

17 • Acid-Base Equilibria

BLUFFER'S GUIDE

- $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$
 $\text{pH} = -\log[\text{H}^+] \quad \text{pH} + \text{pOH} = 14 \quad [\text{H}^+] = 10^{-\text{pH}}$
 Convert between pH, pOH, $[\text{H}^+]$, & $[\text{OH}^-]$
- Acid Ionization Constant (K_a):
 $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$
 Example: $\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$

$$K_a = \frac{[\text{F}^-][\text{H}_3\text{O}^+]}{[\text{HF}]}$$
- Typical question: Given K_a and the starting concentrations of acid, find concentrations (or pH) of $[\text{H}^+]$ at equilibrium.

 Example: K_a for acetic acid = 1.8×10^{-5} .
 Find the pH of 0.100M acetic acid.
- Polyprotic Acids: H_3PO_4 , H_2SO_4 , $\text{H}_2\text{C}_2\text{O}_4$, etc. The 1st dissociation is strong for H_2SO_4 .
 When using Hess's Law with a polyprotic acid: $K_{\text{Overall}} = K_{a1} \times K_{a2}$
 Calculating pH, use K_{a1}
- Bronsted-Lowry Definitions.
 Acids = H+ donors; Bases = H+ acceptors
 Conjugate acid-base pairs.
- Base Ionization Constant (K_b):
 $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$
 Example: $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$

$$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]}$$
- Salt solns can have pH's $\neq 7$ (hydrolysis)
 ions from weak acids \rightarrow basic solutions
 $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^-$
 ions from weak bases \rightarrow acidic solutions
 $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$
- $K_a \times K_b = K_w = 10^{-14}$
 only applies for **conjugate** acids & bases!

 Example: $K_a \text{HC}_2\text{H}_3\text{O}_2 = 1.8 \times 10^{-5}$
 $K_b \text{C}_2\text{H}_3\text{O}_2^- = 10^{-14} / 1.8 \times 10^{-5}$
- Percent ionization =

$$\frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{HA}]_{\text{initial}}} \times 100$$
- Acid Strength-know the 6 strong acids: HCl, HBr, HI, HNO_3 , HClO_4 , and H_2SO_4 (removal of the first H^+ only)
 - binary acids - acid strength increases with increasing size and electronegativity of the "other element". (NOTE: Size predominates over electronegativity in determining acid strength.)
 Examples: $\text{H}_2\text{Te} > \text{H}_2\text{O}$ & $\text{HF} > \text{NH}_3$
 - Oxoacids - Acid strength increases with increasing:
 - electronegativity
 - number of bonded oxygen atoms
 - oxidation state of the "central atom".
 Example: HClO_4 or $[\text{O}_3\text{Cl}(\text{OH})]$
 is very **acidic**
 NaOH is very **basic**
 Acid strength also increases with **decreasing** radii of the "central atom".
 Example:
 HOCl (bond between Cl and OH is covalent--making **HOCl acidic**)
 HOI (bond between I and OH is ionic--making **HOI basic**)
- Lewis Acids and Bases:
(This applies to coordinate covalent bonds.)
 Lewis Acid--electron pair acceptor
 Lewis Base--electron pair donor
 "Have Pair... Will Share" – Lewis Base

 In complex ion formation, metal ions are Lewis acids, and ligands are Lewis bases.
 Example: $\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$
 Cu^{2+} acts as an acid; NH_3 acts as a base.
- Strong Bases: amide ion, NH_2^-
 hydride ion, H^- , methoxide ion, CH_3O^-