Weak Acid Equilibria

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- K_a is a constant for a given acid at a particular temperature regardless of the analytical concentration of the acid.

- The magnitude of K_a indicates acid strength.

  ✓ Strong acids have $K_a >> 1$.

  ✓ Weak acids have $K_a < 1$.

  ✓ The more negative the exponent power of ten, the weaker the acid is and the less tendency it has to dissociate.

Leveling of Strong Acids

☞ When any very strong acid ($K_a >> 1$) is added to water, its strength is said to be **leveled** to that of H_3O^+.

- The hydronium ion is the strongest acid that can exist in molecular form in water.
- Any stronger acid must dissociate to form H_3O^+ and its formal weak conjugate base (which has no real base character).

$HCl + H_2O \rightarrow Cl^- + H_3O^+$ Equilibrium lies right.
⇒ HCl is leveled

$HNO_3 + H_2O \rightarrow NO_3^- + H_3O^+$ Equilibrium lies right.
⇒ HNO_3 is leveled

Weak Base Equilibria

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- K_b is a constant for a particular base in all its solutions.

- The magnitude of K_b indicates base strength.

  - ✓ Strong bases have $K_b >> 1$.

  - ✓ Weak bases have $K_b < 1$.

  - ✓ The more negative the exponent power of ten, the weaker the base is and the less tendency it has to hydrolyze.

Leveling of Strong Bases

☞ When any very strong base ($K_b >> 1$) is added to water, its strength is said to be leveled to that of OH^-.

- The hydroxide ion, OH^-, is the strongest base that can exist in its molecular form in water.
- Any stronger base will be leveled through hydrolysis to make OH^- and the appropriate conjugate acid (which as no real acid strength).

$O^{2-} + H_2O \rightarrow OH^- + OH^-$	Equilibrium lies right ⇒ O^{2-} is leveled
$H^- + H_2O \rightarrow H_2 + OH^-$	Equilibrium lies right ⇒ H^- is leveled

Ordered List of Acids and Conjugate Bases

✔We can construct a table of acids and their conjugate bases, ordered according to acid strength.

- Stronger acids with larger K_a's at the top.
- Weaker acids with smaller K_a's at the bottom.

✔Numerical values of K_a are not listed for the truly strong acids, all of which have $K_a >> 1$.

✔Conjugate base strength runs in the opposite sense of acid strength on the table.

- Weaker conjugate bases at the top right.
- Stronger conjugate bases at the bottom right.

TABLE OF CONJUGATE ACID-BASE PAIRS

Acid	**Base**	**K_a (25 °C)**
$HClO_4$	ClO_4^-	
H_2SO_4	HSO_4^-	
HCl	Cl^-	
HNO_3	NO_3^-	
H_3O^+	H_2O	1.0
H_2CrO_4	$HCrO_4^-$	1.8×10^{-1}
$H_2C_2O_4$ (oxalic acid)	$HC_2O_4^-$	5.90×10^{-2}
$[H_2SO_3] = SO_2(aq) + H_2O$	HSO_3^-	1.71×10^{-2}
HSO_4^-	SO_4^{2-}	1.20×10^{-2}
H_3PO_4	$H_2PO_4^-$	7.52×10^{-3}
$Fe(H_2O)_6^{3+}$	$Fe(H_2O)_5OH^{2+}$	1.84×10^{-3}
$H_2C_8H_4O_4$ (*o*–phthalic acid)	$HC_8H_4O_4^-$	1.30×10^{-3}
$H_2C_4H_4O_6$ (tartaric acid)	$HC_4H_4O_6^-$	1.04×10^{-3}
HF	F^-	6.8×10^{-4}
$Hg(H_2O)_6^{2+}$	$Hg(H_2O)_5OH^+$	2.6×10^{-4}
HCO_2H (formic acid)	HCO_2^-	1.8×10^{-4}
$Cr(H_2O)_6^{3+}$	$Cr(H_2O)_5OH^{2+}$	1.6×10^{-4}
$C_6H_5CO_2H$ (benzoic acid)	$C_6H_5CO_2^-$	6.46×10^{-5}
$HC_2O_4^-$ (hydrogen oxalate)	$C_2O_4^{2-}$	6.40×10^{-5}
$HC_4H_4O_6^-$ (hydrogen tartrate)	$C_4H_4O_6^{2-}$	4.55×10^{-5}
CH_3CO_2H (acetic acid)	$CH_3CO_2^-$	1.76×10^{-5}
$Be(H_2O)_4^{2+}$	$Be(H_2O)_3OH^+$	$\sim 1 \times 10^{-5}$
$Al(H_2O)_6^{3+}$	$Al(H_2O)_5OH^{2+}$	7.9×10^{-6}
$HC_8H_4O_4^-$ (hydrogen phthalate)	$C_8H_4O_4^{2-}$	3.1×10^{-6}
$Cd(H_2O)_6^{2+}$	$Cd(H_2O)_5OH^+$	8.32×10^{-7}
H_2CO_3	HCO_3^-	4.3×10^{-7}
$HCrO_4^-$	CrO_4^{2-}	3.20×10^{-7}
$Cu(H_2O)_6^{2+}$	$Cu(H_2O)_5OH^+$	1.6×10^{-7}
H_2S	HS^-	1.2×10^{-7}
$H_2PO_4^-$	HPO_4^{2-}	6.23×10^{-8}
HSO_3^-	SO_3^{2-}	6.2×10^{-8}
$HOCl$	OCl^-	3.0×10^{-8}
$Pb(H_2O)_6^{2+}$	$Pb(H_2O)_5OH^+$	1.5×10^{-8}
$HOBr$	OBr^-	2.06×10^{-9}
$Co(H_2O)_6^{2+}$	$Co(H_2O)_5OH^+$	1.3×10^{-9}
H_3BO_3 or $B(OH)_3$	$B(OH)_4^-$	7.3×10^{-10}
NH_4^+	NH_3	5.65×10^{-10}
$Zn(H_2O)_4^{2+}$	$Zn(H_2O)_3OH^+$	2.5×10^{-10}
HCO_3^-	CO_3^{2-}	5.61×10^{-11}
$Ni(H_2O)_6^{2+}$	$Ni(H_2O)_5OH^+$	2.5×10^{-11}
HOI	OI^-	2.3×10^{-11}
$Fe(H_2O)_6^{2+}$	$Fe(H_2O)_5OH^+$	$\sim 1 \times 10^{-11}$
$Mn(H_2O)_6^{2+}$	$Mn(H_2O)_5OH^+$	$\sim 6 \times 10^{-12}$
$Mg(H_2O)_6^{2+}$	$Mg(H_2O)_5OH^+$	$\sim 4 \times 10^{-12}$
$Ag(H_2O)_2^+$	$Ag(H_2O)OH(s)$	$\sim 7 \times 10^{-13}$
$Al(H_2O)_3(OH)_3(s)$	$Al(H_2O)_2(OH)_4^-$	$\sim 4 \times 10^{-13}$
HPO_4^{2-}	PO_4^{3-}	3.6×10^{-13}
$Ca(H_2O)_6^{2+}$	$Ca(H_2O)_5OH^+$	3.2×10^{-13}
$Zn(H_2O)_4(OH)_2(s)$	$Zn(H_2O)_3(OH)_3^-$	(?)
H_2O	OH^-	1.0×10^{-14}
HS^-	S^{2-}	$\sim 1 \times 10^{-19}$

Polyprotic Acids

✔ Each hydrolysis step of a polyprotic acid has a separate K_a.

✔ Successive dissociations of polyprotic acids lie progressively less to the right, so K_a's become smaller at each step.

Oxalic Acid:

$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^-$ $K_a = K_1 = 5.90 \text{ x } 10^{-2}$
$HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-}$ $K_a = K_2 = 6.40 \text{ x } 10^{-5}$

Sulfuric Acid:

$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$ $K_a = K_1 >> 1$
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$ $K_a = K_2 = 1.20 \text{ x } 10^{-2}$

☞ Sulfuric acid is a strong acid (leveled) only in its first-step hydrolysis.

Hydrated Cations as Acids

- ✔ Hydrated cations, which have a certain number of H_2O molecules surrounding them (often 6), *may* be acidic.

- ✔ Hydrolysis follows the general pattern of a weak acid equilibrium:

$$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5(OH)^{2+}$$

$$K_a = 7.9 \text{ x } 10^{-6}$$

- ✔ Cations with high charge density, such as Al^{3+} and the transition metal cations, are capable of being acidic.

- ✔ Cations with low charge density, such as alkali metal and heavier alkaline earth metal cations, show no appreciable acidity.
  - The lightest alkaline earth cations in water, $Mg(H_2O)_6^{2+}$ and $Ca(H_2O)_6^{2+}$, are extremely weak acids, as their very small K_a values indicate.

Conjugate Base K_b's

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

✔K_b's for all the conjugates do not need to be listed, because they can be calculated from the K_a's of their conjugate acids.

✔K_b's for conjugate bases become smaller as K_a's of their conjugate acids become larger.

Relationship Between K_a of an Acid HA and K_b of Its Conjugate Base A^-

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_w = [H_3O^+][OH^-]$$

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]}\frac{[HA][OH^-]}{[A^-]}$$

$$= [H_3O^+][OH^-] = K_w$$

Relationship Between K_a and K_b for a Conjugate Pair

- ☞ For an acid HA and its conjugate base A^-, or a base B and its conjugate acid BH^+, the relationship between the hydrolysis constants for the conjugate pair is given by

$$K_a^{\mathrm{HA}} K_b^{\mathrm{A}^-} = K_w$$

$$K_b^{\mathrm{B}} K_a^{\mathrm{BH}^+} = K_w$$

When are conjugate bases real bases?

✔Conjugate bases of weak acids are true bases.

Example: Acetate ion, OAc^-, the conjugate base of acetic acid, HOAc.

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^-$$

$$K_b\,(OAc^-) = K_w/K_a(HOAc) = 5.68 \text{ x } 10^{-10}$$

A solution of sodium acetate, NaOAc, will be basic.

$$NaOAc \rightarrow Na^+ + OAc^-$$

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^-$$

$$pH > 7$$

When are conjugate bases not basic?

- ✔ Aprotic (no ionizable H^+) anions of strong acids are not basic, except in a formal sense.

Example: Chloride ion, Cl^-, the conjugate base of hydrochloric acid, HCl.

$$Cl^- + H_2O \rightleftharpoons HCl + OH^-$$

Equilibrium lies completely left!

$$K_b(Cl^-) = K_w/K_a(HCl) = 1 \text{ x } 10^{-14}/(>>1) = <<1 \text{ x } 10^{-14}$$

A solution of NaCl will be neutral.

$$NaCl > Na^+ + Cl^- \qquad pH = 7$$

Polyprotic Conjugate Bases

✔Aprotic conjugate bases of polyprotic acids can function as polyprotic bases, whose K_b values can be calculated from the K_a values of their conjugate acids.

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$K_b = K_w/K_a(HCO_3^-) = 1.0 \text{ x } 10^{-14}/4.8 \text{ x } 10^{-11} = 2.1 \text{ x } 10^{-4}$$

$$HCO_3^- + H_2O \rightleftharpoons [H_2CO_3] + OH^-$$

$$K_b = K_w/K_a(H_2CO_3) = 1.0 \text{ x } 10^{-14}/4.2 \text{ x } 10^{-7} = 2.4 \text{ x } 10^{-8}$$

✔K_b values become progressively smaller with successive hydrolyses.

Tabulated K_b Values

✔ K_b values for neutral weak bases are frequently given in tables.

Base	NH_3	CH_3NH_2	$C_2H_5NH_2$	$(CH_3)_3N$
K_b	1.8 x 10^{-5}	4.4 x 10^{-4}	6.4 x 10^{-4}	6.4 x 10^{-5}

✔ K_a values for conjugate acids can be calculated from $K_a \times K_b = K_w$.

✔ Sometimes conjugate acids and their K_a's appear in acid tables, from which K_b's for the neutral bases can be calculated, using $K_a \times K_b = K_w$.

pK_a and pK_b

✔ K_a and K_b values are often listed as their negative base-10 logarithms.

$$\mathrm{p}K_a = -\log K_a$$

$$\mathrm{p}K_b = -\log \mathrm{p}K_b$$

✔ The larger the positive value of pK, the smaller the value of K is.

✔ Strong acids and bases have negative values of pK_a and pK_b, respectively.