

Suppose you have $[\text{H}_3\text{O}^+]$ from added $\text{HCl} = 0.1 \text{ M} = 10^{-1} \text{ M}$

Then $[10^{-1}][\text{OH}^-] = 10^{-14}$

In pure H_2O , $[\text{OH}^-] = [\text{H}_3\text{O}^+] = 10^{-7}$, **but**

Weak Acids and Bases

Add acetic acid to H_2O :

$$K = K_a$$

What are $[\text{CH}_3\text{COOH}]$, $[\text{H}_3\text{O}^+]$, $[\text{CH}_3\text{COO}^-]$?

If we ignore H_3O^+ from $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$



we have $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-]$ (Stoichiometry)

{ $[\text{H}_3\text{O}^+]$ from $\text{H}_2\text{O} \approx 10^{-7}$ }

Let $C_0 = \text{initial } [\text{CH}_3\text{COOH}] \equiv [\text{HOAc}]$

$$K = \frac{[\text{H}_3\text{O}^+]^2}{C_0 \cancel{[\text{H}_3\text{O}^+]}} = 1.85 \times 10^{-5}$$

$$K = K_a$$

Small K means
equilibrium is
far to left!

Guess, $[\text{HOAc}] \approx C_0$, since $K = K_a \ll \ll 1$ ($\approx [\text{H}_3\text{O}^+] \ll \ll C_0$)

$$K = \frac{[\text{H}_3\text{O}^+]^2}{C_0 \cancel{[\text{H}_3\text{O}^+]}} = 1.85 \times 10^{-5} \longrightarrow [\text{H}_3\text{O}^+] = \sqrt{KC_0}$$

$$C_0 - [\text{H}_3\text{O}^+] = 0.9957 \text{ M} \approx C_0 = 1 \text{ M} \text{ (0.43\% error)}$$

$$\text{Example : } C_0 = 0.01 \text{ M} \approx [\text{H}_3\text{O}^+] = 4.3 \times 10^{-4}$$

$$C_0 - [\text{H}_3\text{O}^+] = 10 \times 10^{-4} - 1.36 \times 10^{-4} = 8.64 \times 10^{-4} \\ \text{vs } C_0 = 10 \times 10^{-4} \text{ (13.6\% error!!)}$$

*** * *** The approximation that $[\text{HOAc}] \approx C_0$ is good only for **small K_a** , **large C_0** .

Note: In all cases $[\text{H}_3\text{O}^+] \gg 10^{-7}$ Thus, OK to neglect H_3O^+ from $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

Could obtain an exact solution by solving a quadratic:

Such equations are trivial to solve with a modern graphing calculator.

$(K=K_a)$

A powerful, approximate alternative method:



$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = 5.0 \times 10^{-4}$$

Method of Successive Approximations

Take $[\text{OH}^-] \gg 10^{-7}$ (ignore hydrolysis of H_2O)

$$[\text{OH}^-] = [\text{CH}_3\text{NH}_3^+]$$

(Stoichiometry)

Let initial concentration $[\text{CH}_3\text{NH}_2] = C_0 = 0.1$

First Approximation :

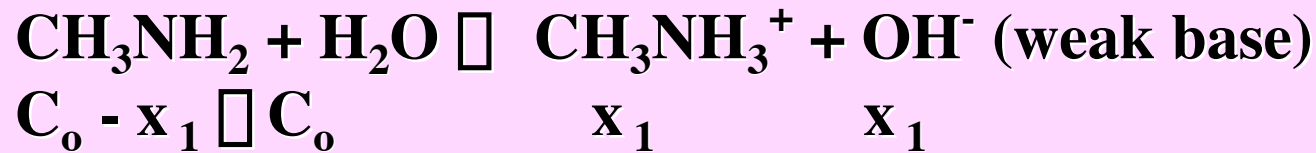
$$[\text{OH}^-] = [\text{CH}_3\text{NH}_3^+] = x_1$$

$$[\text{CH}_3\text{NH}_2] = C_0 - x_1,$$

Assume $x_1 \ll C_0$

$$x_1 = 7.1 \times 10^{-3}$$

$$C_0 - x_1 = (100 - 7.1) \times 10^{-3}$$



$$\% \text{ error in taking } C_0 - x_1 = C_0 \text{ is thus } \left[\frac{7.1}{100} \right] \times 100 = 7.1 \%$$

Second Approximation :

$$[\text{OH}^-] = [\text{CH}_3\text{NH}_3^+] = x_2 \text{ (unknown)}$$

$$K_b = \frac{(x_2)^2}{(C_0 - x_1)} = \frac{(x_2)^2}{92.9 \times 10^{-3}}$$

$$(x_2)^2 = (92.9 \times 10^{-3})(5.0 \times 10^{-4}) = 46.45 \times 10^{-6}$$

Value we chose was only off by 0.3 out of 93.2 (about 0.3%)

Try further iterations (x_3) and will find no change in values to three significant figures.

Hydrolysis



$$K_a = 1.85 \times 10^{-5}$$

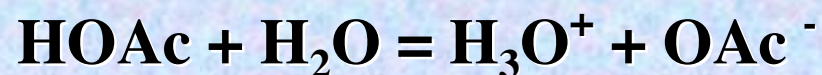


HOAc is an acid, therefore OAc⁻ is a (conjugate) base:

Add NaOAc to H₂O, which dissociates completely to Na⁺, OAc⁻

Multiply K_h by 1 = $\frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]}$

$K_a = [\text{OAc}^-][\text{H}_3\text{O}^+]/[\text{HOAc}]$ is the ionization constant for the reaction:



Note: K_h is very small, indicating that little OAc^- combines with H_2O to form HOAc

Since $K_h = K_w/K_a$, the smaller K_a (weaker the acid) the larger K_h (or OAc^- is more extensively hydrolyzed)

The relative strengths of some acids and their conjugate bases.

$$\text{pK}_a = -\log_{10}(\text{K}_a)$$

Buffer Solutions

Consider acetic acid: $\text{HOAc} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OAc}^-$
 $\text{HOAc} = \text{CH}_3\text{COOH}$, $\text{OAc}^- = \text{CH}_3\text{COO}^-$

$[\text{HOAc}] = [\text{HOAc}]_0$ (initial concentration HOAc)

e.g., add 0.70 mole of HOAc to make 1 liter of solution:

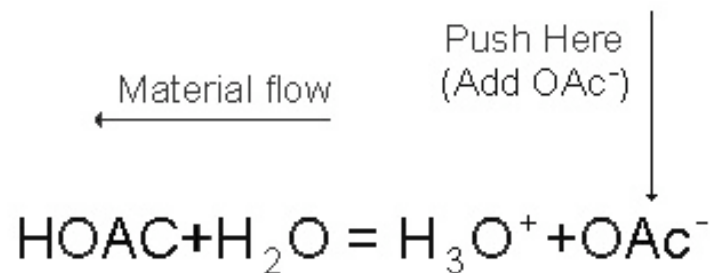
Now suppose add 0.60 moles NaOAc, which dissociates completely to Na^+ , OAc^-

First, look at $\text{HOAc} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OAc}^-$

**How keep $K_a = 1.85 \times 10^{-5}$ when
throw in all of this OAc^- ?**

**This just uses up H_3O^+ that came from ionization of HOAc,
thereby forcing $[\text{HOAc}]$ closer to $[\text{HOAc}]_0$!!**

Inverse teeter-totter effect:



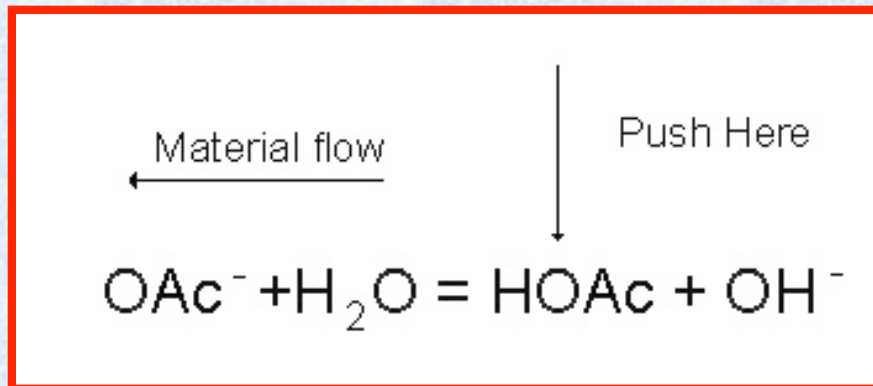
Now, look at: $\text{OAc}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOAc} + \text{OH}^-$

Very little OH^- made this way (lose little OAc^- and make little HOAc) since:

So when put 0.6 moles OAc^- in a liter of pure water have $[\text{OAc}^-] = [\text{OAc}^-]_0 = 0.6 \text{ M}$

How to keep $K_h = [\text{HOAc}] [\text{OH}^-] / [\text{OAc}^-] = 5.4 \times 10^{-10}$ when $[\text{HOAc}]$ is large?

Result is to force OAc^- even closer to its initial value $[\text{OAc}^-]_0 = 0.60 \text{ M}$



Addition of large amounts of a weak acid and its conjugate base to the same solution nullifies both the ionization of the acid and the hydrolysis of the base!!

$$K_a = [\text{OAc}^-][\text{H}_3\text{O}^+] / [\text{HOAc}] = 1.85 \times 10^{-5}$$

$$K_h = [\text{HOAc}][\text{OH}^-] / [\text{OAc}^-] = 5.4 \times 10^{-10}$$

$$[\text{OAc}^-] \approx 0.6 \text{ M and } [\text{HOAc}] \approx 0.7 \text{ M}$$

$[\text{H}_3\text{O}^+] = 2.185 \times 10^{-5} \text{ M}$ } This result is accurate to 4 significant figures (gives same result as solving quadratic to this accuracy)!

A solution containing substantial amounts of a weak acid and its conjugate base is known as a buffer solution.

Thus, have $[\text{H}_3\text{O}^+] = \{[\text{acid}]/[\text{salt}]\} K_a$

Depends only on K_a and the **ratio** of [acid] to [salt]

**Example: 1 liter of 0.25 M HCl, add 0.600 moles of NaOAc(s)
Assume no volume change occurs upon addition of salt.**

Find [OAc⁻], [HOAc], [H₃O⁺], [OH⁻]



$$K_a = \frac{[\text{OAc}^-][\text{H}_3\text{O}^+]}{[\text{HOAc}]} = 1.85 \times 10^{-5}$$

Equation far to the right

**Recognizing a buffer
when you see it. Not
always an easy task.**

Buffer conditions!

$$[\text{OAc}^-] = .350$$

$$[\text{HOAc}] = .250$$