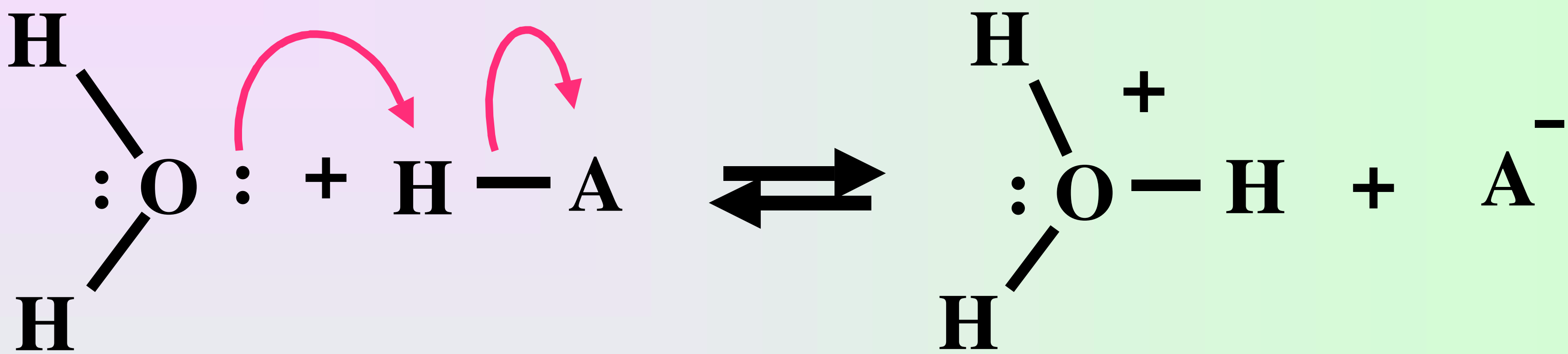
Weak Acids and Acid Ionization Constants

Acid ionization constants are a particular kind of equilibrium constant

Equilibrium constant for proton transfer



$$HA\,(aq) \rightleftharpoons H^{+}\,(aq) + A^{-}\,(aq)$$

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

Acid ionization constant

Ionization Constants of Some Weak Acids at 25°C

Hydrofluoric Acid

$$H-F\,(aq) \rightleftharpoons H^{+}\,(aq) + F^{-}\,(aq)$$

$K_a = 1.71 \times 10^{-4}$

conjugate base

$K_b = 1.4 \times 10^{-11}$

Hydrocyanic Acid

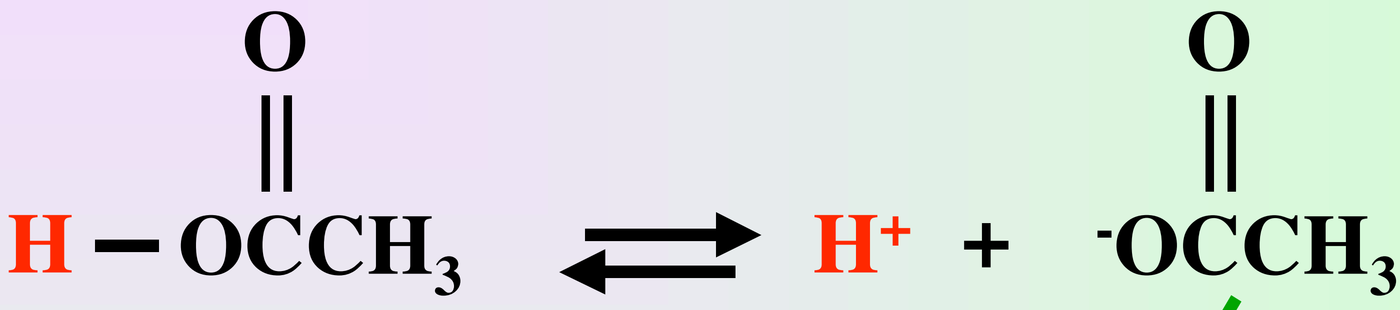
$$H-C\equiv N: \rightleftharpoons H^{+} + :\overset{-}{C}\equiv N:$$

K_a = 4.9 x 10 $^{-10}$

conjugate base

K_b = 2 x 10 $^{-4}$

Acetic Acid



K_a = 1.8 x 10 $^{-5}$

conjugate base

K_b = 5.6 x 10 $^{-10}$

Practice Exercise

What is the pH of a 0 .122 *M* solution of a weak monoprotic acid HA that has $K_a = 5.7 \times 10^{-4}$

$$HA\ (aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

	HA (aq)	H⁺(aq)	A⁻(aq)
Init:	0.122 *M*	0.00*M*	0.00 *M*
final:	- x	+ x	+x
	0.122 - x	+ x	+x

$$K_a = \frac{[H^+]\ [A^-]}{[HA]} = \frac{(x)^2}{(0.122 - x)} = 5.7 \times 10^{-4}$$

$$\frac{[H^+]\ [F^-]}{[HF]} = \frac{(x)^2}{(0.122 - x)} = 5.7 \times 10^{-4}$$

Small K_a

Approximation $.122 - x \approx .122$

$$\frac{x^2}{0.122} = 5.7 \times 10^{-4}$$

$x = [H^+] = .008\ M$

$pH = -\log [H^+]$

$pH = -\log (.008)$

$pH = 2.1$

Percent Ionization

$$HA\ (aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$\text{percent ionization} = \frac{[\,A^-]\ (\text{at equilibrium})}{[\,HA]\ (\text{original})} \times 100$$

Percent Ionization

consider 1.00 *M* HOAc

$K_a = 1.8 \times 10^{-5}$

$$HOAc\,(aq) \rightleftharpoons H^+(aq) + AcO^-(aq)$$

	HOAc	H^+	AcO^-
Init:	1.00 *M*	0.00*M*	0.00 *M*
final:	- x	+ x	+x
	1 - x	+ x	+x

$$K_a = \frac{[H^+]\ [A^-]}{[HOAc]} = \frac{(x)^2}{(1.00 - x)} = 1.8 \times 10^{-5}$$

$$\frac{(x)^2}{(1.00 - x)} = 1.8 \times 10^{-5}$$

$x = 0.0042\ M$

$$\%\ \text{ionization} = 100 \times \frac{[\,AcO^-\,]}{[\,HOAc\,]_o}$$

$[\,AcO^-\,] = 0.0042\ M$

$[HOAc\,]_o = 1.00$

% ionization = 100 (0.0042) / 1.0)

% ionization = 0.42%

Percent Ionization

Is greater in more dilute solution

acetic acid: $K_a = 1.8 \times 10^{-5}$

[acetic acid]	$[H^+]$	%dissoc
1.00 M	0.0042 M	0.42%
0.100 M	0.0013 M	1.3%

Weak Bases and Base Ionization Constants

The Base Ionization Constant K_b

Negatively charged base

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

base	acid		Conjugate acid	Conjugate base

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

base ionization constant

The Base Ionization Constant K_b

neutral base

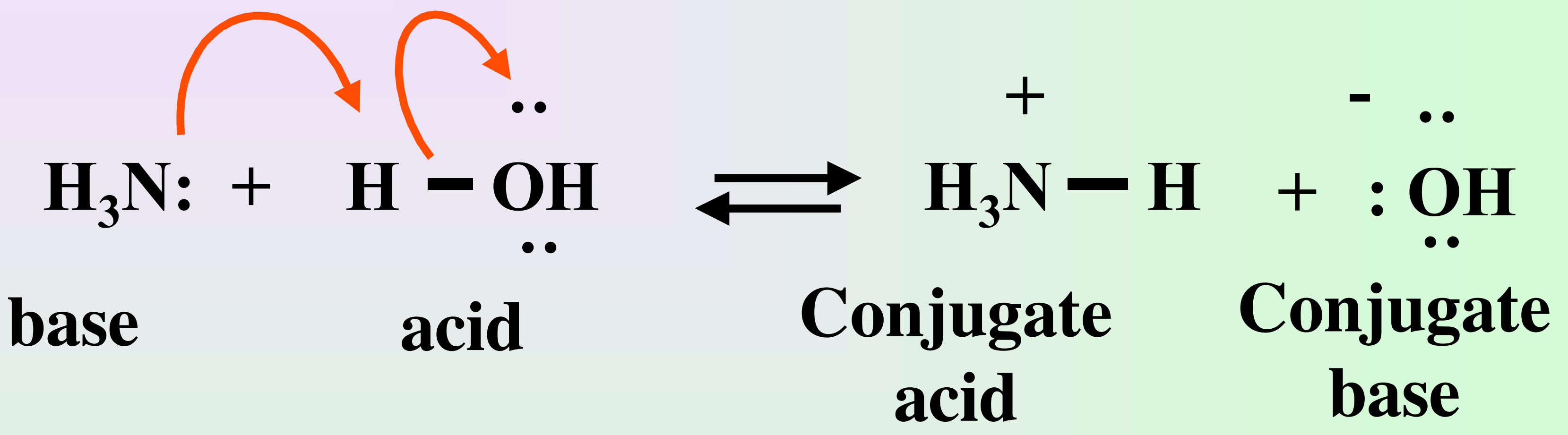
$$:B \quad + \quad H_2O \rightleftharpoons BH^+ \quad + \quad OH^-$$

base	acid		Conjugate acid	Conjugate base

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

base ionization constant

Ammonia is an example of a neutral molecule that is a weak base



$$K_b = \frac{[NH_4^+]\ [OH^-]}{[H_3N]} = 1.8 \times 10^{-5}$$

Example: Methylamine

$$CH_3\ddot{N}H_2 + H-\ddot{\underset{\cdot\cdot}{O}}H \rightleftharpoons CH_3NH_3^{+} + :\ddot{\underset{\cdot\cdot}{O}}H^{-}$$

K_b = 4.4×10^{-4}

Conjugate acid

K_a = 2.3×10^{-11}

Example: Ethylamine

$$CH_3CH_2\ddot{N}H_2 + H{-}\ddot{O}H \rightleftharpoons CH_3CH_2\overset{+}{N}H_3 + :\ddot{O}H^-$$

Conjugate acid

$K_b = 5.6 \times 10^{-4}$

$K_a = 1.8 \times 10^{-11}$

Practice Exercise

What is the pH of a 0 .400 *M* ammonia solution

$K_b = 1.8 \times 10^{-5}$

$$NH_3\ (aq) \rightleftharpoons NH_4^+(aq) + HO^-(aq)$$

	NH_3	NH_4^+	HO^-
Init:	0.400 *M*	0.00*M*	0.00 *M*
final:	- x	+ x	+x
	0.400- x	+ x	+x

$$K_b = \frac{[NH_4^+]\ [HO^-]}{[NH_3]} = \frac{(x)^2}{(0.400 - x)} = 1.8 \times 10^{-5}$$

$$K_a = \frac{[NH_4^+]\ [HO^-]}{[NH_3]} = \frac{(x)^2}{(0.400 - x)} = 1.8 \times 10^{-5}$$

Approximation $.400 - x \approx .400$

$$\frac{x^2}{0.400} = 1.8 \times 10^{-5}$$

$x = [HO^-] = 2.7 \times 10^{-3}\ M$

pOH = -log [OH⁻]

pOH = 2.57

pH = 14.00 - 2.57

pH = 11.43

The Relationship Between Conjugate Acid-Base Equilibrium Constants

For the two equilibria that involve a conjugate acid-base pair in aqueous solution:

$$\text{H}-\text{A} \underset{}{\overset{K_a}{\rightleftharpoons}} \text{H}^+ + :\text{A}^-$$

$$:\text{A}^- + \text{H}_2\text{O} \underset{}{\overset{K_b}{\rightleftharpoons}} \text{H}-\text{A} + :\ddot{\underset{\cdot\cdot}{\text{O}}}\text{H}^-$$

$$K_a \; K_b = K_w$$

At 25° C $K_a \, K_b = 1.0 \times 10^{-14}$

For the two equilibria that involve a conjugate acid-base pair in aqueous solution:

$$\mathrm{H{-}A} \overset{K_a}{\rightleftharpoons} \mathrm{H^+} + \mathrm{{:}A^-}$$

$$\mathrm{{:}A^-} + \mathrm{H_2O} \overset{K_b}{\rightleftharpoons} \mathrm{H{-}A} + \mathrm{{:}OH^-}$$

$$\mathrm{H_2O} \overset{K_w}{\rightleftharpoons} \mathrm{H^+} + \mathrm{{:}OH^-}$$

Recall: when adding two equilibria, multiply their equilibrium constants.

$$K_a K_b = K_w$$

If K_a is small; K_b is large and vice versa

the stronger the acid, the weaker its conjugate base

the stronger the base, the weaker its conjugate acid

Relationships between K_a and K_b

Acid	K_a	Conjugate base	K_b
HF	7.1×10^{-4}	F^-	1.4×10^{-11}
CH_3COOH	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
HCN	4.9×10^{-10}	CN^-	2.0×10^{-5}
Conjugate acid		Base	
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}