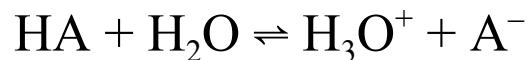


## Weak Acid Equilibria

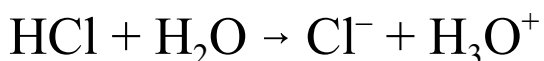


$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

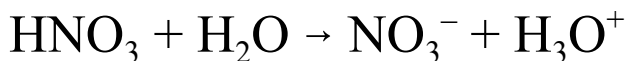
- $K_a$  is a constant for a given acid at a particular temperature regardless of the analytical concentration of the acid.
- The magnitude of  $K_a$  indicates acid strength.
  - ✓ Strong acids have  $K_a \gg 1$ .
  - ✓ Weak acids have  $K_a < 1$ .
  - ✓ The more negative the exponent power of ten, 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  $\text{H}_3\text{O}^+$ .
- The hydronium ion is the strongest acid that can exist in molecular form in water.
  - Any stronger acid must dissociate to form  $\text{H}_3\text{O}^+$  and its formal weak conjugate base (which has no real base character).

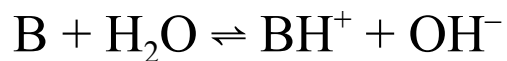


Equilibrium lies right.  
⇒ HCl is leveled



Equilibrium lies right.  
⇒  $\text{HNO}_3$  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  $\text{OH}^-$ .
- The hydroxide ion,  $\text{OH}^-$ , is the strongest base that can exist in its molecular form in water.
  - Any stronger base will be leveled through hydrolysis to make  $\text{OH}^-$  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.

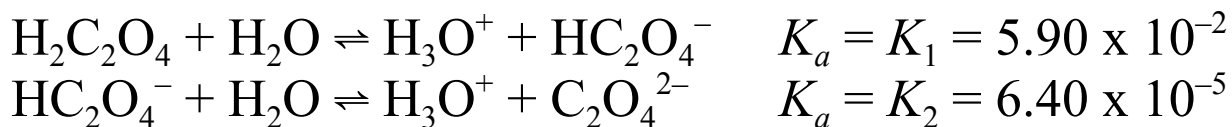
TABLE OF CONJUGATE ACID-BASE PAIRS

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

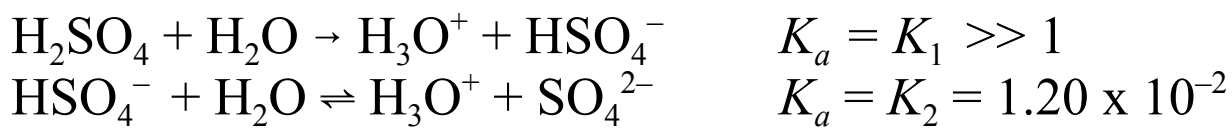
## Polyprotic Acids

- ✓ 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:



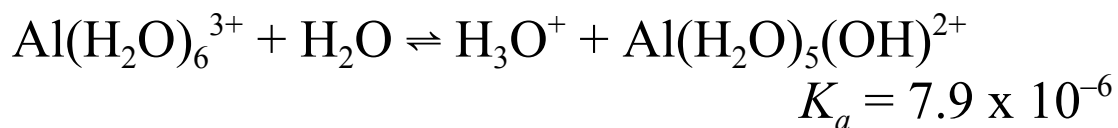
Sulfuric Acid:



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

## Hydrated Cations as Acids

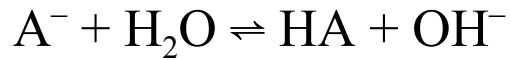
- ✓ Hydrated cations, which have a certain number of H<sub>2</sub>O molecules surrounding them (often 6), *may* be acidic.
- ✓ Hydrolysis follows the general pattern of a weak acid equilibrium:



- ✓ Cations with high charge density, such as Al<sup>3+</sup> 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<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and Ca(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, are extremely weak acids, as their very small *K<sub>a</sub>* values indicate.



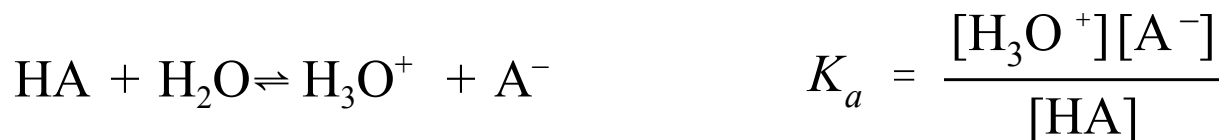
## Conjugate Base $K_b$ 's



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

- ✓  $K_b$ '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

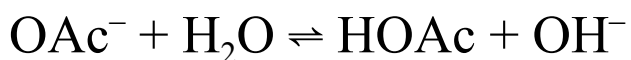
$$K_a^{\text{HA}} K_b^{\text{A}^-} = K_w$$

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

## When are conjugate bases real bases?

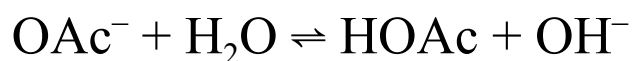
✓ Conjugate bases of weak acids are true bases.

Example: Acetate ion,  $\text{OAc}^-$ , the conjugate base of acetic acid,  $\text{HOAc}$ .



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

A solution of sodium acetate,  $\text{NaOAc}$ , will be basic.

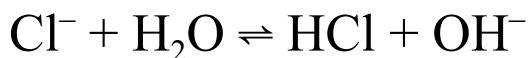


$$\text{pH} > 7$$

## When are conjugate bases not basic?

- ✓ Aprotic (no ionizable H<sup>+</sup>) anions of strong acids are not basic, except in a formal sense.

Example: Chloride ion, Cl<sup>-</sup>, the conjugate base of hydrochloric acid, HCl.



Equilibrium lies completely left!

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

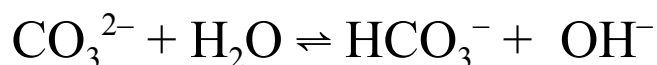
A solution of NaCl will be neutral.



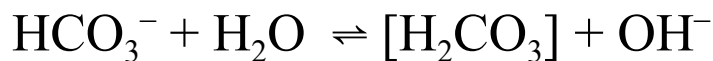
$$\text{pH} = 7$$

## 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	$\text{NH}_3$	$\text{CH}_3\text{NH}_2$	$\text{C}_2\text{H}_5\text{NH}_2$	$(\text{CH}_3)_3\text{N}$
$K_b$	$1.8 \times 10^{-5}$	$4.4 \times 10^{-4}$	$6.4 \times 10^{-4}$	$6.4 \times 10^{-5}$

- ✓  $K_a$  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.