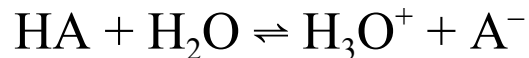


Weak Acid Equilibria

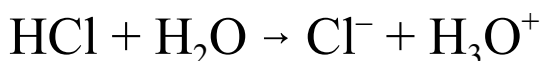


$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

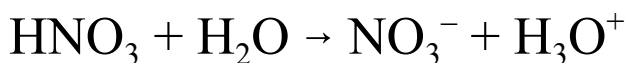
- K_a is a constant for a given acid at a particular temperature regardless of the analytical concentration of the acid.
- The magnitude of K_a indicates acid strength.
 - ✓ Strong acids have $K_a \gg 1$.
 - ✓ Weak acids have $K_a < 1$.
 - ✓ The more negative the exponent power of ten, the weaker the acid is and the less tendency it has to dissociate.

Leveling of Strong Acids

- ☞ When any very strong acid ($K_a \gg 1$) 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).

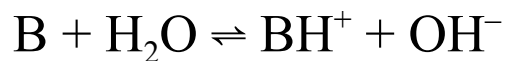


Equilibrium lies right.
⇒ HCl is leveled



Equilibrium lies right.
⇒ HNO_3 is leveled

Weak Base Equilibria



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

- K_b is a constant for a particular base in all its solutions.
- The magnitude of K_b indicates base strength.
 - ✓ Strong bases have $K_b \gg 1$.
 - ✓ 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 ($K_b \gg 1$) 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 has no real acid strength).



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 $K_a \gg 1$.

- ✓ 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.

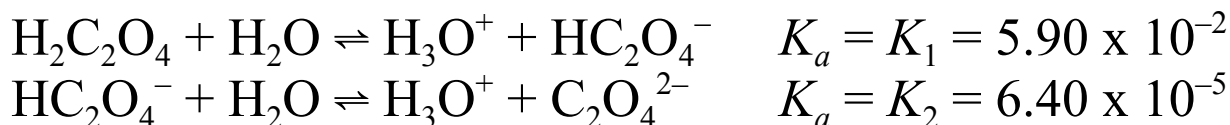
TABLE OF CONJUGATE ACID-BASE PAIRS

Acid	Base	K_a (25 °C)
HClO ₄	ClO ₄ ⁻	
H ₂ SO ₄	HSO ₄ ⁻	
HCl	Cl ⁻	
HNO ₃	NO ₃ ⁻	
H ₃ O ⁺	H ₂ O	1.0
H ₂ CrO ₄	HCrO ₄ ⁻	1.8 x 10 ⁻¹
H ₂ C ₂ O ₄ (oxalic acid)	HC ₂ O ₄ ⁻	5.90 x 10 ⁻²
[H ₂ SO ₃] = SO ₂ (aq) + H ₂ O	HSO ₃ ⁻	1.71 x 10 ⁻²
HSO ₄ ⁻	SO ₄ ²⁻	1.20 x 10 ⁻²
H ₃ PO ₄	H ₂ PO ₄ ⁻	7.52 x 10 ⁻³
Fe(H ₂ O) ₆ ³⁺	Fe(H ₂ O) ₅ OH ²⁺	1.84 x 10 ⁻³
H ₂ C ₈ H ₄ O ₄ (<i>o</i> -phthalic acid)	HC ₈ H ₄ O ₄ ⁻	1.30 x 10 ⁻³
H ₂ C ₄ H ₄ O ₆ (tartaric acid)	HC ₄ H ₄ O ₆ ⁻	1.04 x 10 ⁻³
HF	F ⁻	6.8 x 10 ⁻⁴
Hg(H ₂ O) ₆ ²⁺	Hg(H ₂ O) ₅ OH ⁺	2.6 x 10 ⁻⁴
HCO ₂ H (formic acid)	HCO ₂ ⁻	1.8 x 10 ⁻⁴
Cr(H ₂ O) ₆ ³⁺	Cr(H ₂ O) ₅ OH ²⁺	1.6 x 10 ⁻⁴
C ₆ H ₅ CO ₂ H (benzoic acid)	C ₆ H ₅ CO ₂ ⁻	6.46 x 10 ⁻⁵
HC ₂ O ₄ ⁻ (hydrogen oxalate)	C ₂ O ₄ ²⁻	6.40 x 10 ⁻⁵
HC ₄ H ₄ O ₆ ⁻ (hydrogen tartrate)	C ₄ H ₄ O ₆ ²⁻	4.55 x 10 ⁻⁵
CH ₃ CO ₂ H (acetic acid)	CH ₃ CO ₂ ⁻	1.76 x 10 ⁻⁵
Be(H ₂ O) ₄ ²⁺	Be(H ₂ O) ₃ OH ⁺	~1 x 10 ⁻⁵
Al(H ₂ O) ₆ ³⁺	Al(H ₂ O) ₅ OH ²⁺	7.9 x 10 ⁻⁶
HC ₈ H ₄ O ₄ ⁻ (hydrogen phthalate)	C ₈ H ₄ O ₄ ²⁻	3.1 x 10 ⁻⁶
Cd(H ₂ O) ₆ ²⁺	Cd(H ₂ O) ₅ OH ⁺	8.32 x 10 ⁻⁷
H ₂ CO ₃	HCO ₃ ⁻	4.3 x 10 ⁻⁷
HCrO ₄ ⁻	CrO ₄ ²⁻	3.20 x 10 ⁻⁷
Cu(H ₂ O) ₆ ²⁺	Cu(H ₂ O) ₅ OH ⁺	1.6 x 10 ⁻⁷
H ₂ S	HS ⁻	1.2 x 10 ⁻⁷
H ₂ PO ₄ ⁻	HPO ₄ ²⁻	6.23 x 10 ⁻⁸
HSO ₃ ⁻	SO ₃ ²⁻	6.2 x 10 ⁻⁸
HOCl	OCl ⁻	3.0 x 10 ⁻⁸
Pb(H ₂ O) ₆ ²⁺	Pb(H ₂ O) ₅ OH ⁺	1.5 x 10 ⁻⁸
HOBr	OBr ⁻	2.06 x 10 ⁻⁹
Co(H ₂ O) ₆ ²⁺	Co(H ₂ O) ₅ OH ⁺	1.3 x 10 ⁻⁹
H ₃ BO ₃ or B(OH) ₃	B(OH) ₄ ⁻	7.3 x 10 ⁻¹⁰
NH ₄ ⁺	NH ₃	5.65 x 10 ⁻¹⁰
Zn(H ₂ O) ₄ ²⁺	Zn(H ₂ O) ₃ OH ⁺	2.5 x 10 ⁻¹⁰
HCO ₃ ⁻	CO ₃ ²⁻	5.61 x 10 ⁻¹¹
Ni(H ₂ O) ₆ ²⁺	Ni(H ₂ O) ₅ OH ⁺	2.5 x 10 ⁻¹¹
HOI	OI ⁻	2.3 x 10 ⁻¹¹
Fe(H ₂ O) ₆ ²⁺	Fe(H ₂ O) ₅ OH ⁺	~1 x 10 ⁻¹¹
Mn(H ₂ O) ₆ ²⁺	Mn(H ₂ O) ₅ OH ⁺	~6 x 10 ⁻¹²
Mg(H ₂ O) ₆ ²⁺	Mg(H ₂ O) ₅ OH ⁺	~4 x 10 ⁻¹²
Ag(H ₂ O) ₂ ⁺	Ag(H ₂ O)OH(s)	~7 x 10 ⁻¹³
Al(H ₂ O) ₃ (OH) ₃ (s)	Al(H ₂ O) ₂ (OH) ₄ ⁻	~4 x 10 ⁻¹³
HPO ₄ ²⁻	PO ₄ ³⁻	3.6 x 10 ⁻¹³
Ca(H ₂ O) ₆ ²⁺	Ca(H ₂ O) ₅ OH ⁺	3.2 x 10 ⁻¹³
Zn(H ₂ O) ₄ (OH) ₂ (s)	Zn(H ₂ O) ₃ (OH) ₃ ⁻	(?)
H ₂ O	OH ⁻	1.0 x 10 ⁻¹⁴
HS ⁻	S ²⁻	~1 x 10 ⁻¹⁹

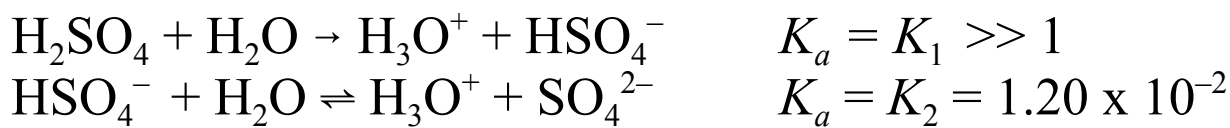
Polyprotic Acids

- ✓ 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:



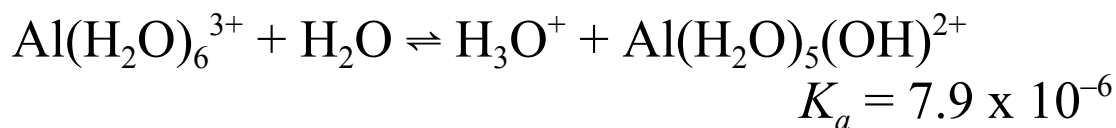
Sulfuric Acid:



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

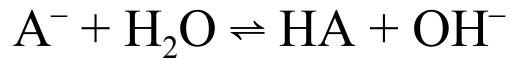
Hydrated Cations as Acids

- ✓ Hydrated cations, which have a certain number of H₂O molecules surrounding them (often 6), *may* be acidic.
- ✓ Hydrolysis follows the general pattern of a weak acid equilibrium:



- ✓ Cations with high charge density, such as Al³⁺ 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(H₂O)₆²⁺ and Ca(H₂O)₆²⁺, are extremely weak acids, as their very small *K_a* values indicate.

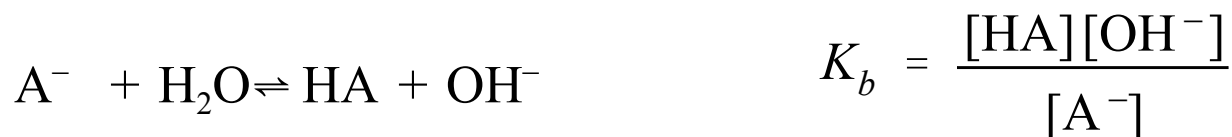
Conjugate Base K_b 's



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

- ✓ 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^-



$$\begin{aligned} K_a \times K_b &= \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \\ &= [\text{H}_3\text{O}^+][\text{OH}^-] = K_w \end{aligned}$$

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

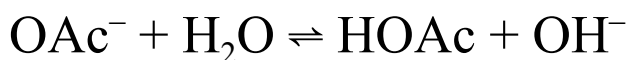
$$K_a^{\text{HA}} K_b^{\text{A}^-} = K_w$$

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

When are conjugate bases real bases?

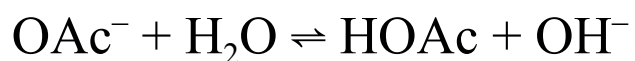
✓ Conjugate bases of weak acids are true bases.

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



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

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

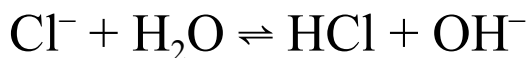


$$\text{pH} > 7$$

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.



Equilibrium lies completely left!

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

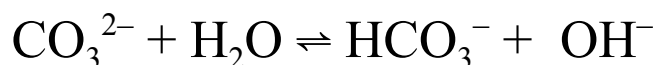
A solution of NaCl will be neutral.



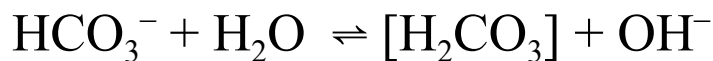
$$\text{pH} = 7$$

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.



$$K_b = K_w / K_a(\text{HCO}_3^-) = 1.0 \times 10^{-14} / 4.8 \times 10^{-11} = 2.1 \times 10^{-4}$$



$$K_b = K_w / K_a(\text{H}_2\text{CO}_3) = 1.0 \times 10^{-14} / 4.2 \times 10^{-7} = 2.4 \times 10^{-8}$$

- ✓ 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 ₃ NH ₂	C ₂ H ₅ NH ₂	(CH ₃) ₃ N
K_b	1.8×10^{-5}	4.4×10^{-4}	6.4×10^{-4}	6.4×10^{-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.

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

- ✓ 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.