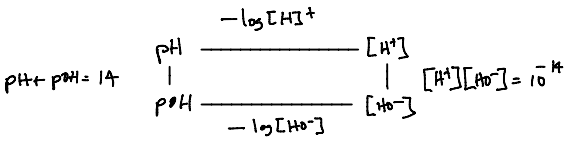
1412 - E2

CH 14 - Acid-Base Equilibria

Notes

14

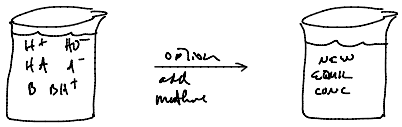
Cheat Sheet (Stephenson)

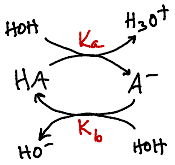


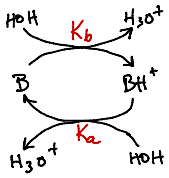
① $C_a/K_a > 100$; $C_a > 100\,K_a$ "C_a is at least 2 orders greater than K"
② $C_a/x > 20$; $C_a > 20\,x$ "C_a is at least 20x larger than x"
(NOTE: #1 does not require problem be worked out; #2 does)

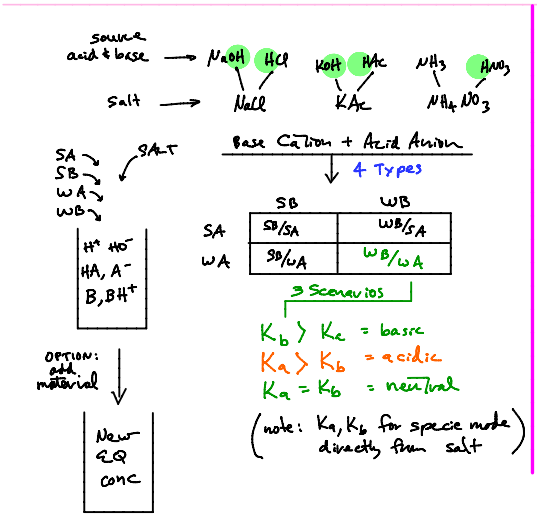
(strong acid)	$[H^+]$	=	C_a
(weak acid)	$[H^+]$	=	$\sqrt{C_a K_a}$
(weak acid buffer)	$[H^+]$	=	$\frac{C_a K_a}{C_b}$

$[HO^-]$	=	C_b	(strong base)
$[HO^-]$	=	$\sqrt{C_b K_b}$	(weak base)
$[HO^-]$	=	$\frac{C_b K_b}{C_a}$	(weak base buffer)









$$K_a K_b = K_w = 10^{-14}$$
$$pK_a + pK_b = pK_w = 14$$
$$[H^+][HO^-] = 10^{-14}$$
$$pK_a + pK_b = 14$$

CHAPTER 14: ACID-BASE EQUILIBRIA

Bronsted-Lowry Acids & Bases [14.1]

Examples of Acids

H_2SO_4 = car battery
$NaOH$ = drano
$NaHCO_3$ = baking soda
AcH = vinegar (5%)
HCO_2H = formic = ant bite

$CaCO_3$ = Tums
$MgCO_3$ =
$KHCO_3$ =
$Mg(OH)_2$ = Alka-Seltzer
$Al(OH)_3$ =

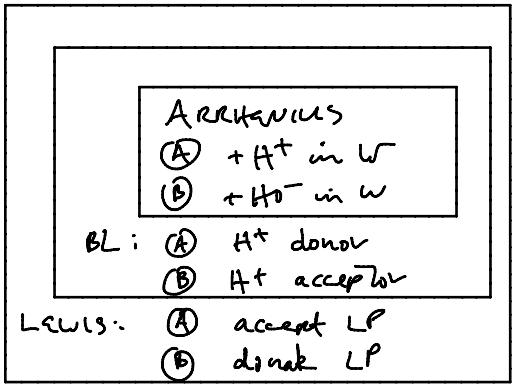
B–L Acid Definition

Acid – donates proton

$$HX \rightarrow H^+ + X^-$$

Base – accepts proton

$$B^- + H^+ \rightarrow BH$$

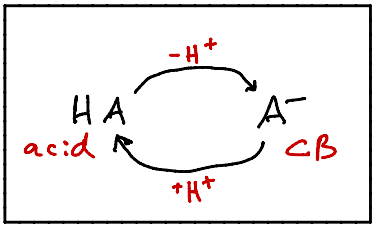


Conjugate Acid–Base Pairs

- acid = 1 proton + conj. base
- conjugate acid-base pair

ACID		CB
HA	$\rightarrow$	$A^- + H^+$
HF	$\rightarrow$	$F^- + H^+$
H_2SO_4	$\rightarrow$	$HSO_4^- + H^+$
HSO_4^-	$\rightarrow$	$SO_4^{2-} + H^+$
NH_4^+	$\rightarrow$	$NH_3 + H^+$

ASIDE: CONSERVATION OF CHARGE



Acid Equilibrium Constant: Ka

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

proton / hydrogen ion

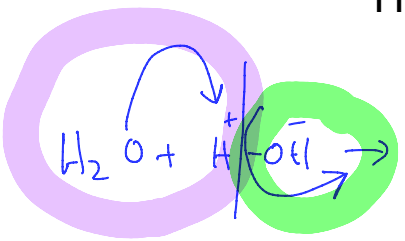
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

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

hydronium ion

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

Autoionization of Water: Kw



$$H_2O + H_2O \rightarrow H_3O^+ + A^-$$

Hydronium ion (alt version of H^+)

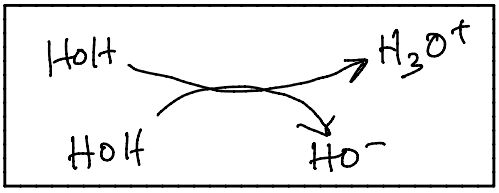
Hydroxide ion

an acid-base reaction, in which water is both the acid and the base

$$K_a = K_w = \frac{[H_3O^+][HO^-]}{[H_20]} = [H_3O^+][HO^-] = 1.0 \times 10^{-14}$$

$K_{a,w}$

…so… in a glass of water at 25 °C, 1-in-100 billion water molecules break apart into ions



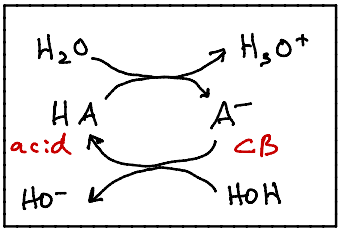
$TEMP$		K_a
$0\,°C$	=	0.11×10^{-14}
$10\,°C$	=	0.29×10^{-14}
$25\,°C$	=	1.0×10^{-14}
$37\,°C$	=	2.4×10^{-14}
$60\,°C$	=	9.6×10^{-14}

Relationship between Water & an Acid: Acid Ionization Constant, Ka

$$HF + H_2O \rightleftharpoons F^- + H_3O^+$$

CA/CB — CB/CA

$$K_{a,HF} = \frac{[H_3O^+][F^-]}{[HF]}$$

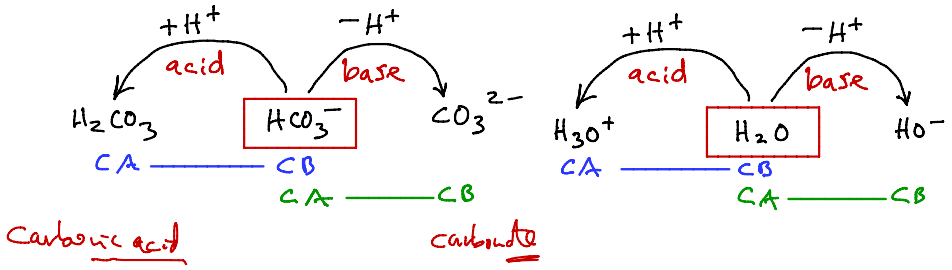


Abbreviated version …

$$HF \rightleftharpoons F^- + H^+$$

$$K_{a,HF} = \frac{[H^+][F^-]}{[H_20]}$$

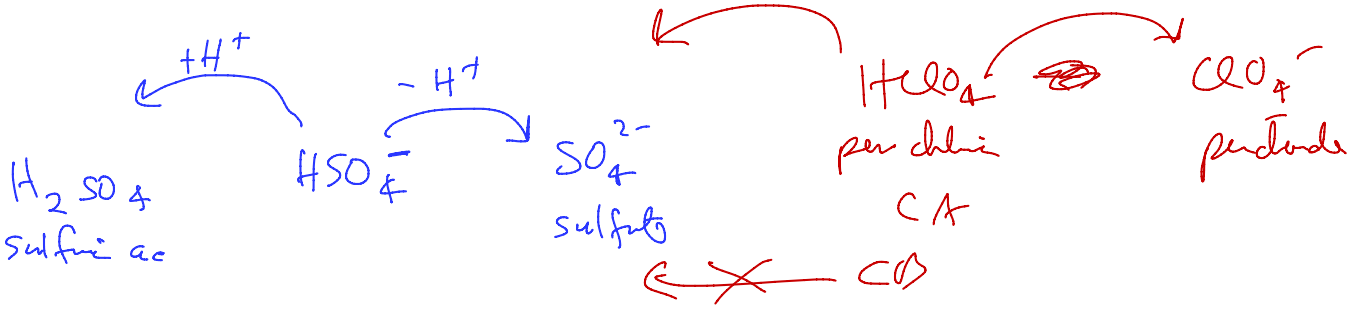
Amphiprotic Species – “It’s an acid AND a base!”



(EX) ¿Which of the folling is/are amphiprotic?

HNO_3 CH_3CO_2H HSO_4^- H_3PO_4 ClO_4^-

answer: HSO4–



pH and pOH [14.2]

The "–logX" function

$$pX = -\log X$$

$$pH = -\log[H^+]$$

$$pOH = -\log[HO^-]$$

$$pK = -\log K$$

$$pK_a = -\log K_a$$

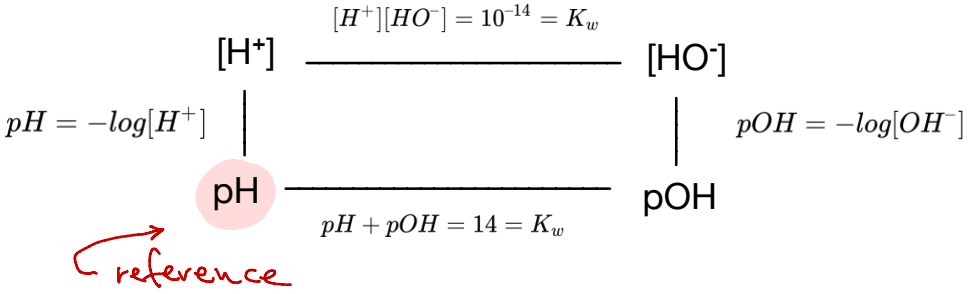
pH vs. pOH vs. pKw

earlier

$$K_w = [H^+][HO^-] = 10^{-14}$$

$$-\log[H^+] + -\log[HO^-] = -\log 10^{-14} = -\log K_a$$

$$\boxed{pH + pOH = 14 = pK_W}$$



(EX) Calc of pH of basic solution
¿What is the pH of a basic solution with a hydroxide conc. of 0.0125 M?

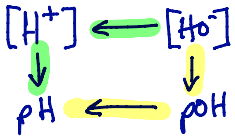
$[HO^-] = 0.0125$

$[H^+] = \frac{10^{-14}}{[HO^-]} = \frac{10^{-14}}{0.0125} = 8.0 \times 10^{-13}$

$pH = -\log[H^+]$

$= -\log(8.0 \times 10^{-13})$

$pH = 12.10$



Relative pH Scale (pH = 7 = neutral)

$HOH \rightleftharpoons H^+ + HO^-$

$K_a = [H^+][HO^-] = 10^{-14}$

↓ @ $[H^+] = [HO^-]$ = neutral

$K_a = (x)(x) = 10^{-14}$

$x^2 = 10^{-14}$

$x = 10^{-7}$

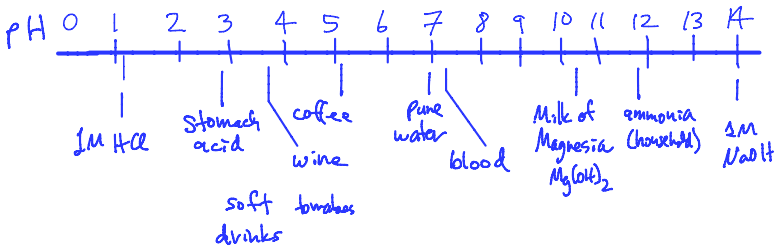
↓

$x = [H^+] = 10^{-7}$

$-\log[H^+] = -\log(10^{-7})$

$\boxed{pH = 7}$ @ neutral.

Acidic	pH < 7	$[H^+] > [HO^-]$
Neutral	pH = 7	$[H^+] = [HO^-]$
Basic	pH > 7	$[H^+] < [HO^-]$

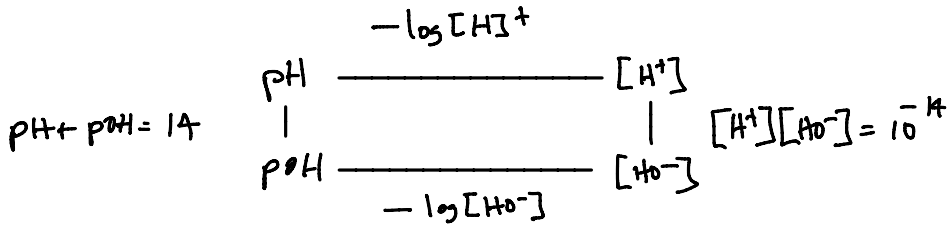


Acid Rain

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
$$H_2CO_3 \longrightarrow H^+ + HCO_3^-$$

$$SO_3(g) + H_2O \longrightarrow H_2SO_4$$
$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

Relative Strengths of Acids & Bases: Ka and Kb [14.3]

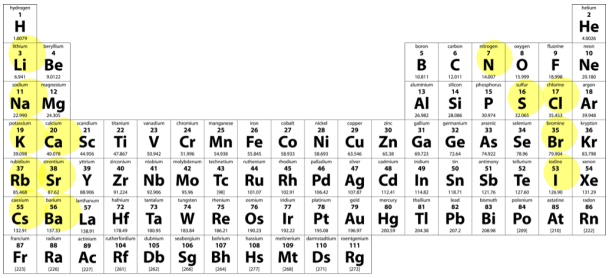


$(strong\ acid)$	$[H^+]$	$=$	C_a
$(weak\ acid)$	$[H^+]$	$=$	$\sqrt{C_a K_a}$
$(weak\ acid\ buffer)$	$[H^+]$	$=$	$\frac{C_a K_a}{C_b}$

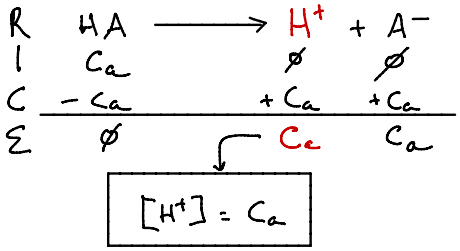
$[HO^-]$	$=$	C_b	$(strong\ base)$
$[HO^-]$	$=$	$\sqrt{C_b K_b}$	$(weak\ base)$
$[HO^-]$	$=$	$\frac{C_b K_b}{C_a}$	$(weak\ base\ buffer)$

7 Strong Acids and 8 Strong Bases

Strong Acids (Dissociate 100%)



Calc of [H⁺] for Strong Acid



Shortcut formulas for relating $[H^+]$ and $[HO^-]$ to inital acid and base concentrations

$HA \longrightarrow H^+ + A^-$ $\quad [H^+] = C_a$

NOT IN BOOK "C_a" is the INITIAL concentration of the acid.

$MOH \longrightarrow M^+ + HO^-$ $\quad [HO^-] = C_b$

Shortcut formulas NOT in OpenStax

(EX) pH of SA solution

Calc the pH of a 0.050 M HNO_3 solution?

$[H^+] = C_a = 0.050$

$pH = -\log[H^+]$

$= -\log(0.050)$

$pH = 1.3$

Weak Acids

	HA	$\longrightarrow$	H^+	+	A^-
R	HA		H^+		A^-
I	C_a		∅		∅
C	$-x$		$+x$		$+x$
E	$C_a - x$		x		x

$$K_a = \frac{x^2}{C_a - x}$$ where $x = [H^+]_{eq}$

$C_a > 100\ K_a$?
$C_a > 20\ x$?

$$K_a = \frac{x^2}{C_a}$$

$$[H^+] = \sqrt{C_a K_a}$$

Mon, Oct 14

Weak Bases

$$B + HOH \rightleftharpoons BH + HO^-$$

$$[HO^-] = \sqrt{C_b K_b}$$

Shortcut: Estimating Values

① $C_a/K_a > 100$; $C_a > 100\ K_a$ "C_a is at least 2 orders greater than K"

② $C_a/x > 20$; $C_a > 20x$ "C_a is at least 20x larger than x"

(NOTE: #1 does not require problem be worked out; #2 does)

(EX) Calc pH for WA

¿(a) What is the pH of a 0.10 M hypochlorous acid, HOCl. For HOCl, Ka = 3.5E-8 M

	HOCl	+ H_2O ⇌	H_3O^+	+ OCl^-
initial	0.10 M		≈0 M	0 M
change due to rxn	$-x$ M		$+x$ M	$+x$ M
at equil	$(0.10 - x)$ M		x M	x M

Substituting these algebraic representations into the K_a expression gives

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} = \frac{(x)(x)}{(0.10 - x)} = 3.5 \times 10^{-8}$$

This is a quadratic equation, but it is not necessary to solve it by the quadratic formula. The small value of the equilibrium constant, K_a, tells us that not very much of the original acid ionizes. Thus we can assume that $x \ll 0.10$. If x is small enough compared with 0.10, it will not matter (much) whether we subtract it, and we can assume that $(0.10 - x)$ is very nearly equal to 0.10. The equation then becomes

$$\frac{x^2}{0.10} \approx 3.5 \times 10^{-8} \qquad x^2 \approx 3.5 \times 10^{-9} \qquad \text{so} \qquad x \approx 5.9 \times 10^{-5}$$

In our algebraic representation we let

$$[H_3O^+] = x\ M = 5.9 \times 10^{-5}\ M\ ;\ [OCl^-] = x\ M = 5.9 \times 10^{-5}\ M$$

$$[HOCl] = (0.10 - x)\ M = (0.10 - 0.000059)\ M = 0.10\ M$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-5}} = 1.7 \times 10^{-10}\ M$$

(b) $pH = -\log(5.9 \times 10^{-5}) = 4.23$

$[H^+] = \sqrt{C_a K_a}$

$= \sqrt{(0.1)(3.5E-8)}$

$[H^+] = 5.91 \times 10^{-5}$

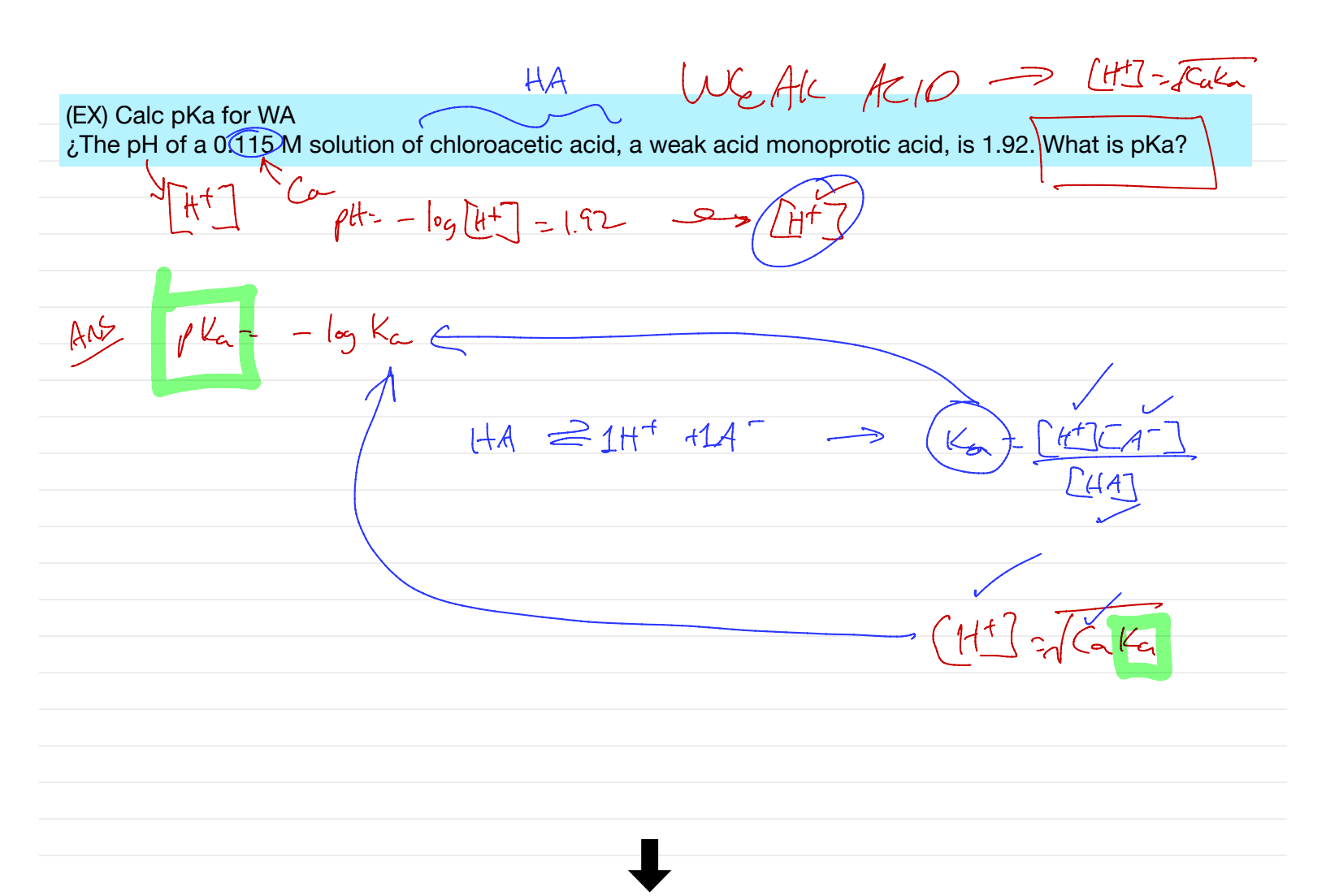
$pH = -\log 5.91 \times 10^{-5}$

$= -(-4.22)$

$pH = 4.22$

(EX) Calc pKa for WA

¿The pH of a 0.115 M solution of chloroacetic acid, a weak acid monoprotic acid, is 1.92. What is pKa?



⬇

(EX) Calc pKa for WA

¿The pH of a 0.115 M solution of chloroacetic acid, a weak acid monoprotic acid, is 1.92. What is pKa?

	$HA \rightleftharpoons$	H^+	$+ A^-$
R			
I	0.115	∅	∅
C	$-x$	x	x
E	$0.115-x$	x	x

$$-\log[H^+] = pH$$

$$-\log x = pH$$

$$x = 10^{-pH} = 10^{-1.92}$$

$$x = 0.012$$

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

$$K_a = \frac{x^2}{0.115 - x}$$

$$K_a = \frac{(0.012)^2}{(0.115 - 0.012)}$$

$$K_a = 0.0014$$

$$pK_a = -\log(0.0014) = 2.85$$

Fails short cut test

~~$C_a > 100\,K_a$~~ don't know K_a

$C_a > 20\,x$

$0.115 > 2\,(0.012)$

$0.115 > 0.24$ ← FALSE !!!

-or-

$$\frac{0.012}{0.015} = 10\% > 5\%$$

END LECTURE #2

% Ionization

$$\%\ \text{Ionization} = \frac{[H^+]}{C_a} \times 100$$

eq (p769)

C_a ← Initial conc.

(EX) Calc % Ionization for a Weak Acid [whitten]

¿Calc the pH and % ionization for 0.10 M solution of acetic acid ($K_a = 1.8E{-}5$)

ⓐ $\frac{C_a}{K_a} > 100?$ $\quad \frac{0.10 \times 10^0}{1.8 \times 10^{-5}} = \frac{10{,}000 \times 10^{-5}}{1.8 \times 10^{-5}} \approx 5{,}000$ ∴ use "shortcut"

ⓑ $[H^+] = \sqrt{C_a K_a} = \sqrt{(1.8E{-}5)(0.10)} = 1.3 \times 10^{-3}$

ⓒ $pH = -\log [H^+] = -\log (1.3 \times 10^{-3}) = \boxed{2.87}$

ⓓ $\%_{ioniz} = \frac{\text{part}}{\text{whole}} = \frac{[HAc]_{ion}}{[HAc]_{init}} = \frac{[H^+]}{C_a} = \frac{1.3 \times 10^{-3}}{0.10} \times 100 = \boxed{1.3\%}$

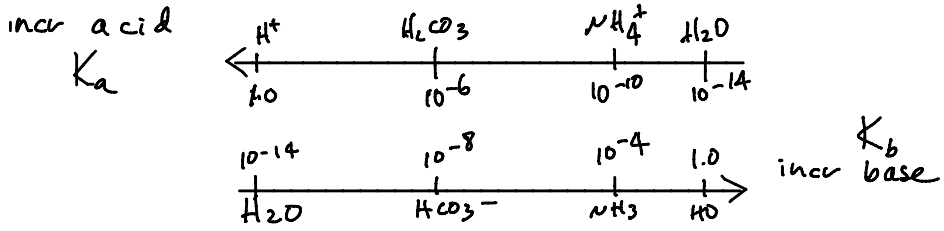
Relationship among Ka, Kb, and Kw

$$K_a \cdot K_b = \frac{[H^+][A^-]}{[HA]} \cdot \frac{[HA][HO^-]}{[A^-]} = [H^+][HO^-] = K_w$$

$$\boxed{K_a K_b = K_w}$$

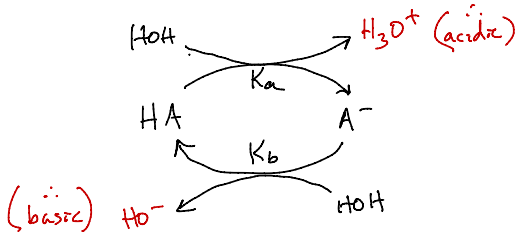
$pK_a + pK_b = 14$ alt. version

Relative CA–CB Strengths



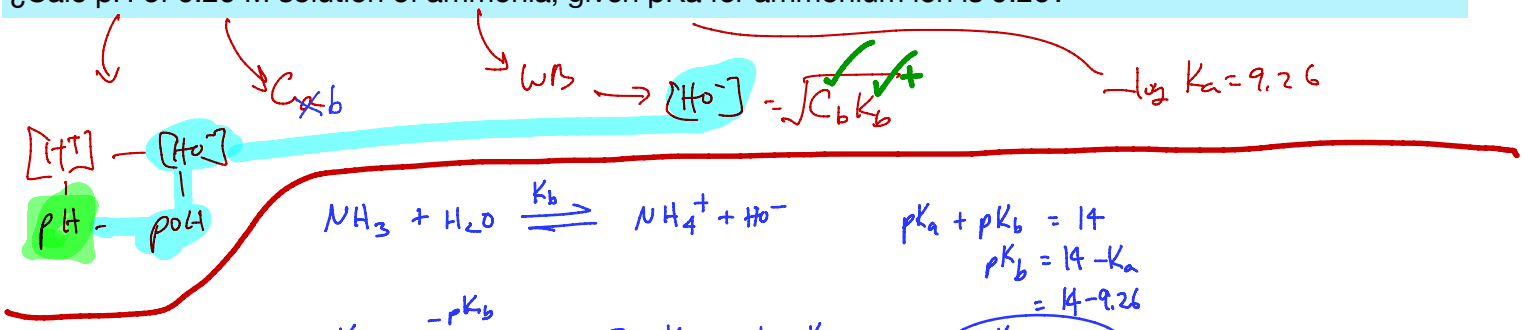
See next page ⇒

Acid				Base			
Increasing acid strength ↑	perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion	Increasing base strength ↓
	sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion	
	hydrogen iodide	HI			I^-	iodide ion	
	hydrogen bromide	HBr			Br^-	bromide ion	
	hydrogen chloride	HCl			Cl^-	chloride ion	
	nitric acid	HNO_3			NO_3^-	nitrate ion	
	hydronium ion	H_3O^+			H_2O	water	
	hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion	
	phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion	
	hydrogen fluoride	HF			F^-	fluoride ion	
	nitrous acid	HNO_2			NO_2^-	nitrite ion	
	acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion	
	carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion	
	hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion	
	ammonium ion	NH_4^+			HN_3	ammonia	
	hydrogen cyanide	HCN			CN^-	cyanide ion	
	hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion	
	water	H_2O			OH^-	hydroxide ion	
	hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion	
	ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion	
	ammonia	NH_3			NH_2^-	amide ion	
	hydrogen	H_2			H^-	hydride ion	
	methane	CH_4			CH_3^-	methide ion	



(EX) Calc pH of WB solution [whitten]

¿Calc pH of 0.20 M solution of ammonia, given pKa for ammonium ion is 9.26?



$NH_3 + H_2O \rightleftharpoons NH_4^+ + HO^-$ (K_b)

$pK_a + pK_b = 14$

$pK_b = 14 - K_a$

$= 14 - 9.26$

$pK_b = 4.74$ ← $pK_b = -\log_2 K_b$

$K_b = 10^{-pK_b}$

$= 10^{-4.74}$

$K_b = 1.8 \times 10^{-5}$

⇓

$C_a > 100\,K_a$?

$0.20 \times 10^{0} > 100\,(1.8 \times 10^{-5})$

$200 \times 10^{-3} > 1.8 \times 10^{-3}$

$200 > 1.8$ YES

⇒

$[HO^-] = \sqrt{C_b K_b}$

$= \sqrt{(0.20)(1.8E\text{-}5)}$

$[HO^-] = 1.9 \times 10^{-3}$

⇓

$pOH = -\log_2 [HO^-] = -\log(1.9E\text{-}3)$

$pOH = 2.72$

⇐

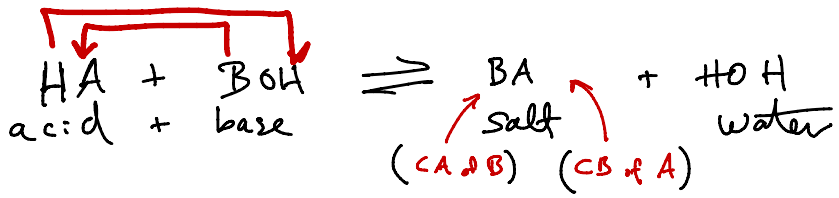
$pH + pOH = 14$

$pH = 14 - pOH$

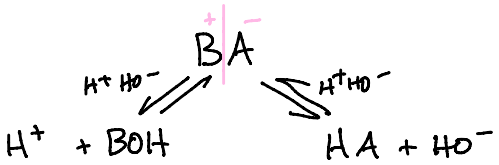
$pH = 14 - 2.72$

$pH = 11.28$ ← Makes sense ... NH_3 is known weak base.

Salt Solutions [14.4]

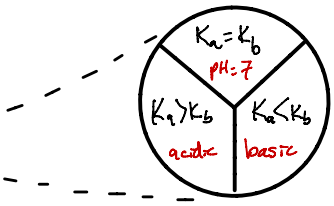


Deconstruct Salt into original acids and bases (using H+ and HO–)

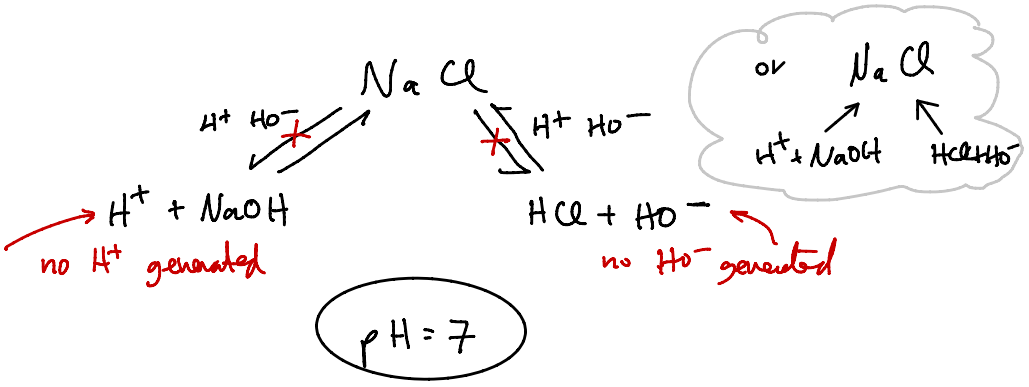


4 Sources of Salts from Acids & Bases

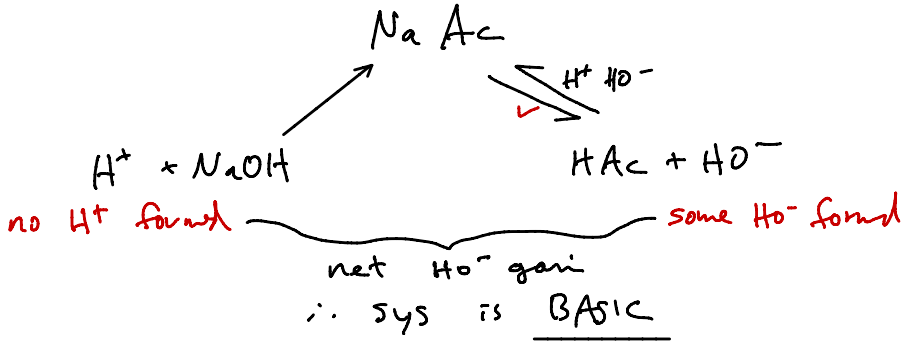
	SB	WB
SA	SB/SA (pH=7)	WB/SA (acidic)
WA	SB/WA (basic)	WB/WA Ka vs. Kb?



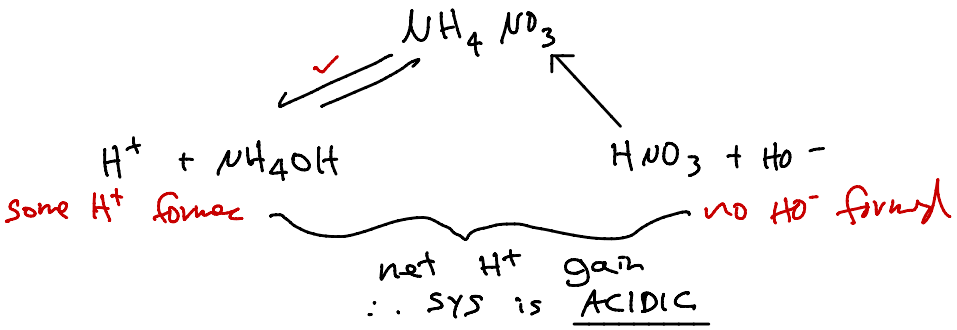
SA/SB [Q1]



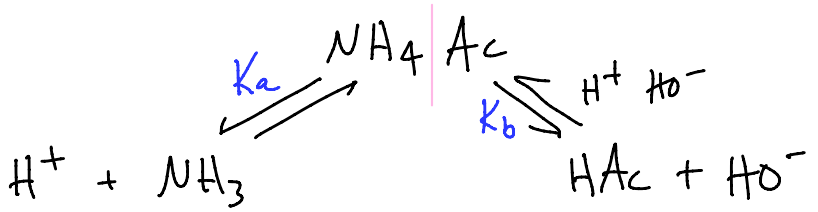
WA/SB [Q4]



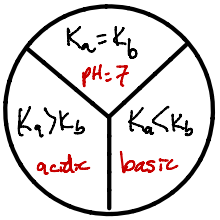
SA/WB [Q2]



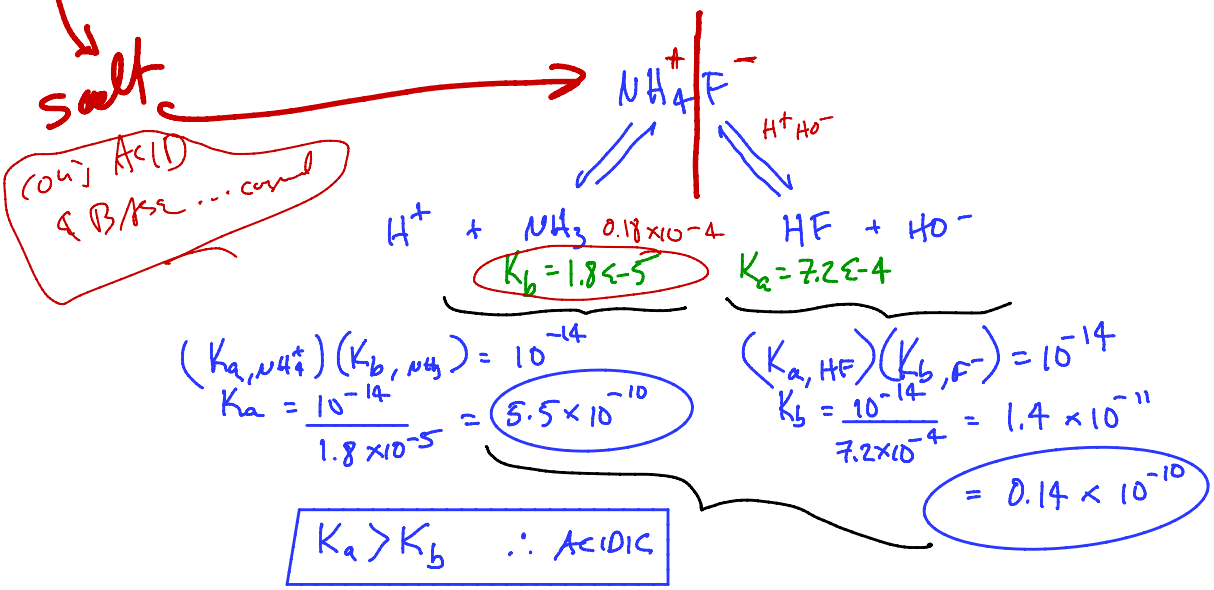
WA/WB [Q3]



if $K_a > K_b$, then ACIDIC
$K_a < K_b$, then BASIC
$K_a = K_b$, then NEUTRAL ($pH = 7$)



(EX) WA/WB Salt — Acidic, Basic, or Neutral?
¿NH4F is added to water. It the resulting solution acidic, basic, neutral, or not enough infomation to determine. (Kb,NH3 = 1.8E–5, Ka,HF = 7.2E–4)



(EX) SB/WA Salt System

¿Calc pH for 0.10 M solution of NaCN? (Kb,CN = 2.5E–5)

SALT

① The divergence from neutral must be due exclusively to CN^-

② ANS will be basic

③ TRy: $[HO^-] = \sqrt{C_b K_b}$ → Yes

④ $C_b > 100\ K_b$

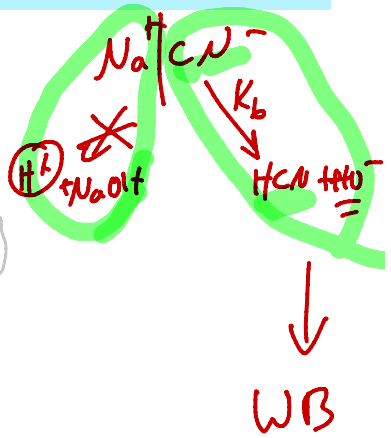
$1E{-}1 > 2.5E{-}3 = 250E{-}1$

$[HO^-] = \sqrt{(0.10)(2.5E{-}5)}$

$[HO^-] = 0.0016$

$pOH = 2.8$

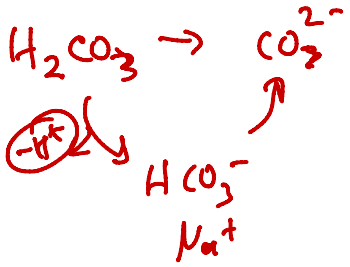
$pH = 14 - 2.8 = 11.2$



Wed 10/16/2019

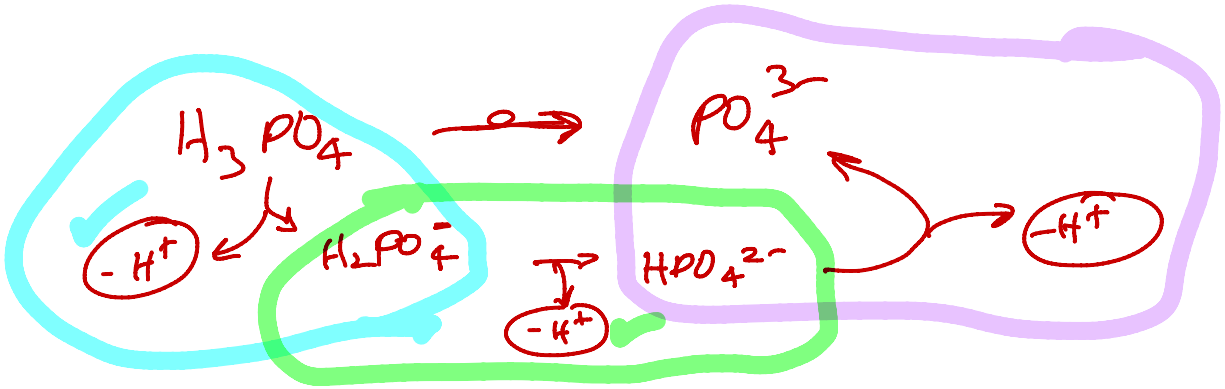
Polyatomic Acids [14.5]

$$H_3A \rightleftharpoons H_2A^- + H^+ \qquad K_{a1}$$
$$H_2A^- \rightleftharpoons HA^{2-} + H^+ \qquad K_{a2}$$
$$HA^{2-} \rightleftharpoons A^{3-} + H^+ \qquad K_{a3}$$



EC: $H_3PO_4 \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} H_2PO_4^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} HPO_4^{2-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} PO_4^{3-}$

	K_{a1}	K_{a2}	K_{a3}
$K_a(H_3PO_4)$	7.5E-3	6.2E-8	3.6E-13



(EX) ¿Calc concentration of all species in 0.10 M H3PO4 solution?

① $C_a/K_a = 0.10/7.5E\text{-}3 = 13 < 100$, ∴ RICE / QUADRATIC Yuck!

$K_{a_1} = \dfrac{[H^+][H_2PO_4^{2-}]}{0.1-[H_3PO_4]} = 7.5E\text{-}3$ Solve QUADRATIC → $[H^+]=[H_2PO_4^-] = 2.4E\text{-}2\,M$

$[H_3PO_4] = 10.\times10^{-2} - 2.4\times10^{-2}$

$[H_3PO_4] = 7.6\times10^{-2}$

② $K_{a_2} = \dfrac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = \dfrac{(y)(2.4\times10^{-2}+y)}{(2.4\times10^{-2}-y)} = 6.2\times10^{-8}$ → $[H^+] = 6.2\times10^{-8} = y$

$\Sigma[H^+] = 2.4E\text{-}2 + 6.2E\text{-}8 = 2.4E\text{-}2 = \Sigma[H^+]$

③ $K_{a_3} = \dfrac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \dfrac{(z)(2.4E\text{-}2+z)}{(6.2E\text{-}8-z)} = 3.6\times10^{-13}$

$z = 9.3\times10^{-19} = [H^+] = [PO_4^{3-}]$

$[H^+] = \Sigma[H^+] = (2.4E\text{-}2)+(6.2E\text{-}8)+(9.3\times10^{-19}) = \boxed{0.024\,M}$

	$H_3A \rightleftharpoons H_2A^- + H^+$			$H_2A^- \rightleftharpoons HA^{2-} + H^+$			$HA^{2-} \rightleftharpoons A^{3-} + H^+$
R	H_3A	H_2A^-	H^+	H_2A^-	HA^{2-}	H^+	
I	C_a	∅	∅	X	∅	X	
C	$-x$	$+x$	$+x$	$-y$	$+y$	$+y$	
E	(C_a-x)	x	x	$(x-y)$	y	$(x+y)$	

Buffers [14.6]

Def: $WA + CB$ (or $WB + CA$)

eg: $AcH + Ac^-$

How it works:

M^+A^- (salt)

	HA	$+ HOH$	$\rightleftharpoons$	A^-	$+ H^+$
I	C_a			C_b	$\emptyset$
C	$-x$			$+x$	$+x$
E	$(C_a - x)$			$(C_b + x)$	x

$$K_a = \frac{(x)(C_b + x)}{(C_a - x)}$$

$C_a > 100 K_a$

$C_a > 20x$

$$K_a = \frac{[H^+] C_b}{C_a} \rightarrow \boxed{[H^+] = \frac{C_a K_a}{C_b}}$$

HH equation

likewise: $\boxed{[HO^-] = \frac{C_b K_b}{C_a}}$

(EX) Calc pH of Buffer Soln of WA

Calc pH of a solution that is 0.10 M in HAc and 0.20 M in NaAc? (Ka,HAc = 1.8E–5)

WA + SALT

WA + K_aC_a

buff

$[H^+] = \frac{K_aC_a}{C_b}$

	HAc	⇌	Ac^-	+	H^+
I	0.10		0.20		∅
C	−x		+x		+x
E	(0.10−x)		(0.20+x)		x

$K_c = \frac{x(0.20+x)}{(0.10-x)} = 1.8E\text{-}5$ (H^+; Ac^- (CB); HAc (CA))

$C_a > 100K_a$ | $0.10 > 1.8E\text{-}3 = 0.0018$ ✓

$K_c = \frac{0.20\,x}{0.10} = 1.0E\text{-}5$

$[H^+] = 9.0E\text{-}6$

pH = 5.05

% ionization = $([H^+]/C_a) \times 100$

= $(9.0E\text{-}6 / 0.10) \times 100$

= 0.0090% ionized

or 9-in-100,000 ≈ 1-in-10,000

SHORT CUT

Assumptions = YES, ∴

$[H^+] = \frac{C_aK_a}{C_b} = \frac{0.1}{0.2} \mid 1.03E\text{-}5$

$[H^+] = 9.0E\text{-}6$ → pH = 5.05

Hendersen-Hasselbalch Equation

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

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

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

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \leftarrow pH = pK_a - \log\frac{[HA]}{[A^-]}$$

at the midpoint $[A^-] = [HA]$ → $\log 1 = 0$

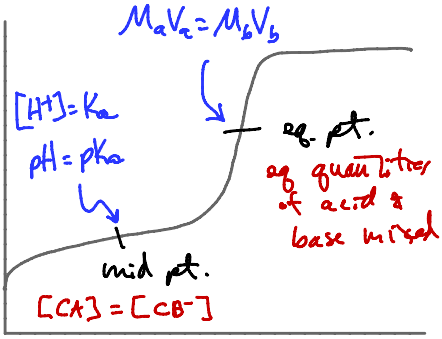
$pH = pK_a$

$[H^+] = K_a$

$M = \frac{mol}{L} \rightarrow mol = M \cdot L$

$mol_a = mol_b$

$M_a V_a = M_b V_b$



$[H^+] = \frac{K_a C_a}{C_b}$

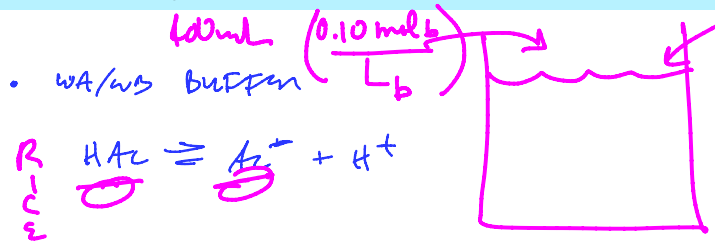
$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

variant of $[H^+] = \frac{C_a K_a}{C_b}$

(EX) ¿Calc pH of a solution that is created by adding 100 mL of 0.20 M in HAc and 400 mL of 0.10 M NaAc? (Ka,HAc = 1.8E–5)

WA

SALT



- WA/WB Buffer

Common ion effect

$$HAc \rightleftharpoons Ac^- + H^+$$

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

$$pK_a = -log(1.8E-5) = 4.74$$

$$[H^+] = \frac{C_a K_a}{C_b} = \frac{(0.20)(100)\cdot 1.8E-5}{(0.10)(400)}$$

$$= \frac{20}{40}\Big|\frac{1.8E-5}{}$$

$$= \frac{1.8E-5}{2} =$$

$$[H^+] = 9.00E-6$$

$$pH = 5.05$$

$$pH = 4.74 + log\frac{0.10(400/500)}{0.20(100/500)}$$

$$pH = 4.74 + log\frac{0.10(400)}{0.20(100)}$$

$$pH = 4.74 + log\frac{40.}{20.}$$

$$pH = 4.74 + log\,2$$

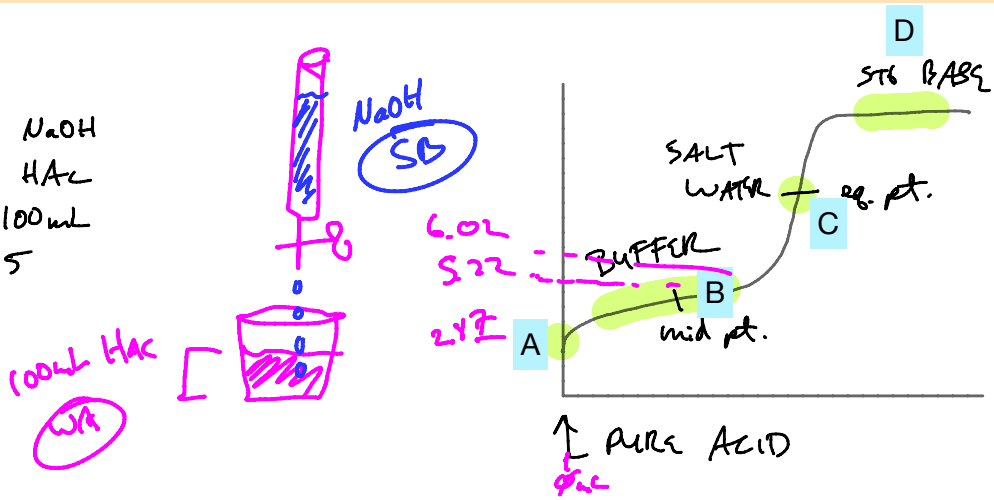
$$pH = 5.04$$

$[H^+] = \frac{C_a K_a}{C_b}$ or HH

Full Acid Titration
(pure weak acid → buffer → salt → stg base)

The Players:

- $[Titrant] = 0.100\ M$ NaOH
- $[Titrand] = 0.100\ M$ HAc
- starting vol HAc = 100 mL
- K_a (HAc) = $1.8\ E-5$



I. Before any base added

$$HAc \rightleftharpoons Ac^- + H^+$$

$C_a = 0.100 > 100\,K_a = 0.0018$ ✓

$$[H^+] = \sqrt{CaKa} = \sqrt{(0.100)(1.8E-5)} = 1.34E-3 \Rightarrow \boxed{pH = 2.87}$$

II. 75 mL strong base added

mol = M · L

mmol = M · mL

mmol HA_c = (0.100 M)(100 mL) = 10.0

mmol HO = (0.100 M)(75 mL) = 7.5

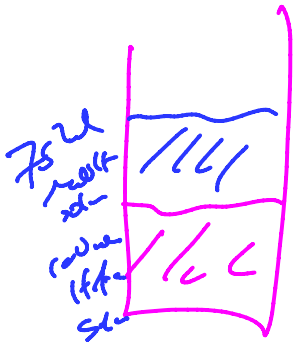
R	HO^-	+ HA_c	⇌	A_c^-	+ HOH
I	7.5	10.0		ø	
C	-7.5	-7.5		+7.5	
E	ø	2.5		7.5	

↓

Buffer Soln

$$[H^+] = \frac{C_a K_a}{C_b} = \frac{2.5}{7.5} \Big| \frac{1.8E\text{-}5}{} = 6.0E\text{-}6$$

← pH = 5.22



mmol = M · mL

$$M = \frac{mol \cdot 1000}{L \cdot 1000} = \frac{mmol}{mL}$$

$$M = \frac{mol}{L}$$

$$mol = M \cdot L$$

$$mmol = M \cdot mL$$

III. 95 mL base added

Approach 1: Add 95 mL base to original pure acid sample ("starting over")

$\text{mmol } HA_2 = (0.100\,M)(100\,mL)$

$= 10.0$

$\text{mmol } HO^- = (0.100\,M)(95\,mL)$

$= 9.5$

	HO^-	+ HA_2	⇌ A_2^-	+ H_2O
	9.5	10.0		
	−9.5	−9.5	+9.5	
	∅	0.5	9.5	

BUFFER

$[H^+] = \frac{C_a K_a}{C_b} = \frac{0.5}{9.5} \mid 1.8\times10^{-5} = 9.47\times10^{-7}$ →

$pH = 6.02$

Approach 2: Add 20 mL of base to previous buffer solution ("continuation")

$\text{mmol } HA_2 = 2.5\,\text{mmol}$

[in previous solution]

$\text{mmol } HO^- = (0.100\,M)(20\,mL)$

$= 2.0\,\text{mmol}$

[amt added to buffer]

	HO^-	+ HA_2	⇌ A_2^-	+ H_2O
	2.0	2.5	7.5	
	−2.0	−2.0	+2.0	
	∅	0.5	9.5	

SAME!!!

IV. At Equivalence Point

	HO^-	+ HAc	⇌ Ac^-	+ HOH
	10.0	10.0		
	−10.0	−10.0	+10.0	
	∅	∅	10.0	

Salt of sb/wA : NaAc

	HOH +	Ac^-	$\overset{K_b}{\rightleftharpoons}$	HAc +	HO^-
I		0.050		∅	∅
C		−x		+x	+x
E		(0.050 − x)		x	x

Conc of Salt

$$M = \frac{\text{mol}}{L} = \frac{10.0\ \text{mol}}{200.0\ \text{mL}} = 0.050\ M$$

100 mL HAc + 100 mL NaOH = 200 mL TOTAL VOL

weak base system ↓

$$[HO^-] = \sqrt{C_b K_b}$$

$$= \sqrt{\frac{C_b}{K_a} K_w} = \sqrt{\frac{0.050}{1.8\text{E}-5} 1\text{E}-14} = 5.27\text{E}-6 = [HO^-]$$

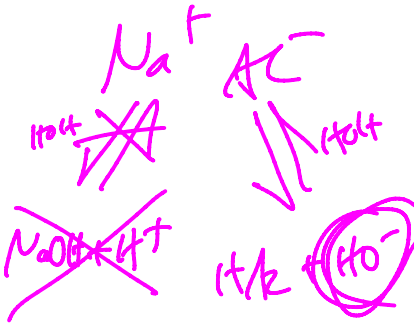
↓

$$pOH = 5.28$$

↓

$$pH = 8.72$$

Reasonable : expect EQ PT for Sb/wA sys to be >7



V. Excess base after equivalence point … 110 mL base added

	HO^-	+ HAc	⇌ Ac^-	+ HOH
I	11.0	10.0	∅	
C	−10.0	−10.0	+10.0	
E	1.0	∅	10.0	

SB (1.0) — WB (10.0)

↓ neglect weak base

$$[HO^-] = C_b = \frac{1.0\ mmol}{(110\ mL + 100\ mL)} = 4.76E\text{-}3$$

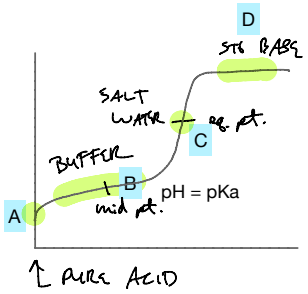
→ pOH = 2.32

↓

pH = 11.68

VI. Summary

$mL\ base$	pH
0	2.87
75	5.22
95	6.02
100	8.72
110	11.62



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

@MIDPOINT
[A-] = [HA]
so, [A-] /[HA] = 1
so, Log 1 = 0
therefore, @midpoint: pH = pKa

Mon, Oct 21

Buffer vs. Unbufferd Systems: Illustrated

UNbuffered

R	$HAc \rightleftharpoons$	$Ac^- + H^+$
I	0.100	∅ ∅
C	−x	+x +x
E	0.100−x	x x

$[H^+] = \sqrt{C_a K_a} = (0.100)(1.8\text{E}{-5})$

$= 1.3\text{E}{-3} \rightarrow pH = 2.87$

↓ + 0.010 mmol NaOH

R	HO^- +	$HAc \rightleftharpoons$	$Ac^- + H_2O$
I	0.010	0.100	∅
C	−0.010	−0.010	+0.010
E	∅	0.090	0.010

↓ Buffer C_A/C_B

$HAc \rightleftharpoons Ac^- + H^+$

0.090 0.010 ∅

$[H^+] = \frac{C_a K_a}{C_b} = \frac{0.090}{0.010} \Big| 1.8\text{E}{-5}$

$= 1.6\text{E}{-4} \rightarrow pH = 3.79$

$\Delta(\text{unbuffered}) = 3.79 - 2.87$

$\Delta = +0.92$ UN buffered

Buffered

$HAc \rightleftharpoons Ac^- + H^+$

0.100 0.100 ∅

−x +x +x

0.100−x 0.100+x x

$[H^+] = \frac{C_a K_a}{C_b} = \frac{0.100}{0.100} \Big| 1.8\text{E}{-5}$

$= 1.85\text{E}{-5} \rightarrow pH = 4.74$

↓

$HO^- + HAc \rightleftharpoons Ac^- + H_2O$

−0.010 0.100 0.100

−0.010 −0.010 +0.010

∅ 0.090 0.110

↓ Buffer C_A/C_B

$HAc \rightleftharpoons Ac^- + H^+$

0.090 0.110 ∅

$[H^+] = \frac{C_a K_a}{C_b} = \frac{0.090}{0.110} \Big| 1.8\text{E}{-5}$

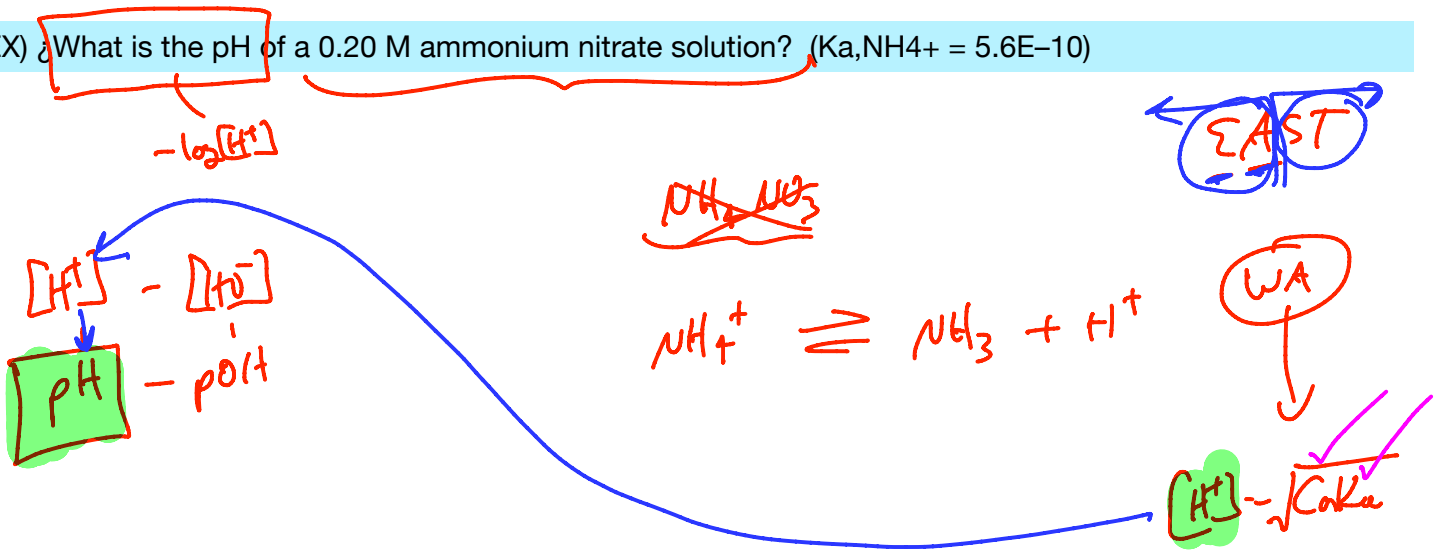
$= 1.5\text{E}{-5} \rightarrow pH = 4.82$

$\Delta(\text{Buffered}) = 4.82 - 4.78$

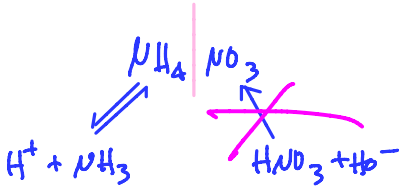
$\Delta = +0.08$ Buffered

Exam Practice Problems

(EX) ¿What is the pH of a 0.20 M ammonium nitrate solution? (Ka,NH4+ = 5.6E–10)



(EX) ¿What is the pH of a 0.20 M ammonium nitrate solution? (Ka,NH4+ = 5.6E−10)



- Reduces to a weak acid problem

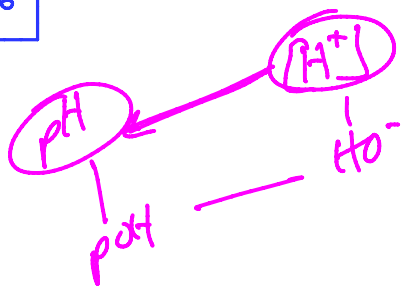
$$NH_4 \rightleftharpoons NH_3 + H^+$$

$$[H^+] = \sqrt{C_a K_a}$$

$$= \sqrt{(0.20)(5.6E-10)}$$

$$[H^+] = 1.1E-5\ M$$

$pH = 4.96$



(EX) ¿the pH of household ammonia is 11.50. What is the Molarity? (Kb,NH3 = 1.8E–5)

NH_3

$pH = -\log[H^+] = 11.50$

$pH + pOH = 14$

$M = \frac{mol}{L}$ x calc

~~$M = \frac{mol}{L_{soln}}$~~ No VOL given

C_b ✓

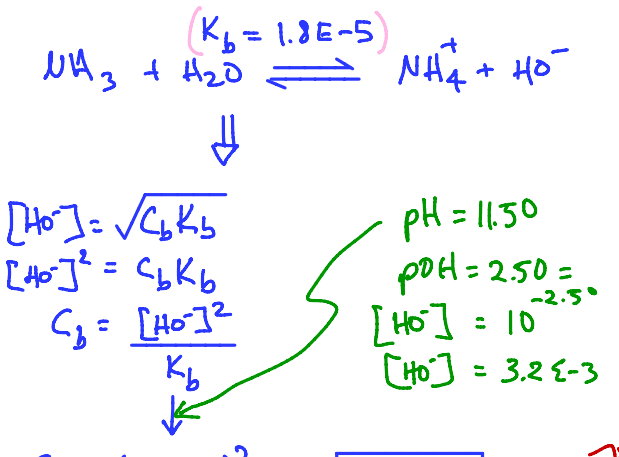
this is the answer!! Ques could have been worded, "what is C_b"

$[HO^-] = \sqrt{C_b K_b}$ (x ✓ 2)

$C_b = \frac{[HO^-]^2}{K_b}$

H^+ HO^- pH pOH

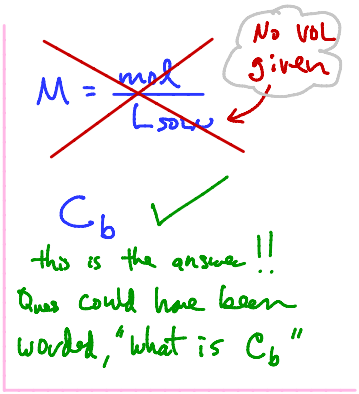
(EX) ¿the pH of household ammonia is 11.50. What is the Molarity? (Kb,NH3 = 1.8E–5)



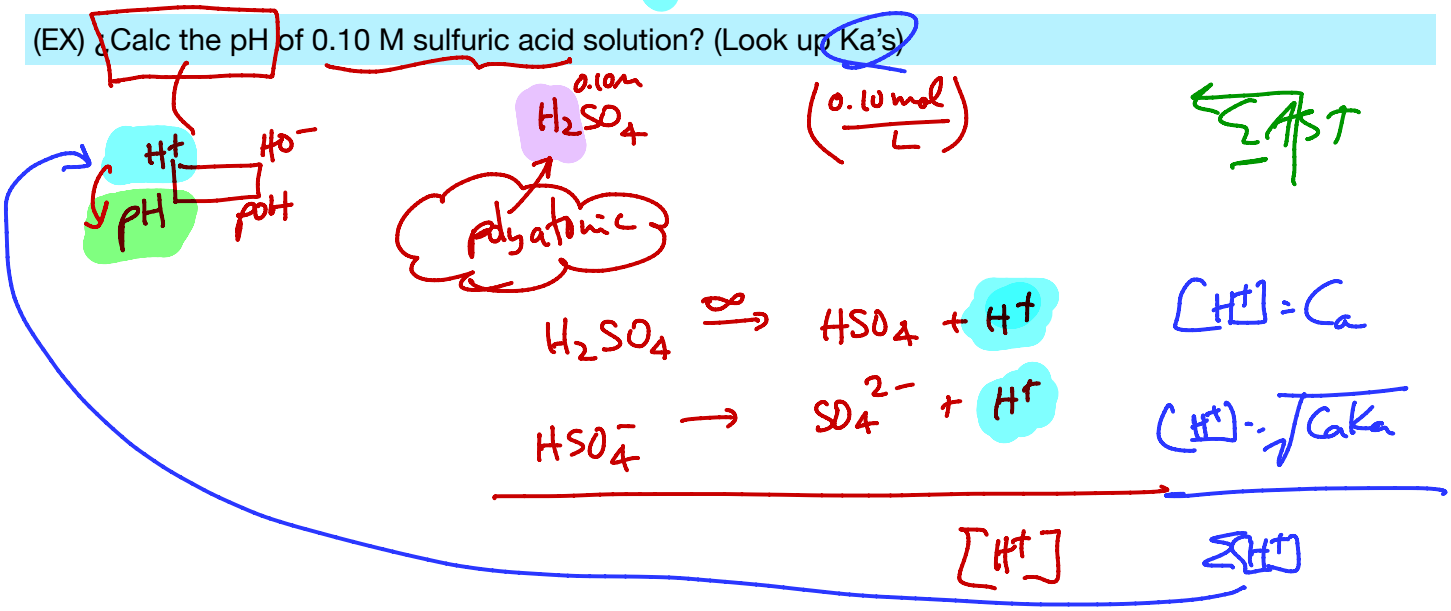
Assumption check

$0.57 > 100(1.8E-5) = 1.8E-3 = 0.0018$

$0.57 > 0.0018$ ∴ Assumption = YES



(EX) Calc the pH of 0.10 M sulfuric acid solution? (Look up Ka's)



(EX) ¿Calc the pH of 0.10 M sulfuric acid solution? (Look up Ka's)

$$H_2SO_4 \xrightarrow[K_{a1}=\infty]{-H^+} HSO_4^- \underset{K_{a2}=0.012}{\overset{-H^+}{\rightleftharpoons}} SO_4^{2-}$$

① STEP 1 = Str Acid, ∴ $[H^+]_{STEP\,1} = C_a = \boxed{0.10\ M} = [HSO_4^-]$

② STEP 2 : $K_{a2} = \dfrac{[SO_4^{2-}][H^+]}{[HSO_4^-]}$

R	H_2SO_4	$\rightarrow$	HSO_4^-	+	H^+
I	0.10		ø		ø
C	−0.10		+0.10		+0.10
E	ø		+0.10		+0.10

R	HSO_4^-	$\rightleftharpoons$	SO_4^{2-}	+	H^+
I	0.10		ø		0.10
C	−y		+y		+y
E	(0.10−y)		y		(0.10+y)

$C_a > 100\,K_a$? $\rightarrow$ $[H^+] = \sqrt{C_a K_a}$

$0.10 > 100(0.012) = 1.2$ FAIL !!!

$$K_a = \frac{(y)(0.10+y)}{(0.10-y)} \quad (y = [SO_4^{2-}],\ 0.10 + y = [H^+],\ 0.10 - y = [HSO_4^-])$$

QUADRATIC

$y = [SO_4^{2-}] = 0.010 = [H^+]_{STEP\,2}$ (1:1 ratio)

③ $\Sigma[H^+] = 0.10 + 0.01 = 0.11\,M = [H^+]$

pH = 0.96

(EX) Calc pH of a solution of 0.15 M HF and 0.20 M KF? (Ka,HF = 7.2E–4)

$C_a = 100\ K_a$

$0.15 = 7.2E{-}2 = 0.072$

YES

$\rightarrow [H^+] = \frac{C_a K_a}{C_b} = \frac{0.15 \mid 7.2E{-}4}{0.20}$

$[H^+] = 5.4E{-}4 \rightarrow \boxed{pH = 3.27}$

EASY

(EX) ¿Calc the pH of a solution that is 0.20 M NH3(aq) and 0.10 M NH4Cl? (Kb,NH3 = 1.8E–5)

$C_b > 100\ K_b$

$0.20 > 1.8E{-}3$

$0.20 > 0.0018$

YES $\rightarrow$

$[HO^-] = \frac{K_b C_b}{C_a} = \frac{1.8E{-}5 \mid 0.20}{0.10} = 3.6E{-}5$

$\downarrow$

$pOH = 4.44$

$pH = 14 - pOH$

$= 14 - 4.44$

$\boxed{pH = 9.56}$

(EX) ¿Calc pH of 0.010 M solution of ethanol (pKa,ethanol = 15.9)

Note that the pK_a for water is 14, so EtOH is less acid than water! Therefore, the H^+ contribution from water cannot be neglected.

	$HA \rightleftharpoons$	A^-	+ H^+
R			
I	0.010	ø	10^{-7}
C	$-x$	$+x$	$+x$
E	$(0.010-x)$	x	$(10^{-7}+x)$

$pK_a = -\log K_a = 15.9$

$K_a = 10^{-15.9}$

$K_a = 1.26 \times 10^{-16}$

$C_a = 0.010 > 100K_a = 1.26 \times 10^{-14}$ ✓

$10^{-7} \gg 100K_a$

shortcut 10^{-7} vs K_a = YES

shortcut $C_a vs K_a$ = YES

~~$[H^+] = \frac{C_a K_a}{C_b}$~~

not WA/CB system

∴ use traditional K_a approach

$K_a = \frac{x \mid 10^{-7}+x}{0.010-x}$

$0.010\ K_a = x \cdot 10^{-7}$

$\frac{0.010 \mid 1.26E-16}{10^{-7} \mid} = x$

$1.26E-11 = x = [A^-]$

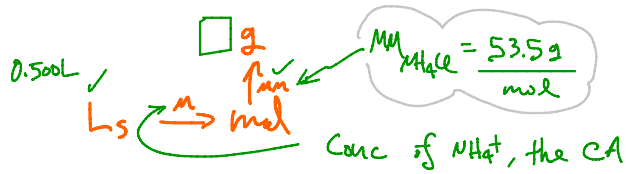
$[H^+] = 10^{-7} + x = 10^{-7} + 1.26 \times 10^{-11} \approx 10^{-7}$

$[H^+] = 10^{-7}$

$\boxed{pH = 7}$

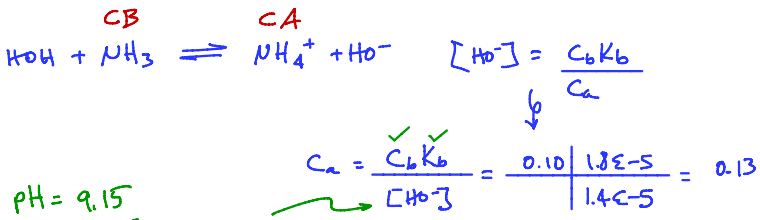
(EX) ¿How many grams of NH4Cl must be added to 500 mL of 0.10 M NH3 to produce a buffer of pH = 9.15? (Kb,NH3 = 1.8E–5)

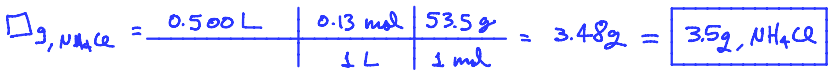
$mol = M \cdot L$

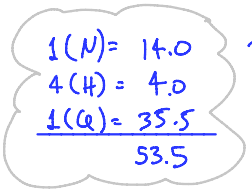


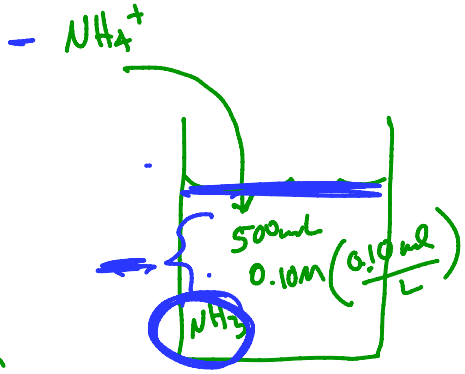
<– Analysis:

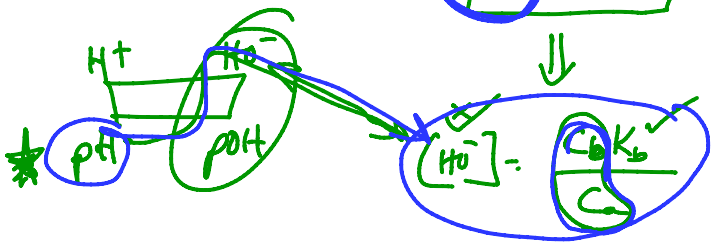
get Grams from Concentration, and get Concentration from pH.











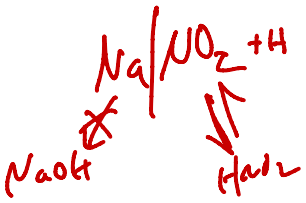
(EX) ¿What is the pH of a 1-liter solution prepared from 0.115 mol NaNO2 and 0.070 mol HCl, followed by a 2-fold dilution in water?

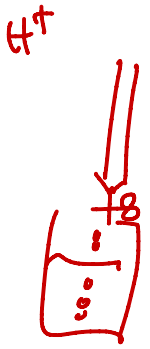
(a)

R	Na^+	+ NO_2^-	+ HCl	→ HNO_2	+ Cl⁻
		0.115	0.070	∅	
C		−0.070	−0.070	+0.070	
E		0.045	∅	0.070	

→ Buffer Solution

<– System?
Salt + SA neutralization, then dilution





$HNO_2 \rightleftharpoons NO_2^- + H^+$ $\quad K_a = 4.5E-4$

0.070 $\quad$ 0.045

$$[H^+] = \frac{C_a K_a}{C_b} = \frac{0.070 \mid 4.5E-4}{0.045} = 7.00 \times 10^{-4} = [H^+] \rightarrow \boxed{pH = 3.15}$$

(b) If dilute 50/50, both C_a and C_b are equally diluted; hence the ratio C_a/C_b does not change; hence, the pH remains the same.

$$\boxed{pH \text{ (aft dilution)} = 3.16}$$

(EX) ¿Calc hydroxide ion concentration of a 0.0105 M $HClO_3$ solution?

7 SA

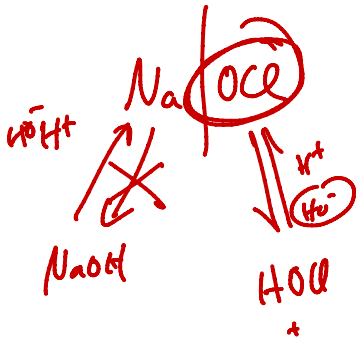
Ca → H^+ → HO^-

pH — pOH

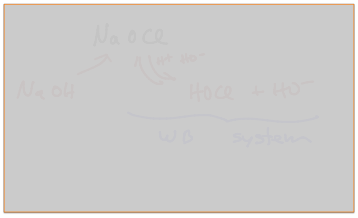
$[H^+] = C_a = 0.0105$

$[HO^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{0.0105} = \boxed{9.52E-13}$

(EX) Calc pH of a 0.12 M solution of NaOCl?



	HOH	+	ClO^-	⇌	$HClO$	+	HO^-
I			0.12		∅		∅
C			−x		+x		+x
E			0.12−x		x		x



$[HO^-] = \sqrt{C_b K_b} = \sqrt{0.12 \left| \frac{K_a}{K_w} \right.} = \sqrt{0.12 \left| \frac{1\times10^{-14}}{3.5\times10^{-8}} \right.} = 1.85\times10^{-4} = [HO^-]$

$pOH = 3.73$ ⟵ $\boxed{pH = 10.27}$

(EX) Calc hydrolysis constant for the hydrated cation 0.10 M Cu(NO3)2 at pH = 4.50?

0.10M

$$Cu(NO_3^-)_2 + HOH \rightleftharpoons Cu(OH)_2 + 2HNO_3^-$$

K = ?

$$Cu^{2+} + HOH \rightleftharpoons Cu(OH)_2 + H^+$$

x/H+ — x/HO−

✓ pH — pOH ✗

	$2NO_3^-$	+ Cu^{2+}	+ HOH ⇌	$Cu(OH)^+$	+ H^+	pH = 4.50
I		0.10		∅	∅	↓
C		−3.16E-5		+3.16E-5	+3.16E-5	[H] = 3.16E-5
E		0.10		3.16E-5	3.16E-5	

$$K = \frac{(3.16E-5)^2}{0.10} = 1.0 \times 10^{-8} = K \rightarrow pK = 8$$

Wed, Oct 23