WEAK ACIDS AND WEAK BASES

Weak acids and weak bases dissociate less than 100%

So far we have used percent ionization to calculate concentration for weak acids, however this is really a stretch. Technically percent ionization is dependent upon concentration...values in the data table are only correct for 0.1 mol/L solutions@ 20^oC

The proper way to calculate ion concentrations in weak acids and weak bases is to use equilibrium constants K

For weak acid systems the following will apply:

$WA + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CB$ **there is always a 1:1 mol ratio between these concentrations**

$$K_a = \frac{[H_3O^+]^2}{[WA]}$$

example:

$HNO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + NO_2^-\,(aq)$

$$K_a = \frac{[H_3O^+]^2}{[HNO_2]}$$ (We can do this because $[H_3O^+] = [NO_2^-]$)

for weak base systems:

$WB(aq) + H_2O\,(l) \rightleftharpoons CA(aq) + OH^-\,(aq)$

$$K_b = \frac{[OH^-]^2}{[WB]}$$

Example:

$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$

$$K_b = \frac{[OH^-]^2}{[NH_3]}$$ (We can do this because $[OH^-] = [NH_4^+]$)

Weak acid and weak base questions might be in multiple choice or constructed response questions. If it is a multiple choice question use the formulas above, but if it's a constructed response, write the two concentrations out separately.

Write the expression for K_b

$$PO_4^{3-}\ (aq) + H_2O\ (l) \rightleftharpoons HPO_4^{2-}\ (aq) + OH^-\ (aq)$$

$$K_b = \frac{[OH^-]^2}{[PO_4^{3-}]} \quad \text{Or} \quad K_b = \frac{[OH^-]\,[HPO_4^{2-}]}{[PO_4^{3-}]}$$

There are many problem types that can be done from simple rearrangement of K, to ones involving pH/pOH/ $[H^+]/[OH^-]$ etc.

Example #1 Calculate the acid ionization (means the same as dissociation) constant (K_a) for benzoic acid (C_6H_5COOH) given the concentration of the acid at equilibrium was 0.45 mol/L and the $[H_3O^+]$ at equilibrium was 0.0058 M

$$C_6H_5COOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + C_6H_5COO^-\ (aq)$$

1:1 mol ratio between H_3O^+ (aq) + $C_6H_5COO^-$ (aq)

$$\therefore K_a = \frac{[H_3O^+]^2}{[C_6H_5COOH]}$$

$$= \frac{(0.0058)^2}{(0.45)} = 7.5 \times 10^{-5}$$

Other questions may require rearranging the K_a expression given 2 of the 3 values, then we could extend the question to do other calculations, like pH or pOH.

Example #2 The K_a of nitrous acid is 1.4×10^{-3}. At equilibrium the concentration of nitrous acid was measured to be 0.056M. Calculate the pH.

$K_a = 1.4 \times 10^{-3}$
$[HNO_2] = 0.056$
pH = ? (but we know it should be < 7)
In order to calculate pH we need $[H_3O^+]$

$$HNO_2(aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + NO_2^-\ (aq)$$

H_3O^+ and NO_2^- have 1:1

$$\therefore K_a = \frac{[H_3O^+]^2}{[HNO_2]}$$

$[H_3O^+]^2 = K_a \times [HNO_2]$

so $[H_3O^+] = \sqrt{K_a \times [HNO_2]}$

$= \sqrt{(1.4 \times 10^{-3})(0.056)}$
$= 8.85 \times 10^{-3}$

and $pH = -\log [H_3O^+]$
$= -\log (8.85 \times 10^{-3})$
$= 2.05$

Try this one: Calculate the pH of a solution of 0.10 mol/L hypochlorous acid, HOCl, if the $K_a = 2.9 \times 10^{-8}$

A NEW TWIST WITH ICE TABLES, TOO!!

In all of the previous examples the equilibrium concentration was assumed to be unaffected by the dissociation... in other words, so little of the acid ionized that the original concentration was the same as the equilibrium concentration.

Consider any acid with a small K_a :

$HX (aq) + H_2O (l) \leftrightarrows X^- (aq) + H_3O^+ (aq)$

	[HX]	$[X^-]$	$[H_3O^{+}]$
Initial	2.0 M	0	0
Change	-0.00001	0.00001	0.00001
Equil.	1.9999	0.00001	0.00001

Once you use significant figures, the equilibrium concentration would still be 2.0M

If the acid dissociates to such a degree that the original concentration changes, then the **quadratic function must be used** ! It also means the $[H_3O^+]$ is not insignificant - it counts!

There is a **magic number** that you need to check to tell you which path to take:

$$\textbf{check } \frac{\textbf{[initial acid]}}{\mathbf{K_a}}$$

IF YOUR ANSWER IS>500, then $[H_3O^+]$ is not significant - it is insignificant, and the initial [acid] is the same as the equilibrium [acid].

IF YOUR ANSWER IS < 500 - you must use the quadratic formula!

Example#1 : Formic acid (HCOOH) is present in the sting of red ants. What is the pH of a 0.015 M solution of HCOOH, given that K_a is 1.8×10^{-9}?

$HCOOH (aq) + H_2O \rightleftarrows H_3O^+ (aq) + HCOO^- (aq)$

	HCOOH		H_3O^+	$HCOO^-$
I	0.015		0	0
C	$-x$		$+x$	$+x$
E	$0.015-x$		x	x

Check the magic number:

$\frac{[acid]}{K_a} = \frac{0.015}{1.8 \times 10^{-9}} = 8.3 \times 10^{6}$ (this is > 500)

so $[H_3O^+]$ is <u>not</u> significant,
∴ $[HCOOH]_i = [HCOOH]_e$

∴ We do not use the quadratic function, and simply calculate.

$$K_a = \frac{[H_3O^+]^2}{[HCOOH]}$$

$$[H_3O^+]^2 = K_a \times [HCOOH]$$

$$[H_3O^+] = \sqrt{K_a \times [HCOOH]}$$

$$= \sqrt{(0.015)(1.8 \times 10^{-9})}$$
$$= 5.20 \times 10^{-6}$$

Now we can calculate pH:

$$pH = -\log [H_3O^+]$$
$$= -\log (5.20 \times 10^{-6})$$
$$= 5.28$$

But check this one out!

Example #2

Formic acid (HCOOH) is present in the sting of red ants. What is the pH of a 0.015 M solution of HCOOH, given that K_a is 1.8×10^{-4}?

$$HCOOH\ (aq) + H_2O \rightleftarrows H_3O^+\ (aq) + HCOO^-\ (aq)$$

	HCOOH		H_3O^+	$HCOO^-$
I	0.015		0	0
C	-*x*		+*x*	+*x*
E	0.015-*x*		*x*	*x*

Check the magic number:

$\frac{[acid]}{K_a} = \frac{0.015}{1.8 \times 10^{-4}} = 83.3$ (this is < 500 so $[H_3O^+]$ is significant)

∴ We must use the quadratic function!

$$K_a = \frac{[H_3O^+]^2}{[HCOOH]}$$

$$= \frac{x^2}{0.015-x}$$

$$1.8 \times 10^{-4} = \frac{x^2}{0.015-x}$$

$$(1.8 \times 10^{-4})(0.015-x) = x^2$$
$$2.7 \times 10^{-6} - 1.8 \times 10^{-4}\,x = x^2$$
$$x^2 + 1.8 \times 10^{-4}\,x - 2.7 \times 10^{-6} = 0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

$$x = \frac{(-1.8 \times 10^{-4}) \pm \sqrt{(-1.8 \times 10^{-4})^2 - 4(1)(-2.7 \times 10^{-6})}}{2(1)}$$

$$x = \frac{(-1.8 \times 10^{-4}) \pm 3.29 \times 10^{-3}}{2}$$

$x = 1.56 \times 10^{-3}$ { Or $x = -1.74 \times 10^{-3}$ throw this one out!}
{can't have a negative concentration}

pH $= -\log[H_3O^+]$
$= -\log(1.56 \times 10^{-3})$
$= 2.81$

Example # 3 Calculate the pH of a 0.0055 M solution of acetic acid (CH_3COOH) given its $K_a = 2.74 \times 10^{-6}$

	CH_3COOH (aq) + H_2O (l) ⇄	H_3O^+ (aq) +	CH_3COO^-(aq)
I	0.0055	0	0
C	$-x$	$+x$	$+x$
E	$0.0055-x$	x	x

Check $\frac{[acid]}{K_a} = \frac{0.0055}{2.74 \times 10^{-6}} = 2007$ (>500)

$\therefore$ $[acid]_{initial} = [acid]_{equil}$

and 1:1 ratio between $[H_3O^+]$ and $[CH_3COO^-]$

so $K_a = \frac{[H_3O^+]^2}{[CH_3COOH]}$

$[H_3O^+] = \sqrt{(K_a)([CH_3COOH])}$

$= \sqrt{(2.74 \times 10^{-6})(0.0055)}$
$= 1.23 \times 10^{-4}$

$pH = -\log [H_3O^+]$
$= -\log (1.23 \times 10^{-4})$
$= 3.91$

Example #4 Calculate the pH of a 0.13 M solution of HCN (aq) ; $K_a = 8.19 \times 10^{-2}$

	$HCN (aq) + H_2O (l) \rightleftarrows$	$CN^- (aq) +$	$H_3O^+ (aq)$
I	0.13	0	0
C	$-x$	$+x$	$+x$
E	$0.13-x$	x	x

check: $\frac{[HCN]}{K_a} = \frac{0.13}{8.19 \times 10^{-2}}$ = 1.59 (<500, use QF)

$K_a = \frac{x^2}{0.13-x}$ $8.19 \times 10^{-2} = \frac{x^2}{0.13 - x}$

$1.06 \times 10^{-2} - 8.19 \times 10^{-2}\, x = x^2$
$0 = x^2 + 8.19 \times 10^{-2}\, x - 1.06 \times 10^{-2}$

$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$x = \frac{8.19 \times 10^{-2} \pm \sqrt{(8.19 \times 10^{-2}) - 4(1)(-1.06 \times 10^{-2})}}{2(1)}$

$x = \frac{8.19 \times 10^{-2} \pm 2.22 \times 10^{-1}}{2}$

$x = 7.01 \times 10^{-2}$ or $x = -0.152$ (use the first one)

$[H_3O^+] = 7.01 \times 10^{-2}$

$$\begin{aligned} pH &= -\log [H_3O^+] \\ &= -\log (7.01 \times 10^{-2}) \\ &= 1.15 \end{aligned}$$

Try this one to make sure you can handle this before you begin your assignment:

Calculate the pH of 0.025 mol/L solution of nitrous acid, given the K_a for HNO_2 (aq) is 7.2×10^{-4}