Chemistry 12
Acid-Base Equilibrium IV

IV 14-15
pg. 148-154

Name:
Date:
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1. K_a / K_b Calculations

Complete the following statements:

1. As a solution becomes more <mark>acidic</mark>...

    Oppositely related

    - $[H_3O^+]$ increases or decreases?
    - pH increases or decreases?
    - [OH-] increases or decreases?
    - pOH increases or decreases?

2. If the pH of a solution equals 5.00, the [OH-] equals $\underline{1.0 \times 10^{-9}}$ M.

    $pOH = 9.00$

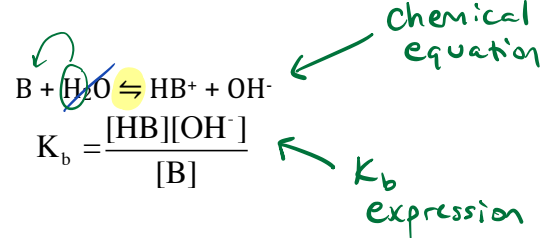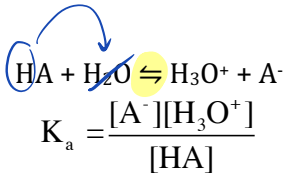 $[OH^-] = 10^{-9.00}$

3. If the pOH of a solution decreases by 5, then the $[H_3O^+]$ has __*decreased*__ (increased or decreased) by a factor of __10^5__.

Calculations Involving K_a and K_b

Weak acids & bases

Recall...

Acid = HA   and   Base = B

chemical equation

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

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

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

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

K_b expression

Write the chemical equation and K_a expression that represents the reaction of <mark>HNO_2</mark> in <mark>water.</mark>

$$HNO_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons NO_{2\,(aq)}^- + H_3O^+_{(aq)}$$

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]}$$

Write the chemical equation and K_b expression that represents the reaction of <mark>NH_3</mark> in <mark>water.</mark>

$$NH_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+ + OH^-_{(aq)}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

CALCULATIONS FOR WEAK ACIDS

Problem Type 1: Calculating pH

→ weak acid
$[WA] \neq [H_3O^+]$

Example: Calculate the (pH) and (pOH) of 0.50 M solution of hydrofluoric acid.

- Is HF a strong or weak acid?

  weak

- What is the chemical equation? (What kind of arrow will you use?)

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons F^-_{(aq)} + H_3O^+_{(aq)}$$

- What is the K_a value (from the table!) and expression?

$$K_a = \frac{[F^-][H_3O^+]}{[HF]} = 3.5 \times 10^{-4}$$

- Since this is a weak acid, equilibrium is established. ICE TABLE!!

	HF $_{(aq)}$	+	H$_2$O $_{(l)}$	$\rightleftharpoons$	F$^-$ $_{(aq)}$	+	H$_3$O$^+$ $_{(aq)}$
Initial	0.50 M				0 M		0 M
Change	- x				+ x		+ x
Equilibrium	0.50 -x				x		x

We don't include the concentration of water because we assume the [H₂O] remains constant.

- Fill out values for the K_a expression.

$$K_a = \frac{(x)(x)}{0.50-x} = 3.5 \times 10^{-4}$$

Must be stated!

assume $0.50 - x \cong 0.50$

- The expression in the denominator: 0.50 M - x can be assumed to be $\cong$ 0.50M.
  - The value of K_a is very small compared to the initial concentration of the acid. This means that the percent of the acid that actually ionizes will not significantly change the original concentration.
  - **If initial [HA] is at least 10³ times larger than the K_a value, the assumption is valid.**

- Solve for unknown.

$$\frac{x^2}{0.50} = 3.5 \times 10^{-4}$$
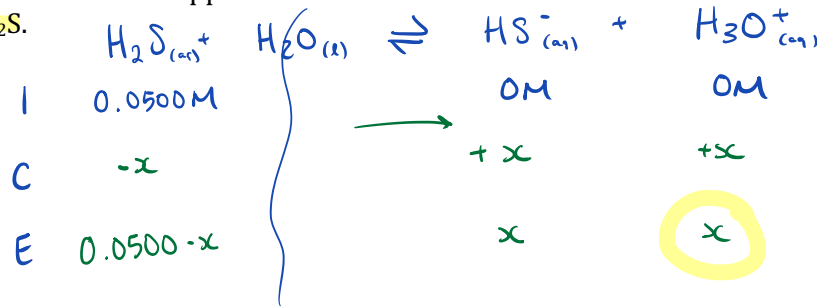
$$x = \sqrt{0.5 \times (3.5 \times 10^{-4})}$$

$$= 0.013 M = [H_3O^+]$$

$$pH = -\log(0.013)$$
$$pH = 1.89$$
$$pOH = 12.11$$

Practice 1: Hydrogen sulphide is a poisonous flammable gas whose "rotten egg" smell is perceptible at concentrations as low as 0.00047 ppm. It is also a weak acid when dissolved in water. Calculate the pH and pOH of 0.0500M H_2S.

$$H_2S_{(aq)} + H_2O_{(l)} \rightleftharpoons HS^-_{(aq)} + H_3O^+_{(aq)}$$

I	0.0500M	0M	0M
C	$-x$	$+x$	$+x$
E	$0.0500-x$	x	x

$$K_a = \frac{[HS^-][H_3O^+]}{[H_2S]} = 9.1 \times 10^{-8}$$

2sf

$$\frac{x^2}{0.0500-x} = 9.1 \times 10^{-8}$$

*assume $0.0500 - x \cong 0.0500$

$$\frac{x^2}{0.0500} = 9.1 \times 10^{-8}$$

$$x = \sqrt{(9.1 \times 10^{-8})(0.0500)}$$

$$= 6.7 \times 10^{-5}M = [H_3O^+]$$

$$pH = -\log(6.7 \times 10^{-5}) = \boxed{4.17}$$

$$pOH = 14 - 4.17 = \boxed{9.83}$$
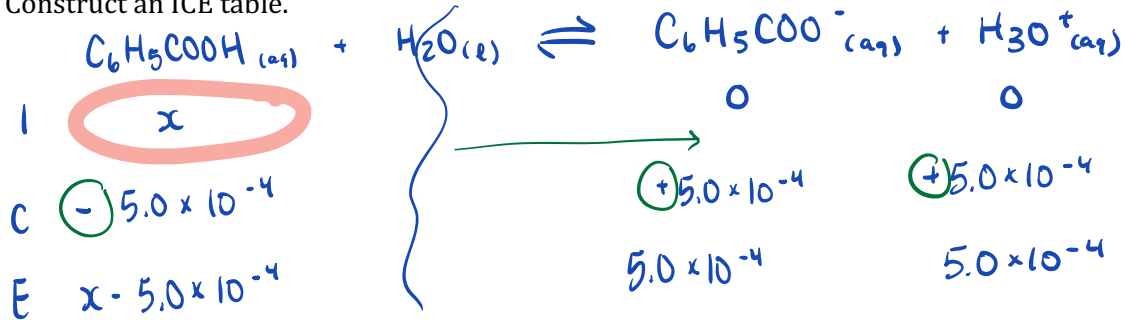
Problem Type 2: Calculating initial [HA]

Example: What concentration of benzoic acid is required to produce a solution with a pOH of 10.70?

- Using given pOH, calculate the $[H_3O^+]$ → equilibrium concentration in ICE table!

$$pH = 14 - 10.70$$
$$= 3.30$$

$$[H_3O^+] = 10^{-3.30} = 5.0 \times 10^{-4}M$$

- Construct an ICE table.

$$C_6H_5COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons C_6H_5COO^-_{(aq)} + H_3O^+_{(aq)}$$

I	x	0	0
C	-5.0×10^{-4}	$+5.0 \times 10^{-4}$	$+5.0 \times 10^{-4}$
E	$x - 5.0 \times 10^{-4}$	5.0×10^{-4}	5.0×10^{-4}

- What is the K_a for benzoic acid?

$$K_a = 6.5 \times 10^{-5} = \frac{(5.0 \times 10^{-4})^2}{x - 5.0 \times 10^{-4}}$$

$$x = 4.3 \times 10^{-3}$$

- Solve for the unknown.

$$(x - 5.0 \times 10^{-4})6.5 \times 10^{-5} = \left(\frac{(5.0 \times 10^{-4})^2}{x - 5.0 \times 10^{-4}}\right)(x - 5.0 \times 10^{-4})$$

$$\boxed{[C_6H_5COOH] = 4.3 \times 10^{-3}M}$$

$$6.5 \times 10^{-5}x - 3.3 \times 10^{-8} = 2.5 \times 10^{-7}$$
$$+3.3 \times 10^{-8} \qquad + 3.3 \times 10^{-8}$$

$$\frac{6.5 \times 10^{-5} x}{6.5 \times 10^{-5}} = \frac{2.83 \times 10^{-7}}{6.5 \times 10^{-5}}$$

Initial [HA]

Problem Type 3: Calculating K_a
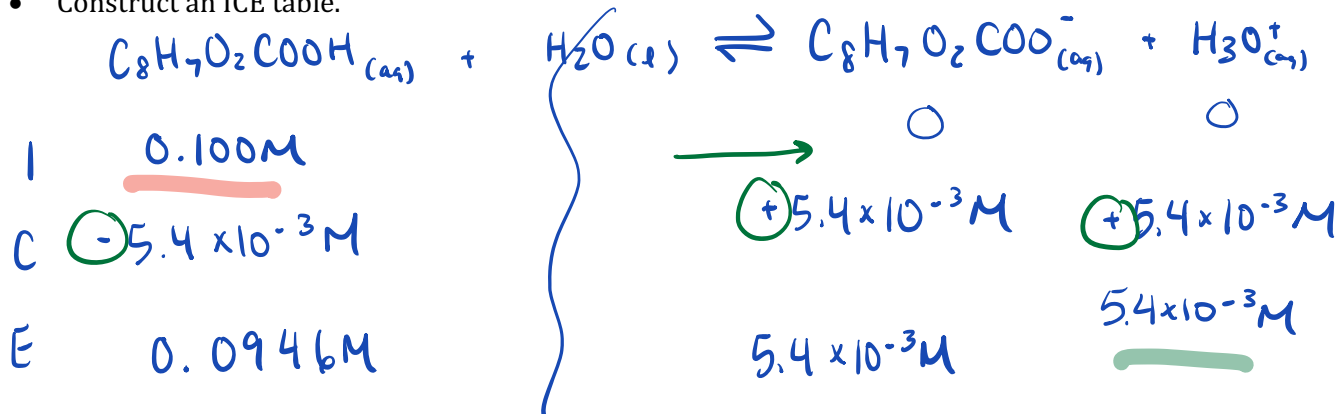
$[H_3O^+]$ At Equilibrium

Example: A 0.100 M solution of acetylsalicylic acid, $C_8H_7O_2COOH$, is found to have a pH of 2.27. Calculate the K_a for this acid.

- Using given pH, calculate the $[H_3O^+]$ at equilibrium

$$[H_3O^+] = 10^{-2.27} = 5.4 \times 10^{-3} M$$

↳ $[H_3O^+]$ at equilibrium

- Construct an ICE table.

$$C_8H_7O_2COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons C_8H_7O_2COO^-_{(aq)} + H_3O^+_{(aq)}$$

I	0.100M	0	0
C	$-5.4 \times 10^{-3}M$	$+5.4 \times 10^{-3}M$	$+5.4 \times 10^{-3}M$
E	0.0946M	$5.4 \times 10^{-3}M$	$5.4 \times 10^{-3}M$

- What is the K_a expression? Solve for K_a.

$$K_a = \frac{[C_8H_7O_2COO^-][H_3O^+]}{[C_8H_7O_2COOH]} = \frac{(5.4 \times 10^{-3})^2}{0.0946}$$

$$= 3.1 \times 10^{-4}$$

Problem Type 1 ($[H_3O^+]$ / pH)
74, 75, 79

Hebden Workbook: Pg. 152 #74-80, 82, 83 HW!

CALCULATIONS FOR WEAK BASES

As with acids, most bases are weak. Using the symbol "B" for a weak base, we can represent the equilibria of weak bases in water:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)} \qquad K_b = \frac{[HB^+][OH^-]}{[B]}$$

We must calculate the K_b for that base by using the K_a value of its conjugate acid

Consider the conjugate acid/base pair of NH$_4^+$ and NH$_3$ and their respective Ka and Kb expressions:

NH$_4^+$ (acid)	NH$_3$ (base)
Reaction: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$	Reaction: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
$K_a = \dfrac{[NH_3][H_3O^+]}{[NH_4^+]}$	$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$

Two common terms appear in each equation.
- Multiply the two expressions together and cancel the common terms...

$$K_a \times K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_3]} = [H_3O^+][OH^-] = K_w !$$
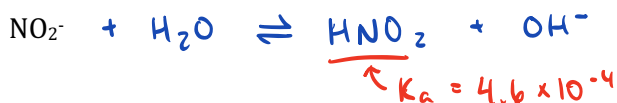
This allows us to formulate the following relationship for conjugate acid-base pairs:

$$K_a \text{ (conjugate acid)} \times K_b \text{ (conjugate base)} = K_w = 1.0 \times 10^{-14}$$

For the following weak bases, write out the equation with water and calculate the K_b.

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$
$$K_a = 4.9 \times 10^{-10}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = \boxed{2.0 \times 10^{-5}}$$

$$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$$
$$K_a = 4.6 \times 10^{-4}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = \boxed{2.2 \times 10^{-11}}$$

The following species are <mark>amphiprotic.</mark> Compare K_a and K_b. → Whichever is greater is what it will act as

$HC_2O_4^-$ (acid)

$K_a = 6.4 \times 10^{-5}$

$HC_2O_4^-$ (base)
$H_2C_2O_4$ (conjugate acid)
$K_a = 5.9 \times 10^{-2}$

$K_b = \dfrac{k_w}{k_a} = 1.7 \times 10^{-13}$

$>$

$HC_2O_4^-$ will act as an acid

$H_2PO_4^-$ (acid) vs

$K_a = 6.2 \times 10^{-8}$

$H_2PO_4^-$ (base)
H_3PO_4 (conjugate acid)

$K_b = \dfrac{1.0 \times 10^{-14}}{7.5 \times 10^{-3}}$

$= 1.3 \times 10^{-12}$

$>$

will act as an acid

HPO_4^{2-} (acid) vs

$K_a = 2.2 \times 10^{-13}$

HPO_4^{2-} (base)
$H_2PO_4^-$ (conjugate acid)
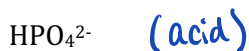
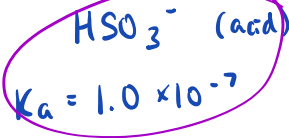$K_b = \dfrac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}}$
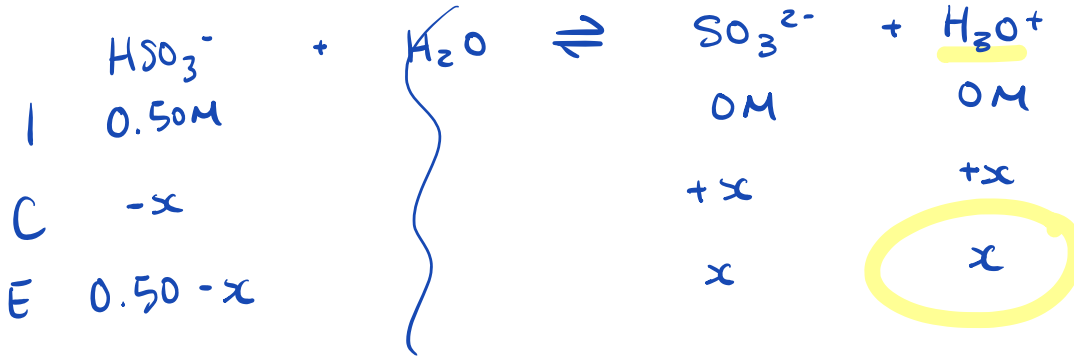
$= 1.6 \times 10^{-7}$

$<$

Will act as a base

Problem Type 1: Calculating pOH

Practice: Calculate the pH and pOH of a 0.50 M solution of HSO_3^-. amphiprotic!

$$HSO_3^- \text{ (acid)} \qquad HSO_3^- \text{ (base)}$$

$$K_a = 1.0 \times 10^{-7} \qquad > \qquad K_b = \frac{K_w}{K_a (H_2SO_3)} \; \xcancel{} \; \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-2}} = 6.7 \times 10^{-13}$$

	HSO_3^-	+	H_2O	⇌	SO_3^{2-}	+	H_3O^+
I	0.50M				0M		0M
C	-x				+x		+x
E	0.50 - x				x		x

$$K_a = 1.0 \times 10^{-7} = \frac{x^2}{0.50 - x} \qquad \text{* assume } 0.50 - x \cong 0.50$$

$$x = \sqrt{(0.50)(1.0 \times 10^{-7})}$$
$$= 2.2 \times 10^{-4} = [H_3O^+]$$

$$pH = -\log(2.2 \times 10^{-4})$$
$$= \boxed{3.65}$$
$$pOH = 14 - 3.65$$
$$= \boxed{10.35}$$

Practice: Calculate the pH of a solution containing 0.20 M CN-. ⤷weak base

	$CN^-_{(aq)}$	+	$H_2O_{(\ell)}$	⇌	$HCN_{(aq)}$	+	$OH^-_{(aq)}$
					$K_a = 4.9 \times 10^{-10}$		
I	0.20M				0M		0M
C	-x				+x		+x
E	0.20 - x				x		x
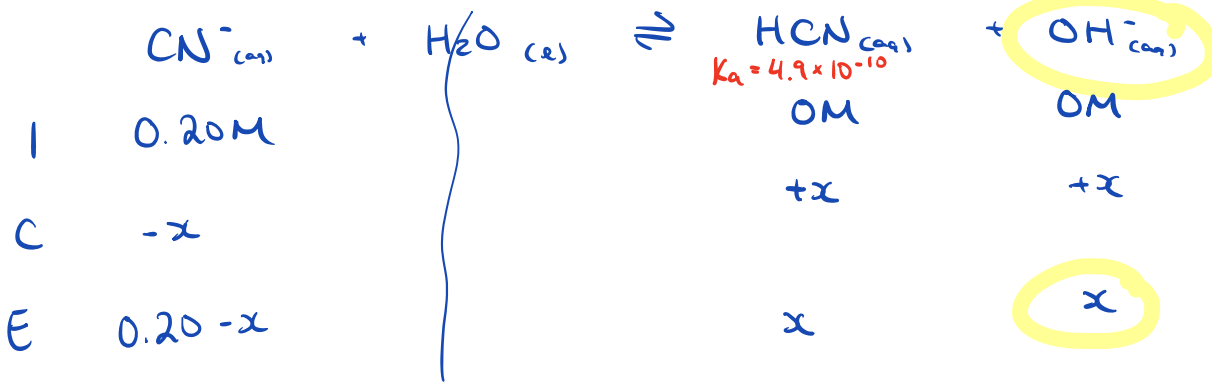
$$K_b = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5} = \frac{x^2}{0.20 - x} \qquad \text{* assume } 0.20 - x \cong 0.20$$

$$x = \sqrt{(0.20)(2.0 \times 10^{-5})}$$
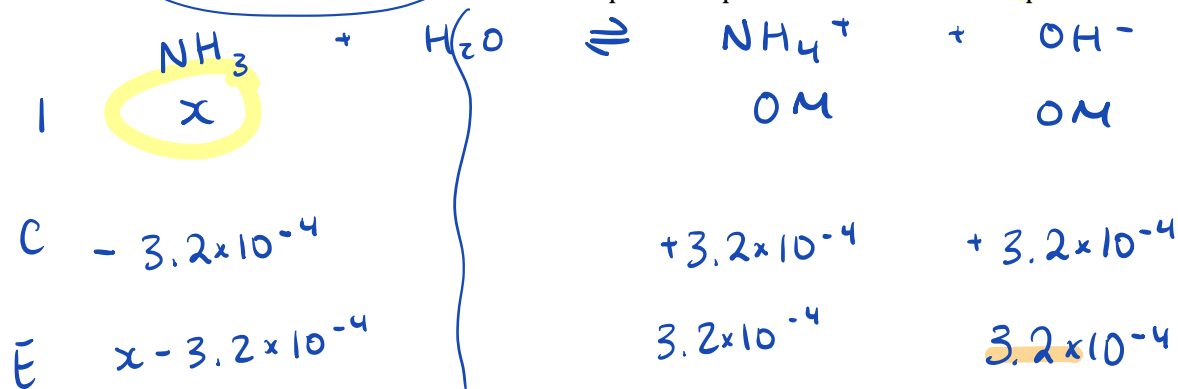$$= 2.0 \times 10^{-3} = [OH^-]$$

$$pOH = -\log(2.0 \times 10^{-3})$$
$$= 2.70$$
$$\boxed{pH = 11.30}$$

Problem Type 2: Calculating initial [B]

→ basic

Practice: What concentration of NH_3 would be required to produce a solution with pH = 10.50?

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

I	x		0M	0M
C	-3.2×10^{-4}		$+3.2\times10^{-4}$	$+3.2\times10^{-4}$
E	$x-3.2\times10^{-4}$		3.2×10^{-4}	3.2×10^{-4}

$pOH = 14 - 10.50$

$\quad = 3.50$

$[OH^-] = 10^{-3.50}$

$\quad = 3.2\times10^{-4}M$

$K_b = \dfrac{(3.2\times10^{-4})^2}{x-3.2\times10^{-4}} = \dfrac{K_w}{K_a(NH_4^+)} = \dfrac{1.0\times10^{-4}}{5.6\times10^{-10}}$
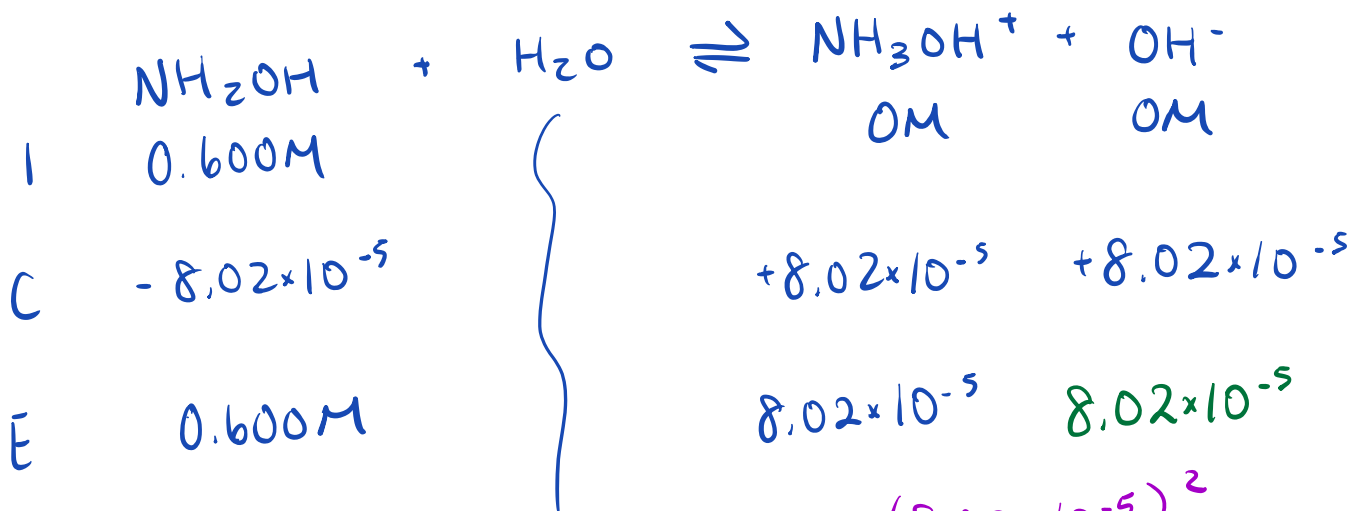
$\dfrac{(3.2\times10^{-4})^2}{x-3.2\times10^{-4}} = 1.8\times10^{-5}$

$$x = \boxed{6.0\times10^{-3}M = [NH_3]}$$

Problem Type 3: Calculating K_b

Practice: A solution is prepared by dissolving 9.90 g of the weak base hydroxylamine, NH_2OH in enough water to produce 500.0 mL of solution. The pH of the solution is found to be 9.904. Calculate the K_b for hydroxylamine.

Initial $[NH_2OH] = \dfrac{9.90g}{0.5000L} \times \dfrac{1\,mol}{33.0g} = 0.600M$

$$NH_2OH + H_2O \rightleftharpoons NH_3OH^+ + OH^-$$

I	0.600M		0M	0M
C	-8.02×10^{-5}		$+8.02\times10^{-5}$	$+8.02\times10^{-5}$
E	0.600M		8.02×10^{-5}	8.02×10^{-5}

$pH = 9.904$

$pOH = 4.096$

$\quad [OH^-] = 10^{-4.096}$

$\quad\quad = 8.02\times10^{-5}$

$K_b = \dfrac{(8.02\times10^{-5})^2}{0.600}$

$\quad = \boxed{1.07\times10^{-8}}$

Practice: A 0.400 M solution of the weak base methylamine, CH_3NH_2, is found to have a pH of 13.30. Calculate the K_b and pK_b of methylamine.

$$pOH = 0.70 \qquad [OH^-] = 10^{-0.70} = 0.20\,M$$

$$CH_3NH_{2(aq)} \ + \ H_2O_{(l)} \ \rightleftharpoons \ CH_3NH_3^+{}_{(aq)} \ + \ OH^-{}_{(aq)}$$

I	0.400M		
C	-0.20M	+0.20M	+0.20M
E	0.20M	0.20M	0.20M

(right side before C/E: 0M and 0M)

$$K_b = \frac{(0.20)^2}{0.20} = \boxed{0.20}$$

*re: $p = -\log$

$$pK_b = -\log K_b$$
$$= -\log(0.20)$$
$$= \boxed{0.70}$$