, H_3O^+, OH^- (add acid to water)
  initial concentrations: [HA]_0 0 10^-7 10^-7
  change: acid dissociation
  water “re”-autoionization
  in equilibrium [HA]_0-x x x+z+10^-7 z+10^-7

  y = z+10^-7

  The equilibrium concentrations do not depend the pathway!

• additional considerations:
  material balance for the acid ⇒ [HA]_{eq} + [A^-]_{eq} = [HA]_0
  charge balance ⇒ [A^-]_{eq} + [OH^-]_{eq} = [H_3O^+]_{eq}
  autoionization ⇒ [H_3O^+]_{eq} [OH^-]_{eq} = K_w

• Measure the pH of the solution:
  \[ \text{pH} = - \log_{10} [H_3O^+] = - \log_{10} (x+y) \]
  \[ \text{pOH} = - \log_{10} [OH^-] = - \log_{10} (y) \]
  \[ [HA] = [HA]_0 - x \]
  \[ [A^-] = [H_3O^+] - [OH^-] = [H_3O^+] - K_w/[H_3O^+] \]

• Without measurement, using the equilibrium constant \( K_a \)
  \[ \begin{align*}
    K_a &= \frac{[H_3O^+][NO_3^-]}{[HA]} = \frac{(x+y)(x)}{[HA]_0-x} = \frac{[H_3O^+]}{[HA]_0} \left( \frac{[H_3O^+] - K_w/[H_3O^+]}{[HA]_0 - ([H_3O^+] - K_w/[H_3O^+])} \right) \\
    &= \frac{[H_3O^+]}{[HA]_0[H_3O^-][H_3O^+]^2 + K_w} \left( [H_3O^+]^2 - K_w[H_3O^+] \right) = \frac{[H_3O^+](x+y)(x)}{[HA]_0-x} \\
    &= \frac{[H_3O^+]^3 - K_w[H_3O^+]^2}{[HA]_0[H_3O^-][H_3O^+]^2 + K_w} = \frac{[H_3O^+]^3 - K_w[H_3O^+]}{[HA]_0[H_3O^-][H_3O^+]^2 + K_w} \\
    &= [H_3O^-]^3 + K_w[H_3O^-]^2 - ([HA]_0 K_a + K_w) [H_3O^-] - K_a K_w = 0
  \end{align*} \]

  exact analytical solution for [H_3O^+]
III. Simplifications (be careful and check the final results):

- if \([H_2O^+]\) is large, \(pH\) is small \(\Rightarrow pH \leq 6 \ [H_2O^+] \geq 10^{-6} \) than \( [H_2O^+] / [H_2O^+ \approx [H_2O^+] \]
  \[
  K_a \approx \frac{[H_2O^+] [H_2O^+]}{[HA]_0 - [H_2O^+]} \Rightarrow [H_2O^+]^2 - K_a [H_2O^+] - K_a [HA]_0 = 0
  \]

- note that the above treatment is equivalent to neglecting the effect of autoionization in the equilibrium process since the \([H_2O^+] \gg [OH^-] \) and considered only the acid dissociation
- autoionization of water is significant in the \(6 < pH < 8\) range

- **strong acids**: \(K_a\) is large (cannot be determined experimentally) and
  the initial concentration is greater than \(10^{-6} \) \(M \Rightarrow pH = - \log_{10} [HA]_0\)

- **weak acids**: non-negligible amount of non-dissociated acid in the equilibrium
  examples: organic acids \(CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_2O^+\)
  cations/conjugate acids of strong bases \(NH_4^+ + H_2O \leftrightarrow NH_3 + H_2O^+\)
  anions of polyprotic acids \(HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_2O^+\)

consider phenol solution (remember why more acidic than ethanol, i.e. EN of C sp^2 vs. C sp^3)
\(C_6H_5OH + H_2O \leftrightarrow C_6H_5O^- + H_2O^+\)
\(K_a = 1.3 \cdot 10^{-10} \ M\)

**species present:** \(HA\) \(A^-\) \(H_2O^+\) \(OH^-\)
**initial concentrations:** \([HA]_0\) \(0\) \(0\)
**change: acid dissociation** \(-x\) \(+x\) \(+x\)
**water autoionization in equilibrium** \(x+y\) \(y\)
\([H_2O^+]^3 + K_a[H_2O^+]^2 - ([HA]_0 K_a + K_w) [H_2O^+] - K_a K_w = 0\)

1. assumption: \(pH\) will be less than 6 \(\Rightarrow\) exclude the contribution of water autoionization
\([H_2O^+]^2 - K_a [H_2O^+] - K_a [HA]_0 = 0\)

2. assumption: if \([HA]_0 \gg 100 K_a \) ignore the dissociated amount of \([A^-]\)
\([H_2O^+]^2 = K_a [HA]_0\)

for example: \([C_6H_5OH] = 0.02 \ M\); and \(0.02 \gg 1.3 \cdot 10^{-5} \ M \Rightarrow pH = 5.8 \Rightarrow [C_6H_5O^-] = 1.6 \cdot 10^{-6} \ M\)

percent of acid dissociation \(= [C_6H_5O^-]/[C_6H_5OH] = 0.008 \%\)

for \(0.02M\) acetic acid solution with \(K_a = 1.8 \cdot 10^{-5} \Rightarrow \sim 3\%\)

IV. Polyprotic acids

- typically \(pK_{a1} - pK_{a2} > 3 \Rightarrow most of the [H_2O^+] is from the 1st acid dissociation (dominant step)\)
- species present:
  \(\begin{array}{cccc}
  \text{species} & \text{H}_2\text{A} & \text{HA} & \text{A}^- & \text{H}_2\text{O}^+ & \text{OH}^- \\
  \text{initial concentrations:} & [HA]_0 & 0 & 0 & 0 \\
  \text{change: 1st acid dissociation} & -x & +x & +x \\
  \text{2nd acid dissociation} & -y & y & +y & +z & +z \\
  \text{water autoionization in equilibrium} & [HA]_0 - x & x - y & y & x + y + z & z \\
  \end{array}\)

1. assumption: \(x \gg y\) if \(\Delta pKa > 3\)
\([HA]_0 - x \ x \ y \ x + z \ z\)

2. assumption \(x \gg z\) if \(pH < 6\)
\([HA]_0 - x \ x \ y \ x \ z\)

obtain \(x\) from \(K_{a1} = x^2/([HA]_0 - x)\)
proton concentration is determined by \(K_{a1}\)

obtain \(z\) from \(K_w\)
autoionization determines the hydroxide concentration
completely ionized acid is determined by \(K_{a2}\)