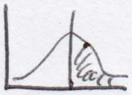
5/29/12

The auto-ionization of water

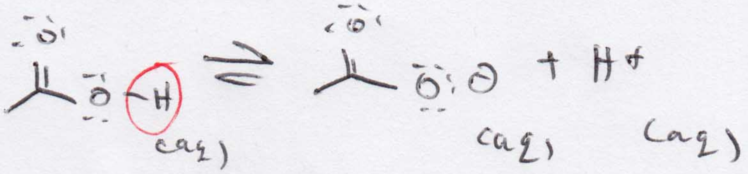
$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$ is unfavorable but happens to a small degree since @ any temperature a few molecules will have enough energy to dissociate.



$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at only one temperature (   )

In pure water @   °C, $[H^+] = [OH^-] = 1.0 \times 10^{-7}\ M$

$pH \equiv -\log_{10}[H^+] = 7.00$ pH=7 means neutral only @ this temperature



$\Rightarrow K_a = \dfrac{[H^+][A^-]}{[HA]}$

$HA \rightleftharpoons A^- + H^+$

conjugate

$\Rightarrow K_b = \dfrac{[OH^-][HB]}{[B]}$

$:NH_3 + H_2O \rightleftharpoons OH^- + NH_4^{\oplus}$

$B + H_2O \rightleftharpoons {}^-OH^- + HB^{\oplus}$

conjugate

If $A^- = B$

$$K_A \cdot K_B = \frac{[H^+]\cancel{[A^-]}}{\cancel{[HA]}} \cdot \frac{[OH^-]\cancel{[HB]}}{\cancel{[B]}} = [H^+][OH^-] = K_w$$

An acid's strength is inversely proportional to its conjugate base's strength.

$1\ M$ HCl → pH $\cancel{=}$ 0

$0.1\ M$ HCl → pH $\cancel{=}$ 1

$0.01\ M$ HCl → pH = 2

When solutions are highly concentrated, interactions between solute particles can cause deviation from predicted solution behavior → activity

Strong acid; Heavy spontaneous dissociation

→ large K_a

→ small pK_a

$pK_{a(HCl)} \ll 0$

Weak acids

Given 1 M Acetic acid (and ignoring activity), what is the pH? $pK_a = 4.76$ $K_a = 1.76 \times 10^{-5}$

	HA	H^+	A^-
Initial	1.00	$\cancel{10^{-7}}$	0
Change	$-x$	$+x$	$+x$
End	$1-x$	x	x

If $x \ll 1$, it (x) can be ignored

$$K_a = \frac{(x)(x)}{1\cancel{-x}} = 1.76 \times 10^{-5}$$

$$x^2 = 1.76 \times 10^{-5}$$

$$x = 4.19 \times 10^{-3} \Rightarrow \boxed{pH = 2.38}$$

Given 0.500 M acetic acid + 0.500 M sodium acetate, what is the pH?

	HA	H^+	A^-
I	.5M	"0"	.5M
C	$-x$	x	x
E	$.5-x$	x	$.5+x$

$$K_a = 1.76 \times 10^{-5} = \frac{(.5+x)(x)}{.5-x}$$

$\underline{\underline{\text{If}}}$ $x \ll .5$

$x = 1.76 \times 10^{-5}$ $pH = 4.76 = pK_a$ $\Rightarrow \frac{.5(x)}{.5} = x$

*If x is <u>not</u> small compared to .5, this simplification is not possible.

* When an acid + a conjugate are added together, a small shift in their concentrations will occur. But, if the acid is weak, that shift can often be ignored.

$$pK_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow -\log_{10}(K_a) = -\log_{10}\left[\frac{[H^+][A^-]}{[HA]}\right].$$

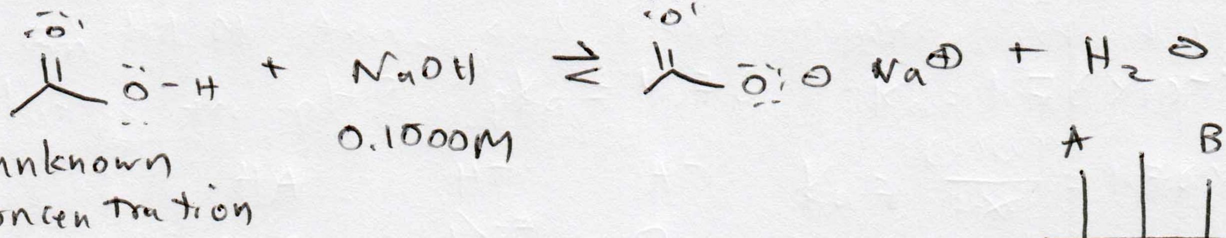
$$pK_a = -\log_{10}[H^+] + \left(-\log_{10}\left(\frac{[A^-]}{[HA]}\right)\right)$$

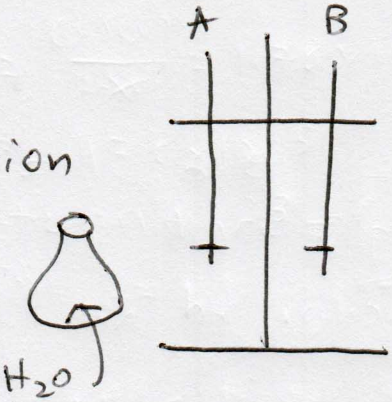
$$pK_a = pH - \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

Henderson-Hasslebach eq.

$$pH = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

Titration





Indicator – The indicator for a titration is chosen such that the pKa of the indicator is the same as the expected pH of the neutralized sol'n,

Neutral ≠ Neutralized

neutral: $[H^+] = [OH^-]$

neutralized: $\underline{n_{acid}} = \underline{n_{base}}$

not H^+ not OH^-

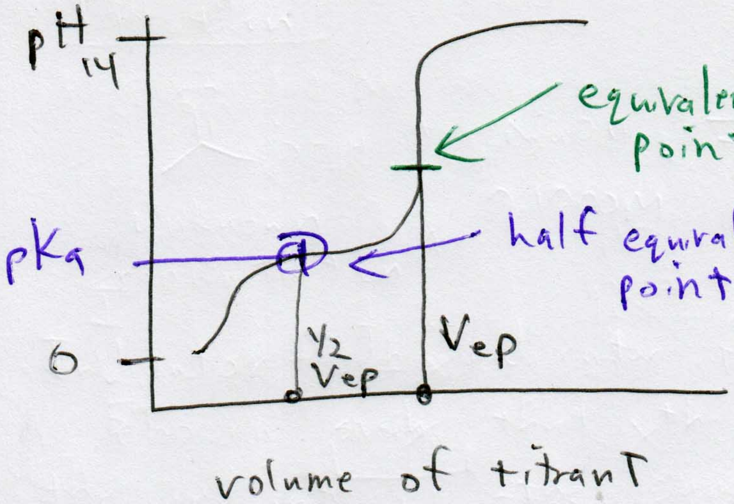
If a weak acid and/or weak base are used in titration, the moles of $[H^+]/[OH^+]$ would not be the same as the moles of acid/base, since incomplete dissociation would occur.

acetic acid + sodium hydroxide → basic sol'n
weak acid strong base

Once acetic acid is fully neutralized by sodium hydroxide, a salt is produced (sodium acetate). This product is the result of the forced complete dissociation of a <u>weak</u> acid. Once formed, the salt will thus want to re-establish equilibrium w/ the acid, so it will react with water, forming hydroxide, resulting in a basic solution.

Equivalence point – When equal moles of acid + base have been reacted.

Endpoint – The <u>visual</u> observation that a titration is complete (color change).



1.0M HCl → pH = 0
.1M HCl → pH = 1
.01M HCl → pH = 2
.001M HCl → pH = 3

90%
99%
99.90%

As titrant is added linearly, pH changes exponentially.

Same simplication used in H.H. equation

@ half equivalence, $[HA] \approx [A^-]$

$$Ka = \frac{[H^+]\cancel{[A^-]}}{\cancel{[HA]}} \Rightarrow Ka = [H^+] \Rightarrow \boxed{pKa = pH}$$

@ equivalence ! $n_{acid} = n_{base}$ $n = M \cdot V$

$$\underline{M_{acid}}\,\underline{V_{acid}} = \underline{M_{base}} \cdot \underline{V_{base}}$$

unknown

measured

calculated (standardized)