Consider an 0.100 M solution of the weak base ammonia:

NH_3 ; $K_b = 1.75 \times 10^{-5}$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = 1.75 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

What is the pH?

	initial	Δ	equilibrium
$[NH_4^+]$	0	$+x$	x
$[OH^-]$	0	$+x$	x
$[NH_3]$	.100	$-x$	$.100 - x$

x = amount of NH_3 that ionizes

$$1.75 \times 10^{-5} = \frac{x^2}{.100 - x}$$

Plug in and solve for "x"!

$$1.75 \times 10^{-5} = \frac{x^2}{.100 - x}$$

Quadratic!

$x \ll 0.100$ Assume $.100 - x \approx .100$

$$1.75 \times 10^{-5} = \frac{x^2}{.100}$$

$$1.322 \times 10^{-3} = x = [OH^-]$$

$$-\log(x) = pOH$$

$$2.88 = pOH$$

$$pH + pOH = 14.00$$

$$\boxed{pH = 11.12}$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

Compare pH to the pH of an 0.100 M solution of the strong base NaOH:

$pH_{NH_3} = 11.12$

$NaOH \longrightarrow Na^+ + OH^-$

$[OH^-] = 0.100$

$pOH = 1.00$

$pH + pOH = 14.00$

$\boxed{pH = 13.00}$

The higher the Ka or Kb value, the stronger the acid or base!

SALTS

- Compounds that result from the reaction of an acid and a base.

- Strong electrolytes (completely dissociate in water) IF SOLUBLE (not all salts dissolve appreciably)

- Most ionic compounds are considered salts (they can be made by some reaction between the appropriate acid and base)

- Salts have acidic and basic properties!

  - Salts made from WEAK ACIDS tend to form BASIC solutions

  - Salts made from WEAK BASES tend to form ACIDIC solutions

$$H_2CO_3 + 2H_2O \rightleftharpoons 2H_3O^+ + CO_3^{-2}$$

acid — conj base

Na_2CO_3

SALT OF A WEAK ACID

$NaA \longrightarrow Na^+ + A^-$ — The salt dissolves completely!

$A^- + H_2O \rightleftharpoons HA + OH^-$ — ... but the ionization of the salt's anion is an EQUILIBRIUM!

The anion is a BASE. It can accept a proton from water to form the weak (therefore stable as a molecule!) acid HA

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$ — This is the base ionixation contant for $\bar{A}$

Since $\bar{A}$ and HA are a conjugate pair, the ionization constants are related!

$$K_w = (K_{a,HA})(K_{b,A^-})$$

You will generally not find both the Ka AND Kb for a conjugate pair in the literature, since one can be easily converted to the other!

SALT OF A WEAK BASE

NH_4Cl

$$BHCl \longrightarrow BH^+ + Cl^-$$

The salt dissociates completely!

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$

... but this ionization is an EQUILIBRIUM process!

$$K_a = \frac{[B][H_3O^+]}{[BH^+]}$$

Acid ionization constant for BH^+

$$K_w = (K_{a,BH^+})(K_{b,B})$$

Find the pH for salt solutions just like you would find pH for any other weak acid or weak base solutions. Only trick is to find out whether the salt is actually acidic or basic!

0.100 M NH_4Cl ... Find pH

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

Acidic, basic, neutral?

weak base: stable in H_2O

NH_4^+: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ ✓

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

strong acid, unstable in H_2O

doesn't exist as HCl molecule

The conjugate of a strong acid or base is NEUTRAL - does not affect pH!

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

p540, Harris

$K_a = \dfrac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.69 \times 10^{-10}$

	initial	Δ	equilibrium
$[NH_3]$	0	$+x$	x
$[H_3O^+]$	0	$+x$	x
$[NH_4^+]$	.100	$-x$	$.100 - x$

"x" = amount of NH_4^+ that reacts

$$\frac{x^2}{.100 - x} = 5.69 \times 10^{-10}$$

$x \ll .100$

$$\frac{x^2}{.100} = 5.69 \times 10^{-10}$$

$$x = 7.54 \times 10^{-6}$$

$7.54 \times 10^{-6} = [H_3O^+]$

$5.12 = pH$

compare to pH = 1 for strong
pH = 2, is for HNO_2

0.100 M $NaC_2H_3O_2$, Find pH

$$NaC_2H_3O_2 \rightarrow Na^+ + C_2H_3O_2^-$$

Na^+: neutral

$C_2H_3O_2^-$: conjugate of $HC_2H_3O_2$

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = ?$$

$$K_{a,\,HC_2H_3O_2} = 1.75 \times 10^{-5}$$

$$K_a \times K_b = K_w$$

$$(1.75 \times 10^{-5})(K_b) = (1.00 \times 10^{-14})$$

$$K_b = 5.71 \times 10^{-10}$$

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = 5.71 \times 10^{-10}$$

	initial	Δ	equilibrium
$[HC_2H_3O_2]$	0	$+x$	x
$[OH^-]$	0	$+x$	x
$[C_2H_3O_2^-]$	0.100	$-x$	$0.100 - x$

"X" = amount of acetate that reacts

$$\frac{x^2}{.100 - x} = 5.71 \times 10^{-10}$$

$\downarrow$ $.100 - x \approx .100$, $x << .100$

$$\frac{x^2}{.100} = 5.71 \times 10^{-10}$$

$$x = 7.56 \times 10^{-6} = [OH^-]$$

$x = 7,56 \times 10^{-6} = [OH^-]$

$pOH = 5,12$

$pH + pOH = 14,00$

$\boxed{pH = 8,88}$

K_a:

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

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

K_b:

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

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

0.150 M NH_4NO_3, find pH

$NH_4NO_3 \longrightarrow NH_4^+ + NO_3^-$

NO_3^-: conjugate of HNO_3, strong acid

NH_4^+: conjugate of NH_3, weak base

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$K_{a,NH_4^+} = \dfrac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.69 \times 10^{-10}$

	initial	Δ	equilibrium
$[NH_3]$	0	$+x$	x
$[H_3O^+]$	0	$+x$	x
$[NH_4^+]$	.150	$-x$	$.150 - x$

x = amount of NH_4^+ that reacts

$$\frac{x^2}{.150 - x} = 5.69 \times 10^{-10}$$

$x << .150$, so $.150 - x \approx .150$

$$\frac{x^2}{.150} = 5.69 \times 10^{-10}$$

$$x = 9.24 \times 10^{-6} = [H_3O^+]$$

$$\boxed{pH = 5.03}$$

BUFFERS

- resist pH change caused by either the addition of strong acid/base OR by dilution

Made in one of two ways:

1. Make a mixture of a weak acid and its conjugate base (as the SALT)
2. Make a mixture of a weak base and its conjugate acid (as the SALT)

For a weak acid, you would:

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

- Add HA (weak acid)
- Add a salt containing A^- (example: NaA)

- This solution actually contains an acid and a base at equilibrium, with a significant concentration of BOTH.

- The acid in the buffer can neutralize bases, while the base can neutralize acids.

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

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

1. Take log of both sides
2. Multiply by -1
3. Rearrange, solving for pH

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

Henderson-Hasselbalch Equation

$[A^-]$ ... from salt

$[HA]$ ... from acid

- We ASSUME that the initial concentrations of both the acid and its conjugate are equal to the equilibrium concentrations. Valid IF there are significant amounts of both species initially.

$$pH = pK_{a,acidic} + \log\left(\frac{[\text{basic species}]}{[\text{acidic species}]}\right)$$

Henderson-Hasselbalch Equation

Ex: $HC_2H_3O_2 / NaC_2H_3O_2$

$$pH = pK_{a,HC_2H_3O_2} + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

NH_3 / NH_4NO_3

$$pH = pK_{a,NH_4^+} + \log\left(\frac{[NH_3]}{[NH_4^+]}\right)$$

$$pK_a + pK_b = 14,00$$