Chemistry 12

Unit V - Acid/Base II

KEY

I) Weak Acid Equilibrium and K_a

Recall that strong acids dissociate 100% in water. For example, a 0.010M solution of HCl will produce a $[H_3O^+]$ = 0.010 M and have a pH of 2.00. Dissociation equation (one way):

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

Weak acids do not dissociate 100% in water, and therefore an equilibrium forms. In fact, a weak acid, by definition, dissociates < 50% (and in Chemistry 12, < 5%). Thus, without knowing the exact percent dissociation, it is more difficult to determine the pH of, say, a 0.010M solution of weak acid than it is to determine that of a 0.010M solution of a strong acid. K_a, or the weak acid equilibrium constant provides a means toward determining the pH of a certain molarity of a weak acid.

Take the weak acid, HF, for example:

pure liquid!

$$HF_{(aq)} + H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + F^-_{(aq)} \qquad K_a = \frac{[P]}{[R]} = \frac{[H_3O^+][F^-]}{[HF]}$$

K_a is a type of K_{eq}, therefore the same rules apply.

The larger the K_a → the more the acid dissociates → the more H_3O^+ produced → the stronger the acid.

Notice the K_a values decrease as you go down the table because the acids are getting progressively weaker.

* It is interesting to note (but not examinable in Chem. 12) that the % dissociation of a weak acid or base changes as the [acid] or [base] changes. Using acids as an example, % dissociation increases (due to Le Chatelier) as an acid is diluted (but K_a remains the same), thus a weak acid at a low enough conc. can act as a strong acid. A basic rule of thumb: if $[H_3O^+] < K_a$, weak acids dissociate more than 'expected'; if $[H_3O^+] > K_a$, weak acids act like 'weak' acids and dissociate very little.

Ka problems can be broken into three types.

1. Calculate the [H_3O^+] and/or pH given the concentration of the weak acid or salt.
2. Calculate the concentration of the weak acid required to produce a given pH.
3. Calculate Ka given pH and the concentration of the weak acid.

Type 1

Calculate the [H_3O^+] in and the pH of a 0.20M solution of acetic acid.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

	CH_3COOH	H_2O	H_3O^+	CH_3COO^-
I	0.20 M		0 M	0 M
C	$-x$		$+x$	$+x$
E	$0.20-x$		x	x

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \Rightarrow 1.8 \times 10^{-5} = \frac{x^2}{0.20-x}$$

Assume $0.20 - x \approx 0.20$

$$1.8 \times 10^{-5} = \frac{x^2}{0.20} \Longrightarrow x = [H_3O^+]_{eq} = 0.001\underline{8}974\ M$$

$$\boxed{= 0.0019\ M}$$

$$pH = -\log[H_3O^+]_{eq} = -\log(0.001\underline{8}974\ M) = \boxed{2.72}$$

To check the validity of the assumption, and to calculate the % dissociation of the acid: $\frac{[H_3O^+]_{eq}}{[HA]_i}$

* if ratio is < 0.05, then the assumption is VALID!

$$\frac{0.0018974\ M}{0.20\ M} = 0.95\ \%\ \text{dissoc.}$$

(VALID)

For the reaction: $H_2S_{(aq)} + H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + HS^-_{(aq)}$; Calculate the $[H_3O^+]$ and pH if the $[H_2S] = 0.050M$. *Note: Consider only the first proton of a polyprotic acid, as the dissociation of the second proton is negligible compared to the first. This is true for any di, tri, or polyprotic acid.

	H_2S	+ H_2O ⇌	H_3O^+	+ HS^-
I	0.050M		0 M	0 M
C	$-x$		$+x$	$+x$
E	$0.050-x$		x	x

$$K_a = \frac{[H_3O^+][HS^-]}{[H_2S]} \Rightarrow 9.1 \times 10^{-8} = \frac{x^2}{0.050-x}$$

* assume $0.050 - x = 0.050$

$$9.1 \times 10^{-8} = \frac{x^2}{0.050}$$

$$x = [H_3O^+]_{eq} = 6.7454 \times 10^{-5} M = \boxed{6.7 \times 10^{-5} M}$$

$$pH = -\log(6.7454 \times 10^{-5} M) = \boxed{4.17}$$

$$* \frac{6.7454 \times 10^{-5} M}{0.050 M} = 0.13\% \text{ dissoc.}$$

(VALID)

What is the pH of a 0.100M NH_4Cl solution?

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

0.100M 0.100M

	NH_4^+	+ H_2O ⇌	H_3O^+	+ NH_3
I	0.100M		0 M	0 M
C	$-x$		$+x$	$+x$
E	$0.100-x$		x	x

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]} \Rightarrow 5.6 \times 10^{-10} = \frac{x^2}{0.100-x}$$

assume $0.100 - x = 0.100$

$$5.6 \times 10^{-10} = \frac{x^2}{0.100}$$

$$x = [H_3O^+]_{eq} = 7.4833 \times 10^{-6} M$$

$$pH = -\log(7.4833 \times 10^{-6} M) = \boxed{5.13}$$

$$\frac{7.4833 \times 10^{-6} M}{0.100 M} = 0.0075\% \text{ dissoc.}$$

(VALID)

What is the pH of a 0.81M solution of the weak acid $H_2C_2O_4$? Does the 'assumption' hold true in this example? What is the difference in the pH answers using/not using the 'assumption'?

$$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^-$$

	$H_2C_2O_4$	H_2O	H_3O^+	$HC_2O_4^-$
I	0.81 M		0 M	0 M
C	$-x$		$+x$	$+x$
E	$0.81-x$		x	x

$$K_a = \frac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]} \Rightarrow 5.9 \times 10^{-2} = \frac{x^2}{0.81-x}$$

* Assume $0.81 - x = 0.81$

$$5.9 \times 10^{-2} = \frac{x^2}{0.81}$$

$$\frac{0.21861}{0.81} = 0.2699 = 26.99\%$$

ASSUMPTION INVALID

$$x = 0.21861\ M$$

$$pH = -\log(0.21861) = \boxed{0.66}$$

using QUAD. FORMULA

$$x^2 + 0.059x - 0.81 = 0$$

$$x = 0.19109\ M$$

$$pH = -\log(0.19109) = \boxed{0.72}$$

difference of 0.06 pH units

Assignment 1: Hebden p. 152 #74, 75, 79, 81

1. Calculate the pH of a 0.50M solution of H_3BO_3. (answer = 4.72)
2. Calculate the pH of a 0.235M solution of NaH_2PO_4. (ans. = 3.92)

Type 2

What $[H_2CO_3]$ would be required to produce a pH of 3.178 ?

	H_2CO_3	$+ \; H_2O$	$\rightleftharpoons H_3O^+$	$+ \; HCO_3^-$
I	x	$\times$	$0\ M$	$0\ M$
C	-6.6374×10^{-4}		$+ \uparrow$	$+ \nearrow$
E	$x - 0.00066374$		$6.6374 \times 10^{-4}\ M \longrightarrow$	

$[H_3O^+]_{eq} = \text{inv log}(-3.178)$
$= 6.6374 \times 10^{-4} M$

$$K_a = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} \Rightarrow 4.3 \times 10^{-7} = \frac{(6.6374 \times 10^{-4})^2}{x - 0.00066374}$$

$$x - 0.00066374 = \frac{(6.6374 \times 10^{-4})^2}{4.3 \times 10^{-7}}$$

$$x - 0.00066374 = 1.02455$$

$$x = [H_2CO_3]_i = 1.0252 = \boxed{1.0\ M}$$

What $[Fe(H_2O)_6^{3+}]$ would be required to produce a pH of 1.120 ?

hexaaquoiron ion (ACIDIC)

	$Fe(H_2O)_6^{3+}$	$+ \; H_2O$	$\rightleftharpoons H_3O^+$	$+ \; Fe(H_2O)_5OH^{2+}$
I	x	$\times$	$0\ M$	$0\ M$
C	-0.075858		$+ \uparrow$	$+ \nearrow$
E	$x - 0.075858$		$0.075858\ M \longrightarrow$	

$[H_3O^+]_{eq} = \text{inv log}(-1.120)$
$= 0.075858 M$

$$K_a = \frac{[H_3O^+][Fe(H_2O)_5OH^{2+}]}{[Fe(H_2O)_6^{3+}]} \Rightarrow 6.0 \times 10^{-3} = \frac{(0.075858)^2}{x - 0.075858}$$

$$x - 0.075858 = 0.95907$$

$$x = [Fe(H_2O)_6^{3+}]_i = 1.03492$$

$$\boxed{= 1.03\ M}$$

Type 3

Calculate the Ka of the weak acid HX if the pH of a 0.100M solution of HX is 3.30.

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

	HX	H_2O	H_3O^+	X^-
I	0.100M		0 M	0M
C	−0.000501187		+ ↑	+ →
E	0.099499M		5.01187×10^{-4}M →	

$[H_3O^+]_{eq}$ = invlog (−3.30)

$= 5.01187 \times 10^{-4}M$

$$K_a = \frac{[H_3O^+][X^-]}{[HX]} = \frac{(5.01187 \times 10^{-4})^2}{0.099499}$$

$$\boxed{= 2.5 \times 10^{-6}}$$

A 2.00M diprotic weak acid has a pH of 0.50. Calculate its Ka value.

$$H_2A + H_2O \rightleftharpoons H_3O^+ + HA^-$$

	H_2A	H_2O	H_3O^+	HA^-
I	2.00M		0 M	0 M
C	−0.31623		+ ↑	+ →
E	1.68377 M		0.31623 M →	

$[H_3O^+]_{eq}$ = invlog(−0.50)

= 0.31623M

$$K_a = \frac{[H_3O^+][HA^-]}{[H_2A]} = \frac{(0.31623)^2}{1.68377} = \boxed{0.059}$$

OR

$$\boxed{5.9 \times 10^{-2}}$$

A 0.20M solution of a weak acid has a pH of 1.32. Using calculations, identify the acid.

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

$$[H_3O^+]_{eq} = \text{invlog}(-1.32) = 0.047863\ M$$

I	0.20M		0 M	0 M
C	-0.047863		+	+
E	0.15214 M		0.047863 M →	

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(0.047863)^2}{0.15214} = 1.5 \times 10^{-2}$$

SULPHUROUS ACID
H_2SO_3

Assignment 2: Hebden p. 152 #76, 77, 78, 80, 82

Also do:

1. A 0.100M solution of an unknown acid HX, has a pH = 1.414. What is the K_a for HX? (answer = 2.4×10^{-2})
2. Red blood cells undergo "hemolysis" (rupture of the cell walls) at a pH of 3.00. In an effort to cause the minimum damage to the cell contents, a biochemist added acetic acid to 100 mL of a suspension of red blood cells in blood plasma in an effort to gently rupture the cell walls. What mass of acetic acid was required? (For answer, see p. 152-3 #83)
3. An acid is known to be either iodic, acetic, or benzoic. A 0.200M solution was found to have a pH of 2.44. Use calculations to identify the acid. (answer – Benzoic acid).

- QUIZ 1 -

II) Weak Base Equilibrium and K_b

Strong **bases** dissociate 100% in solution whereas weak bases do not (analogous to the acid discussion earlier, except that low soluble alkaline earth metal hydroxides are unable to create relatively high pH values, even though they are considered strong bases). Weak base problems can be solved using the K_b constant, which is analogous to K_a and is also a type of K_{eq} value.

Remember:** Weak bases are on the ***right-hand side of the A/B table in the middle section (unshaded region).

The higher the K_b → the STRONGER the base, meaning it accepts A PROTON (H^+) from water to a greater extent, thereby producing more OH^- ions.

Consider the weak base nitrite:

$$NO_2^-{}_{(aq)} + H_2O_{(l)} \Leftrightarrow HNO_{2(aq)} + OH^-{}_{(aq)}$$

$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]}$$

Relationship of K_w, K_a, and K_b for a Conjugate Acid-Base Pair

$$K_a \times K_b = K_w \qquad K_w = 1 \times 10^{-14} \text{ at } 25°C$$

Proof using nitrite and nitrous acid (conjugate pairs):

$$K_a(HNO_2) = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} \; ; \; K_b(NO_2^-) = \frac{[HNO_2][OH^-]}{[NO_2^-]}$$

$$K_a \cdot K_b = K_w \quad ???$$

$$\frac{\cancel{[NO_2^-]}[H_3O^+]}{\cancel{[HNO_2]}} \cdot \frac{\cancel{[HNO_2]}[OH^-]}{\cancel{[NO_2^-]}} = [H_3O^+][OH^-]$$

$$\Downarrow$$

$$K_w!!!$$

The acid-base table only lists K_a values for the acids. To get the K_b value for the conjugate base, you must divide the K_w by the K_a of the conjugate acid.

Determine K_b of the weak base SO_4^{2-}. → find SO_4^{2-} in 'BASE' column

$$K_b = \frac{K_w}{K_a(HSO_4^-)} = \frac{1\times10^{-14}}{1.2\times10^{-2}} = \boxed{8.3\times10^{-13}}$$

Determine K_b of HCO_3^-.

$$K_b = \frac{K_w}{K_a(H_2CO_3)} = \frac{1\times10^{-14}}{4.3\times10^{-7}} = \boxed{2.3\times10^{-8}}$$

Determine the K_b values of the following:

a) NH_3 b) HPO_4^{2-} c) $H_2PO_4^-$ d) $HC_2O_4^-$

a) $K_b = \frac{1\times10^{-14}}{5.6\times10^{-10}} = \boxed{1.8\times10^{-5}}$

b) $K_b = \frac{1\times10^{-14}}{6.2\times10^{-8}} = \boxed{1.6\times10^{-7}}$

c) $K_b = \frac{1\times10^{-14}}{7.5\times10^{-3}} = \boxed{1.3\times10^{-12}}$

d) $K_b = \frac{1\times10^{-14}}{5.9\times10^{-2}} = \boxed{1.7\times10^{-13}}$

Types of K_b Problems

1. Calculate $[OH^-]$ and pH (or pOH) given the concentration of a weak base.
2. Calculate the concentration of a weak base given the pH of a solution.
3. Calculate K_b given the concentration of a weak base and pH.

Type 1

Calculate the $[OH^-]$ and pH for a 0.25M solution of the weak base $HCOO^-$.

$$HCOO^- + H_2O \rightleftharpoons OH^- + HCOOH \qquad K_b = \frac{1\times10^{-14}}{1.8\times10^{-4}} = 5.5556\times10^{-11}$$

I	0.25 M		0 M	0 M
C	$-x$		$+x$	$+x$
E	$0.25-x$		x	x

$$K_b = \frac{[OH^-][HCOOH]}{[HCOO^-]} \Rightarrow 5.5556\times10^{-11} = \frac{x^2}{0.25-x}$$

*assume $0.25-x = 0.25$

$$5.5556\times10^{-11} = \frac{x^2}{0.25}$$

$\% \text{ dissoc.} = \frac{3.7268\times10^{-6}}{0.25} = 0.00149\%$

ASSUMPTION VALID!

$$x = [OH^-] = 3.7268\times10^{-6}\ M = \boxed{3.7\times10^{-6}\ M}$$

$$pOH = -\log(3.7268\times10^{-6}) = 5.4287 \rightarrow pH = \boxed{8.57}$$

Calculate the pH of a 0.100M solution of $C_2O_4^{2-}$.

$$C_2O_4^{2-} + H_2O \rightleftharpoons OH^- + HC_2O_4^- \qquad K_b = \frac{1\times10^{-14}}{6.4\times10^{-5}} = 1.5625\times10^{-10}$$

I	0.100 M		0 M	0 M
C	$-x$		$+x$	$+x$
E	$0.100-x$		x	x

$$K_b = \frac{[OH^-][HC_2O_4^-]}{[C_2O_4^{2-}]} \Rightarrow 1.5625\times10^{-10} = \frac{x^2}{0.100-x}$$

*assume $0.100-x = 0.100$

$$1.5625\times10^{-10} = \frac{x^2}{0.100}$$

$\% \text{ dissoc.} = \frac{3.9528\times10^{-6}}{0.100} = 0.00395\%$ VALID!

$$x = [OH^-] = 3.9528\times10^{-6}\ M$$

$$pOH = -\log(3.9528\times10^{-6}) = 5.4031 \rightarrow pH = \boxed{8.60}$$

Assignment 3: Hebden p. 153-154 #85, 88, 90, 92

Type 2

A solution of NO_2^- has a pH of 8.900. Calculate the $[NO_2^-]$ that created this pH value.

$$NO_2^- + \cancel{H_2O} \rightleftharpoons OH^- + HNO_2$$

I	x		$0\,M$	$0\,M$
C	-7.9433×10^{-6}		$+\uparrow$	$+\nearrow$
E	$x-7.9433\times10^{-6}$		$7.9433\times10^{-6}\,M \rightarrow$	

$K_b = \dfrac{1\times10^{-14}}{4.6\times10^{-4}}$

$K_b = 2.\underline{1}739\times10^{-11}$

$[OH^-]_{eq} = \text{invlog}(-5.100)$
$= 7.9\underline{4}33\times10^{-6}\,M$

$$K_b = \frac{[OH^-][HNO_2]}{[NO_2^-]} \Rightarrow 2.\underline{1}739\times10^{-11} = \frac{(7.9433\times10^{-6})^2}{x-7.9\underline{4}33\times10^{-6}}$$

$$x - 0.00000079\underline{4}33 = 2.\underline{9}024$$

$$x = [NO_2^-]_i = \boxed{2.9\,M}$$

A solution of ammonia, NH_3, has a pH of 10.50. Calculate the $[NH_3]$ at equilibrium in the solution.

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

I			$0\,M$	$0\,M$
C			$+\uparrow$	$+\nearrow$
E	x		$3.\underline{1}623\times10^{-4} \rightarrow$	

$K_b = \dfrac{1\times10^{-14}}{5.6\times10^{-10}}$
$= 1.\underline{7}857\times10^{-5}$

$[OH^-]_{eq} = \text{inv.log}(-3.50)$
$= 3.\underline{1}623\times10^{-4}\,M$

$$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]} \Rightarrow 1.\underline{7}857\times10^{-5} = \frac{(3.\underline{1}623\times10^{-4})^2}{x}$$

$$\boxed{x = 0.0056\,M = [NH_3]_{eq}}$$

Type 3

A 0.44M solution of the weak base B⁻ has a pH of 11.12. Calculate the K_b for this base, and the K_a for the conjugate acid, HB at 25°C.

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

$[OH^-]_{eq} = \text{invlog}(-2.88)$
$= 1.3183 \times 10^{-3} M$

I	0.44 M		0 M	0 M
C	−0.0013183		+	+
E	0.43868		1.3183×10^{-3} M	

$$K_b = \frac{[OH^-][HB]}{[B^-]} = \frac{(1.3183 \times 10^{-3})^2}{0.43868} = \boxed{4.0 \times 10^{-6}}$$

A 0.25M solution of benzyl amine, $C_7H_7NH_2$, has a pH of 11.38. Calculate the K_b of benzyl amine. (Benzyl amine is a weak base).

$$C_7H_7NH_2 + H_2O \rightleftharpoons OH^- + C_7H_7NH_3^+$$

$[OH^-]_{eq} = \text{invlog}(-2.62)$
$= 2.3988 \times 10^{-3} M$

I	0.25 M		0 M	0 M
C	−0.0023988		+	+
E	0.2476 M		2.3988×10^{-3} M	

$$K_b = \frac{[OH^-][C_7H_7NH_3^+]}{[C_7H_7NH_2]} = \frac{(2.3988 \times 10^{-3})^2}{0.2476} = \boxed{2.3 \times 10^{-5}}$$

Assignment 4: Hebden p. 153/154 #84, 86, 87, 89, 91, 93

- quiz 2 -

III) Writing Molecular, Complete Ionic, and Net Ionic Equations for Acid/Base Reactions

* In Chemistry 12, we will not deal with net ionic equations involving polyprotic acids EXCEPT when the reaction is a STRONG ACID-STRONG BASE. This is because within this curriculum, net ionic equations involve the transfer of one proton only.

1. Strong Acid/Strong Base (Neutralization):

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow \underline{NaCl_{(aq)}} + \underline{H_2O_{(l)}}$ (molecular)

$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O_{(l)}$ (compl. ionic) * treat as if 'alone' in water.

$H^+ + OH^- \Leftrightarrow H_2O_{(l)}$ (net ionic)

* $\underline{\underline{\text{ALL}}}$ STRONG - STRONG!

2. Strong Acid/Weak Base:

$HCl_{(aq)} + NaCN_{(aq)} \rightarrow \underline{NaCl_{(aq)}} + \underline{HCN_{(aq)}}$ (molecular)

$H^+ + Cl^- + Na^+ + CN^- \rightarrow Na^+ + Cl^- + HCN$ (compl. ionic)

(weak acid ⇒ majority is undissociated)

$H^+ + CN^- \Leftrightarrow HCN$ (net ionic)

3. Weak Acid/Strong Base:

$HF_{(aq)} + KOH_{(aq)} \rightarrow \underline{KF_{(aq)}} + \underline{H_2O_{(l)}}$ (molecular)

$HF + K^+ + OH^- \rightarrow K^+ + F^- + H_2O$ (compl. ionic)

(weak acid)

$HF + OH^- \Leftrightarrow F^- + H_2O$ (net ionic)

4. Weak Acid/Weak Base:

$HF_{(aq)} + NaCN_{(aq)} \rightarrow NaF_{(aq)} + HCN_{(aq)}$ (molecular)

$HF + Na^+ + CN^- \rightarrow Na^+ + F^- + HCN$ (compl. ionic)

$HF + CN^- \Leftrightarrow F^- + HCN$ (net ionic)

HINT (prior to Assignment 5): $NH_4OH_{(aq)}$ does NOT exist!!! It decomposes to NH_3 and H_2O immediately…see #6 below.

Assignment 5

Write Molecular (Formulae), Complete Ionic, and Net Ionic Equations for the following Acid/Base reactions (Use a separate sheet of paper, if need be):

1. $HClO_{4\,(aq)} + KOH_{(aq)} \rightarrow KClO_4 + H_2O$

$H^+ + ClO_4^- + K^+ + OH^- \longrightarrow K^+ + ClO_4^- + H_2O$

$H^+ + OH^- \rightleftharpoons H_2O$

2. $HBr_{(aq)} + NaCH_3COO_{(aq)} \rightarrow NaBr + CH_3COOH$

$H^+ + Br^- + Na^+ + CH_3COO^- \longrightarrow Na^+ + Br^- + CH_3COOH$

$H^+ + CH_3COO^- \rightleftharpoons CH_3COOH$

3. $HCOOH_{(aq)} + LiOH_{(aq)} \rightarrow LiHCOO + H_2O$

$HCOOH + Li^+ + OH^- \longrightarrow Li^+ + HCOO^- + H_2O$

$HCOOH + OH^- \rightleftharpoons HCOO^- + H_2O$

4a. $HI_{(aq)} + NH_{3\,(aq)} \rightarrow NH_4I$

$H^+ + I^- + NH_3 \longrightarrow NH_4^+ + I^-$

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

4b. **HCN** (aq) **+ NH_3** (aq) → NH_4CN

$HCN + NH_3 \longrightarrow NH_4^+ + CN^-$

$HCN + NH_3 \rightleftharpoons NH_4^+ + CN^-$

5. $Sr(OH)_2$ (aq) **+ 2HNO_3** (aq) → $Sr(NO_3)_2 + 2H_2O$

$Sr^{2+} + 2OH^- + 2H^+ + 2NO_3^- \longrightarrow Sr^{2+} + 2NO_3^- + 2H_2O$

$\cancel{2}H^+ + \cancel{2}OH^- \rightleftharpoons \cancel{2}H_2O$

6. NaOH (aq) **+ NH_4Cl** (aq) → $NaCl + NH_4OH$

$Na^+ + OH^- + NH_4^+ + Cl^- \longrightarrow Na^+ + Cl^- + NH_3 + H_2O$

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

You can make up your own examples as well; except, stay away from polyprotic acids unless the rxn is STRONG-STRONG.

IV) Hydrolysis

When an acid reacts with a strong hydroxide base, it is called a NEUTRALIZATION reaction, and the products are SALT and WATER.

@ EQUIV. PT.

$2HBr + Ca(OH)_2 \Rightarrow CaBr_2 + 2H_2O$ NEUTRAL pH

strong strong

$CH_3COOH + KOH \Rightarrow KCH_3COO + H_2O$ BASIC pH

weak strong

When a strong acid reacts with a base that does not contain hydroxide, it is still a neutralization reaction, however the only product is a weak acid, or a salt that hydrolyzes acidically.

$HCl + CN^- \Rightarrow HCN + Cl^-$ or $HCl + NH_3 \Rightarrow NH_4Cl \longrightarrow NH_4^+ + Cl^-$

weak acid salt weak acid

The salts that are produced can be soluble or insoluble. The insoluble salts will form a solid and precipitate out of solution. The soluble salts will remain as cations and anions and may react with water in a process called **hydrolysis,** causing the resulting solution to be acidic, basic, or neutral.

The ions that make up the salts produced from the neutralization reactions may or may not undergo hydrolysis. Here are the guidelines:

1. a) Conjugate bases of STRONG acids do not undergo basic hydrolysis
eg: Cl^-, I^-, Br^-, ClO_4^-, NO_3^-, HSO_4^-

b) Conjugate acids of STRONG bases do not undergo acidic hydrolysis
eg: OH^-, NH_3, Na^+, Li^+, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}, etc...
(any alkali/alkaline earth cation)

2. Weak acids undergo hydrolysis to produce H_3O^+, thereby creating an ACIDIC solution.

3. Weak bases undergo hydrolysis to produce OH^-, thereby creating a BASIC solution.

Predict whether the following salt solutions will be acidic, basic, or neutral.

$KCl \longrightarrow K^+ + Cl^-$

K^+ does not hydrolyze (conj. acid of strong base).

Cl^- does not hydrolyze (conj. base of strong acid).

∴ solution is NEUTRAL.

$NH_4NO_3 \longrightarrow NH_4^+ + NO_3^-$

NH_4^+ hydrolyzes ACIDICALLY: $NH_4^+ + H_2O \rightleftharpoons \boxed{H_3O^+} + NH_3$

NO_3^- does not hydrolyze (conj. base of str. acid).

∴ solution is ACIDIC.

$Na_2CO_3 \longrightarrow 2\,Na^+ + CO_3^{2-}$

Na^+ does not hydrolyze (conj. acid of strong base).

CO_3^{2-} hydrolyzes BASICALLY: $CO_3^{2-} + H_2O \rightleftharpoons \boxed{OH^-} + HCO_3^-$

∴ solution is BASIC (alkaline)

$NaHSO_3 \longrightarrow Na^+ + HSO_3^-$

Na^+ does not hydrolyze (conj. acid of str. base).

HSO_3^- is AMPHIPROTIC ⇒ it hydrolyzes both ACIDICALLY and BASICALLY.

Acidically: $HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$ $K_a = 1.0\times10^{-7}$

Basically: $HSO_3^- + H_2O \rightleftharpoons OH^- + H_2SO_3$ $K_b = \frac{K_w}{K_a(H_2SO_3)} = \frac{1\times10^{-14}}{1.5\times10^{-2}} = 6.7\times10^{-13}$

$K_a > K_b$ ∴ $\boxed{\text{ACIDIC solution}}$

$KHCO_3 \longrightarrow K^+ + HCO_3^-$

K^+ does not hydrolyze (conj. acid of str. base)

HCO_3^- is AMPHIPROTIC → hydrolyzes ACIDICALLY and BASICALLY

Acidically: $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$ $K_a = 5.6\times10^{-11}$

Basically: $HCO_3^- + H_2O \rightleftharpoons OH^- + H_2CO_3$ $K_b = \frac{K_w}{K_a(H_2CO_3)} = \frac{1\times10^{-14}}{4.3\times10^{-7}}$
$= 2.3\times10^{-8}$

$K_b > K_a$ ∴ $\boxed{\text{BASIC solution}}$

$NH_4NO_2 \longrightarrow NH_4^+ + NO_2^-$

NH_4^+ hydrolyzes ACIDICALLY: $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$
$K_a = 5.6\times10^{-10}$

NO_2^- hydrolyzes BASICALLY: $NO_2^- + H_2O \rightleftharpoons OH^- + HNO_2$
$K_b = \frac{K_w}{K_a(HNO_2)} = \frac{1\times10^{-14}}{4.6\times10^{-4}} = 2.2\times10^{-11}$

$K_a > K_b$ ∴ $\boxed{\text{ACIDIC}}$

$Al(NO_2)_3 \longrightarrow Al^{3+} + ③\,NO_2^-$

Al^{3+} hydrolyzes ACIDICALLY: $Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5OH^{2+}$
$K_a = 1.4\times10^{-5}$

NO_2^- hydrolyzes BASICALLY: $NO_2^- + H_2O \rightleftharpoons OH^- + HNO_2$
$K_b = \frac{1\times10^{-14}}{4.6\times10^{-4}} = 2.2\times10^{-11}$

$K_a > K_b$ (by greater than a factor of ③) ⇒ $\boxed{\text{ACIDIC}}$

Summary of Possibilities:

Scope of Ch.12

1. Neither cation nor anion hydrolyzes. ⇒ NEUTRAL salt
2. Cation hydrolyzes acidically, anion does not hydrolyze ⇒ ACIDIC salt.
3. Cation does not hydrolyze, anion hydrolyzes basically ⇒ BASIC salt.
4. Both cation (acidically) and anion (basically) hydrolyze ⇒ compare K_a to K_b
5. Cation does not hydrolyze, anion is amphiprotic ⇒ compare K_a to K_b.
6. next year! * Cation hydrolyzes acidically, anion is amphiprotic ⇒ involves concentrations being known

Assignment 6: Hydrolysis Exercises

1. Write the hydrolysis (if any) reaction(s) occurring when the following salts are added to water and predict whether the resulting solution will be acidic, basic, or neutral.
a) Na_2SO_3 b) K_2SO_3 c) $LiHCO_3$ d) LiBr e) Na_2HPO_4 f) $NaNO_2$
g) $Al(NO_3)_3$ h) NH_4Cl i) CaF_2 j) NH_4CH_3COO k) $Al_2(SO_4)_3$
l)NH_4Br m) Na_3PO_4

2. Calculate the pH of a 0.20M KCN solution.

3. The salt AB contains the ions A^+ and B^-. A^+ acts as an acid in aqueous solution while B^- acts as a base. Explain how it is possible for a solution AB to have a pH less than 7.

4. Calculate the pH of a 0.40M $NaCH_3COO$ solution.

5. In a titration, which of the following combinations would result in an equivalence point with pH greater than 7.0 ?

A. HCl and NaOH
B. HNO_3 and NH_3
C. HBr and $NaCH_3COO$
D. CH_3COOH and NaOH

Also: p.148 #71-73 (and #69 d, f-j; #70 b-h, j – for extra practice only)

– QUIZ 3 –

V) Acid-Base Indicators

Acid-Base indicators are used to signal the equivalence point (where moles of H_3O^+ = moles of OH^-) during an acid-base titration by changing the colour of the solution in the flask/beaker. They can also be used to determine the pH range of a particular solution.

An indicator is a mixture of a weak organic acid, **HIn**, and its conjugate base, **In⁻**, at equilibrium. The acid form of the indicator is a different colour than the conjugate base form, which is why these chemicals are so usable in determining pH changes etc. The following is the general equilibrium for any acid-base indicator:

$$\underset{\text{yellow}}{HIn} + H_2O \Leftrightarrow \underset{\text{blue}}{In^-} + H_3O^+$$

Suppose HIn creates a yellow solution while the In^- creates a blue solution.

If a few drops of indicator are added to a flask containing a stronger acid (ie. an acid with a higher $[H_3O^+]$ than the indicator), the above equilibrium will shift LEFT, thereby favouring HIn over In^- and producing a 'YELLOWISH' colour.

In a basic (or weaker acidic) solution, the $[H_3O^+]$ of the solution is lower than that of the indicator, thereby causing a shift RIGHT, producing a 'BLUISH' colour.

ASSIGNMENT 5: HYDROLYSIS EXERCISES

①

a) $Na_2SO_3 \longrightarrow 2Na^+ + SO_3^{2-}$

$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-$ ∴ BASIC

b) $K_2SO_3 \rightarrow 2K^+ + SO_3^{2-}$

$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-$ ∴ BASIC

c) $LiHCO_3 \longrightarrow Li^+ + HCO_3^-$

$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \quad Ka = 5.6\times10^{-11}$

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^- \quad K_b = \frac{1.0\times10^{-14}}{4.3\times10^{-7}} = 2.3\times10^{-8}$

$Kb > Ka$ ∴ BASIC

d) $LiBr \rightarrow Li^+ + Br^-$

∴ NEUTRAL

e) $Na_2HPO_4 \rightarrow 2Na^+ + HPO_4^{2-}$

$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+ \quad Ka = 2.2\times10^{-13}$

$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^- \quad K_b = \frac{1.0\times10^{-14}}{6.2\times10^{-8}} = 1.6\times10^{-7}$

$K_b > Ka$ ∴ BASIC

f) $NaNO_2 \longrightarrow Na^+ + NO_2^-$

$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$ ∴ BASIC

g) $Al(NO_3)_3 \longrightarrow Al^{3+} + 3NO_3^-$

$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$

∴ ACIDIC

h) $NH_4Cl \longrightarrow NH_4^+ + Cl^-$

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

∴ ACIDIC

i) $CaF_2 \rightarrow Ca^{2+} + 2F^-$

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

∴ BASIC

j) $NH_4CH_3COO \rightarrow NH_4^+ + CH_3COO^-$

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ $K_a = 5.6\times10^{-10}$

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ $K_b = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$

$K_a = K_b$ ∴ NEUTRAL

K) $Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$

$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$ $K_a = 1.4\times10^{-5}$

$SO_4^{2-} + H_2O \rightleftharpoons HSO_4^- + OH^-$ $K_b = \frac{1.0\times10^{-14}}{1.2\times10^{-2}} = 8.3\times10^{-13}$

$K_a > K_b$ ∴ ACIDIC

~~l) $Fe_2S_3 \rightarrow 2Fe^{3+} + 3S^{2-}$~~

~~$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$ ← NOT ON A/B TABLE~~

~~∴ OMIT QUESTION~~

l) $NH_4Br \rightarrow NH_4^+ + Br^-$

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

∴ ACIDIC

m) $Na_3PO_4 \rightarrow 3Na^+ + PO_4^{3-}$

$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$

∴ BASIC

2) $\underset{0.20M}{KCN} \rightarrow K^+ + \underset{0.20M}{CN^-}$ * 100% dissoc. due to alkali metal ion (Solution Chem.)

	CN^- + H_2O ⇌	HCN +	OH^-
i	0.20	0	0
c	$-x$	$+x$	$+x$
e	$0.20-x$	x	x

Let $x = \Delta[OH^-]$

$K_b = \frac{[OH^-]^2}{[CN^-]}$ $K_b = \frac{1.0\times10^{-14}}{4.9\times10^{-10}} = 2.04\times10^{-5}$

$2.04\times10^{-5} = \frac{x^2}{0.20-x}$ ASSUME $0.20-x \cong 0.20$

$2.04\times10^{-5} = \frac{x^2}{0.20}$ $x = \sqrt{(2.04\times10^{-5})(0.20)}$

$x = 2.02\times10^{-3}$

$[OH^-] = 2.02\times10^{-3}M$

$pOH = 2.69$

$pH = \underline{11.31}$

3) $AB \longrightarrow A^+ + B^-$

$pH < 7$ IS AN ACIDIC SOLUTION

~~2 POSSIBILITIES:~~ ~~① A^+ HYDROLYZES ACIDICALLY AND B^- DOES NOT HYDROLYZE ∴ ACIDIC SOL'N & $pH<7$~~

~~②~~ $\boxed{\text{A}^+ \text{ HYDROLYZES ACIDICALLY AND B}^- \text{ HYDROLYZES BASICALLY. BUT K}_a \text{ OF A}^+ > \text{K}_b \text{ OF B}^- \text{ ∴ SOLUTION IS ACIDIC AND pH<7.}}$

4) $NaCH_3COO \longrightarrow Na^+ + CH_3COO^-$

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

	CH_3COO^-	CH_3COOH	OH^-
i	0.40	0	0
c	$-x$	$+x$	$+x$
e	$0.40-x$	x	x

Let $x = \Delta[OH^-]$

$K_b = \frac{[OH^-]^2}{[CH_3COO^-]}$

$K_b = \frac{1.0\times10^{-14}}{1.8\times10^{-5}}$

$= 5.56\times10^{-10}$

$5.56\times10^{-10} = \frac{x^2}{0.40-x}$ ASSUME $0.40-x \cong 0.40$

$5.56\times10^{-10} = \frac{x^2}{0.40}$

$x = \sqrt{(5.56\times10^{-10})(0.40)}$

$x = 1.49\times10^{-5}$

$[OH^-] = 1.49\times10^{-5} M$

$pOH = 4.83$

$pH = 9.17$

5) D

eg: What colour will Orange IV be when placed into a solution with pH 3.5?

$$\underset{\text{RED}}{HIn} + H_2O \rightleftharpoons \underset{\text{YELLOW}}{In^-} + H_3O^+ \qquad \text{RANGE} \Rightarrow pH\ 1.4 - 2.8$$

(lower than 3.5)

So... ORANGE IV is being placed into a solution with a LOWER $[H_3O^+]$. Shift will be $\boxed{\text{RIGHT}}$

$$[H_3O^+]\downarrow\ \underset{\text{shift } (R)}{\uparrow} = \downarrow\ [HIn]\downarrow\ \ [In^-]\uparrow$$

$\boxed{\text{Solution turns YELLOW}}$

During a titration, pH is constantly changing as base is being added to acid (or vice versa). If an indicator is present, it will undergo a colour change at a certain point due to the change in $[H_3O^+]$ which causes the indicator equilibrium to shift as the titration proceeds.

When base is added to an acidic solution (which is yellow in our example), eventually $[HIn] = [In^-]$ (mol HIn = mol In^-), and the solution will turn 'perfect' green as we have equal moles of yellow and blue coloured indicator. If any more base is added, the solution will turn 'BLUISH'.

The point at which $[HIn] = [In^-]$ is called the ENDPOINT or TRANSITION POINT. It is also defined as the point at which the 'perfect' intermediate colour is observed (and the 'halfway' point of the pH ranges provided on the Indicator Data Table).

This point occurs at different pHs for different indicators.

It is very important to be able to distinguish between the two terms, **equivalence point** and **endpoint**. The equivalence point is the point in the titration where moles of H_3O^+ = moles of OH^-. The endpoint is the point in the titration where the colour of the indicator changes (ie. where moles HIn equals moles In^-). If the indicator is chosen correctly, it will change the colour of the solution at or near the equivalence point.

The Chemistry 12 Data Booklet has a table called Acid-Base Indicators. It shows the pH ranges at which different indicators change colour. Most indicators change colour over a range of about 2 pH units. For example, Bromthymol Blue is yellow at pH 6.0 and blue at pH 7.6. Thus, the endpoint is in the middle of the range (pH 6.8) and is a perfect combination of the two colours - green.

Assignment 7: Indicator Exercises

1. A weak acid is titrated with a strong base using the indicator phenolphthalein to detect the endpoint. What is the approximate pH at the transition point?

A. 7.0 B. 8.0 [✓ C. 9.0] D. 10.0

Phenolphthalein range: 8.2 - 10 ∴ transition pt.
colourless pink
pH = 9.1

2. Which of the following indicators is red at pH 13 ?

A. Orange IV 1.4 → 2.8 → yellow
[✓ B. Alizarin Yellow] 10.1 → 12.0 → red
C. Indigo Carmine 11.4 → 13.0 → yellow
D. Thymol Blue 8.0 - 9.6 → blue

chat about why on table twice.

3. What colour is a 1 x 10^{-3} M NaOH solution containing the indicator Neutral Red?

$$\underset{0.001\,M}{NaOH} \longrightarrow Na^+ + \underset{0.001\,M}{OH^-}$$

$pOH = -\log(0.001\,M) = 3.0$

$pH = 11.0$ Neutral Red (6.8 - 8.0)

$\boxed{\text{AMBER}}$

Recall that the general equilibrium equation for an indicator is as follows:

$$HIn + H_2O_{(l)} \Leftrightarrow In^- + H_3O^+$$

Write the K_a equation for the above:

$$K_a = \frac{[In^-][H_3O^+]}{[HIn]}$$

At the endpoint, [HIn] = [In⁻], and therefore...

$$K_a = \frac{\cancel{[In^-]}[H_3O^+]}{\cancel{[HIn]}} = [H_3O^+]$$

Therefore, at the endpoint (time of colour change to 'perfect' colour), the $[H_3O^+]$ equals the value of the K_a for the indicator.
If $K_a = [H_3O^+]$ and $pH = -\log [H_3O^+]$, then **$pH = -\log K_a$**

OR **$pH = pK_a$**

Assignment 8: More Indicator Exercises

1. Which of the following chemical indicators has a $K_a = 2.5 \times 10^{-5}$?
   A. methyl orange
   B. phenolphthalein
   C. thymolphthalein
   [✓ D. bromcresol green]

Assume ENDPOINT so that $K_a = [H_3O^+]$

pK_a = pH at ENDPOINT

$-\log(2.5 \times 10^{-5}) = \underline{4.60}$ ← halfway-pt. of Bromcr. Green.

2. Find the K_a of Alizarin Yellow. Assume endpoint. (pH @ endpt = pK_a)

Endpt. pH = 11.05 = pK_a; invlog(−11.05) = $\boxed{9 \times 10^{-12}}$

3. Read p. 161 (bottom) and 162 on Universal Indicators
   Hebden p. 162 #108-112 and p. 163 #114-118 (Try 120)

VI) Buffers

Buffers are acid-base equilibrium systems that can maintain an almost constant pH when acid or base is added. Our blood contains a buffer system using bicarbonate/carbonic acid to maintain a steady pH. $K_b > K_a$ (basic blood)

Blood buffering system:

$$CO_2 + H_2O + OH^- \rightleftharpoons H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O$$

blood pH 7.4

* 7% CO_2 dissolves in plasma
* 23% as $HbCO_2$
* 70% as HCO_3^-

Buffers are made up of EQUAL (or near equal) concentrations of a WEAK ACID and its CONJUGATE BASE. A 'perfect' buffer has ***equal*** concentrations.

Two Hydrolysis reactions occur **simultaneously** within a buffer system:

Acidic hydrolysis:

$HSO_3^- + H_2O \Leftrightarrow SO_3^{2-} + H_3O^+$

2.0M 2.0M <<2.0M

Basic hydrolysis

$SO_3^{2-} + H_2O \Leftrightarrow HSO_3^- + OH^-$

2.0M 2.0M <<2.0M

In order to make a buffer like the equilibrium shown above, why can't 2.0 M HSO_3^- simply be added directly to water?

HSO_3^- is a weak acid and will only dissociate < 5%. AT BEST, $[HSO_3^-] : [SO_3^{2-}] = 20 : 1$

not equal enough in conc. to be an efficient buffer.

So, one must add $NaHSO_3$ to water and then add extra SO_3^{2-} in the form of a soluble salt (Na_2SO_3) to make the $[HSO_3^-]$ and $[SO_3^{2-}]$ equal. As well, $[H_3O^+]$ and $[OH^-]$ will be comparatively low as only a very small amount is produced by reacting HSO_3^- and SO_3^{2-} respectively with water.

How a Buffer Works

The key to a functional buffer is the large, equal (or near equal) concentrations of a weak acid and its conjugate base. The weak acid is present to buffer any 'contaminant' OH^- that may come in contact with the buffered solution. The conjugate base is present to buffer any 'contaminant' H_3O^+ that may come in contact with the buffered solution.

Remember that pH is dependent on only two substances: H_3O^+ and OH^-. A buffer reacts with and depletes any added H_3O^+ and OH^-, thereby keeping the pH very close to (but not the same as) the original value.

Scenarios (assume 'perfect' buffer):

Contaminant acid:

If H_3O^+ is added to our HSO_3^- / SO_3^{2-} buffer, it will react with SO_3^{2-}, causing a shift to the left of the acid hydrolysis equilibrium:

$$HSO_3^- + H_2O \Leftrightarrow SO_3^{2-} + H_3O^+$$

$[H_3O^+] \uparrow \underset{\text{buffering}}{\downarrow} = \uparrow$ (a little) $[SO_3^{2-}] - \downarrow = \downarrow$ $[HSO_3^-] - \uparrow = \uparrow$

$\boxed{\text{pH} \downarrow \text{ a bit}}$

or, viewed in a different way, it will cause a shift to the right of the base hydrolysis equilibrium:

$$SO_3^{2-} + H_2O \Leftrightarrow HSO_3^- + OH^- \text{ (base hydrolysis)}$$

$[H_3O^+] \uparrow \Rightarrow [OH^-] \downarrow \underset{\text{buffering}}{\uparrow} = \downarrow$ (a little) $[SO_3^{2-}] - \downarrow = \downarrow$ $[HSO_3^-] - \uparrow = \uparrow$

$\boxed{\text{pH} \downarrow \text{ a bit}}$

Not all of the H_3O^+ added will directly affect pH (thanks to LeChatelier's Principle), so the pH will only *slightly* lower. If too much H_3O^+ is added, the buffer will eventually ***collapse*** as all moles of the SO_3^{2-} (which is the source of OH^-) will be used up.

Contaminant base:
If OH^- is added to our buffer, we can view its effect in two ways (each of which producing the same result => a *slight* increase in pH)

SO_3^{2-} + H_2O ⇔ HSO_3^- + OH^- (base hydrolysis)

$[OH^-]$ ↑↓ = ↑ $[SO_3^{2-}]$—↑=↑ $[HSO_3^-]$—↓=↓   pH ↑ slightly.

shift Ⓛ
(buffering)

OR… HSO_3^- + H_2O ⇔ SO_3^{2-} + H_3O^+ (acid hydrolysis)

$[H_3O^+]$ ↓↑ = ↓ $[HSO_3^-]$—↓=↓ $[SO_3^{2-}]$—↑=↑   pH ↑ slightly

shift Ⓡ
(buffering)

Not all of the OH^- added will directly affect pH (LeChatelier), thus the pH will rise only slightly. If too much OH^- is added, all moles of HSO_3^- (source of H_3O^-) will be used up and the buffer will collapse.

Diluting a Buffer
Take the example used previously:

HSO_3^-	+	H_2O	⇔	SO_3^{2-}	+	H_3O^+
2.0M				2.0M		~0.05M

Adding water to the above equilibrium system will cause each concentration to decrease. But we still have a buffer possessing the exact same buffering capabilities because we still have the same original amount of *moles* of each of the weak acid and base. So, buffer capacity is still the same after dilution.

A buffer's capacity, therefore, depends upon how the buffer was ***originally*** produced with respect to the amount of moles of conjugate acid and base.

Acidic, Basic, and Neutral Buffers

Each buffer system has a unique pH that it buffers. The pH can be found by using K_a. For example:

$HSO_3^- + H_2O \Leftrightarrow SO_3^{2-} + H_3O^+$ -- therefore, a 'perfect' buffer…
2.0M 2.0M v. small

$$K_a = \frac{[SO_3^{2-}][H_3O^+]}{[HSO_3^-]} = \frac{(2.0)[H_3O^+]}{(2.0)} = [H_3O^+]$$ …if 'perfect' buffer…

For HSO_3^-:

$$K_a = 1.0 \times 10^{-7} = [H_3O^+]$$

Therefore: pH of HSO_3^-/SO_3^{2-} buffer system $= -\log[H_3O^+]$
$= -\log(1.0 \times 10^{-7})$
$= 7.00$ (neutral buffer)

Wouldn't K_a change with different [acids]? NO

The higher [acid], the higher [conjugate base] - in order to maintain the 'perfect' buffer. The increase in $[H_3O^+]$ is offset by the increase in $[OH^-]$; K_a remains same.
Also, only a TEMPERATURE change alters K_a!

The example used above is a neutral buffer because the K_a of HSO_3^- is 1.0×10^{-7} and therefore has a buffer pH of 7.00.

In fact: $K_a(HSO_3^-) = K_b(SO_3^{2-})$

Weak acids that have K_a values greater than 1.0×10^{-7} have a buffer pH in the acidic region, and weak acids that have K_a values less than 1.0×10^{-7}, have a buffer pH in the basic region.

$CH_3COOH + H_2O \Leftrightarrow CH_3COO^- + H_3O^+$
1.0M 1.0M v. small

$K_a = 1.8 \times 10^{-5} = [H_3O^+]$ therefore $pH = -\log(1.8 \times 10^{-5}) = 4.74$

Therefore, acetic acid/acetate creates an acidic buffer.

$HCN + H_2O \Leftrightarrow CN^- + H_3O^+$
1.0M 1.0M v. small

$K_a = 4.9 \times 10^{-10} = [H_3O^+]$ therefore $pH = -\log(4.9 \times 10^{-10}) = 9.31$

Therefore, hydrocyanic acid/cyanate creates a basic buffer.

Assignment 9: Buffer Exercises

1. What is the buffering pH in your blood? The weak acid is carbonic acid (H_2CO_3) and the conjugate base is bicarbonate (HCO_3^-).

Hebden p. 181 -182 #131-140

Read Hebden p. 182-183 *Buffers in Biological Systems* (Try #141-143)

① $K_a(H_2CO_3)$ room temp. $= 4.3 \times 10^{-7}$
pH of room temp. blood ⇒ 6.37 (if $K_a = [H_3O^+]$ (ie. perfect buffer))

② $K_a(H_2CO_3)$ body temp. $= 7.9 \times 10^{-7}$
pH of body temp blood = 6.10 (again, if 'perfect' buffer)

BUT, pH of blood = 7.4
Why? b/c $[HCO_3^-] > [H_2CO_3]$ ∴ more OH^- than H_3O^+ in blood

Humans ingest and metabolically produce many more acids than bases. Blood is ready for that.

HOW A BUFFER WORKS (Quantitative):

$$\underset{1.0\,M}{CH_3COOH} + H_2O \rightleftharpoons H_3O^+ + \underset{1.0\,M}{CH_3COO^-}$$

* a "PERFECT" <u>acidic</u> buffer : $K_a = [H_3O^+] \Rightarrow pH = \underline{\underline{4.74}}$

Assume we have 1.0 L of this buffered solution and we add 100.0 mL of 2.0 M HCl.

After Addition: mol H_3O^+ added $= MV = (2.0M)(0.1000L) = 0.20$ mol H_3O^+

mol CH_3COO^- before $= MV = (1.0M)(1.0L) = 1.0$ mol CH_3COO^-;

mol CH_3COO^- after HCl addition $= 1.0 - 0.20$ mol $= 0.80$ mol CH_3COO^- after.

$$[CH_3COO^-]_f = \frac{mol_f}{V_f} = \frac{0.80\text{ mol}}{1.1\text{ L}} = 0.727\text{ M}$$

mol CH_3COOH before $= MV = (1.0M)(1.0L) = 1.0$ mol CH_3COOH;

mol CH_3COOH after HCl addition $= 1.0 + 0.20$ mol $= 1.2$ mol CH_3COOH after

$$[CH_3COOH]_f = \frac{mol_f}{V_f} = \frac{1.2\text{ mol}}{1.1\text{ L}} = 1.09\text{ M } CH_3COOH$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \Rightarrow [H_3O^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = \frac{(1.8\times10^{-5})(1.09M)}{0.727\ M}$$

$$= 2.7\times10^{-5}\text{ M}$$

$pH_f = -\log(2.7\times10^{-5}) = 4.57$ (pH down by 0.17 ONLY)

Without buffer: Add 100 mL of 2.0 M HCl to 1 L WATER (pH 7).

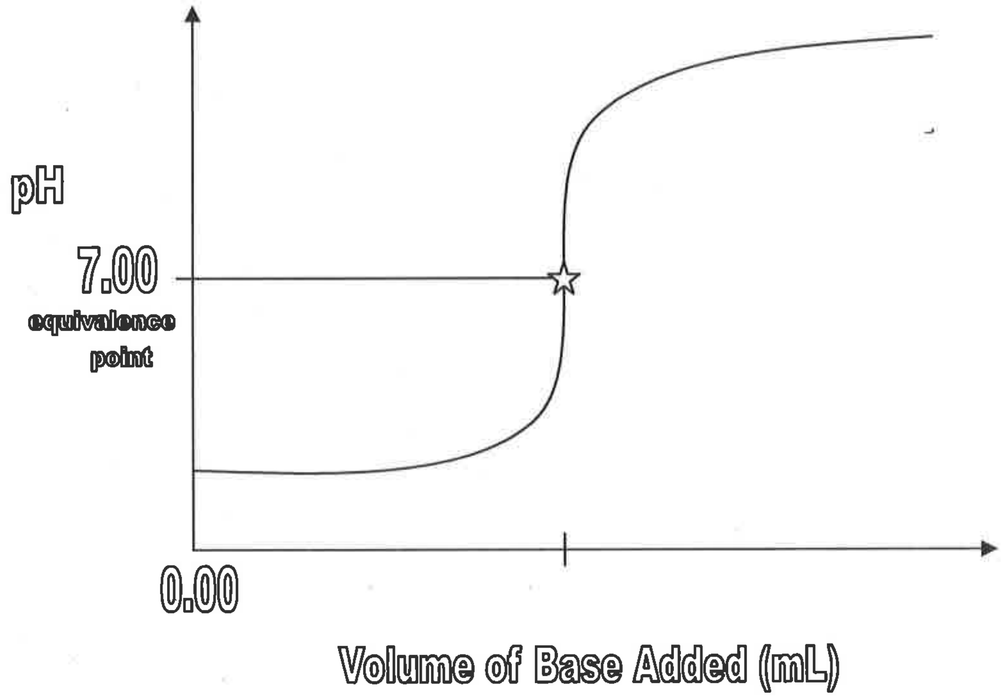
mol $H_3O^+ = MV = 0.200$ mol H_3O^+

$[H_3O^+] = \frac{0.200\text{ mol}}{} = 0.182$ M $H_3O^+ \rightarrow pH = \boxed{0.74}$ DOWN 6.26

VII) Acid/Base Titration Curves

A standard titration curve plots Volume of Base (or Acid) added from the burette on the *x axis* versus pH on the *y axis*.

Strong Acid/Strong Base Titration Curve



Notice the general shape of a titration curve. The pH rises very slowly at the start of the titration, and then very drastically in the middle region, and then very slowly again at the end. This is because pH is a logarithmic function.

For example, to change from a pH 2 to pH 3, $[H_3O^+]$ must change from 0.01M to 0.001M. This will take a significant amount of $[OH^-]$ from the burette, much more that changing pH from 6 to 7 ($[H_3O^+]$ goes from 0.000 001M to 0.000 000 1M).

TITRATION CURVES
EXPLANATION

① 10 mL of 0.1 M (∴ pH 1) HCl in flask. 0.1 M NaOH in burette.

VOLUME NaOH added	Moles of Greater Quantity Ion (H_3O^+ / OH^-)	pH of substance in flask
0 mL	0.0010 mol H_3O^+	1
1 mL	0.0009 mol H_3O^+	1.09
2 mL	______ mol H_3O^+	______
3 mL	______ mol H_3O^+	______
4 mL	______ mol H_3O^+	______
5 mL	______ mol H_3O^+	______
6 mL	______ mol H_3O^+	______
7 mL	______ mol H_3O^+	______
8 mL	______ mol H_3O^+	______
9 mL	______ mol H_3O^+	______
10 mL	______ mol H_3O^+/OH^-	______
11 mL	______ mol OH^-	______
12 mL	______ mol OH^-	______
13 mL	______ mol OH^-	______
14 mL	______ mol OH^-	______
15 mL	______ mol OH^-	______
⋮		
20 mL	______ mol OH^-	______

One must add $NaHSO_3$ to water and then add extra SO_3^{2-} in the form of a salt solution (Na_2SO_3) to make the $[HSO_3^-]$ and $[SO_3^{2-}]$ equal. As well, $[H_3O^+]$ and $[OH^-]$ will be comparatively low as only a very small amount is produced by reacting HSO_3^- and SO_3^{2-} respectively with water. Now you have a buffer system.

How a Buffer Works

The key to a functional buffer is the large (compared to $[H_3O^+]$ and $[OH^-]$), equal concentrations of a weak acid and its conjugate base. The weak acid is there in large amounts to react with any OH^- added to the buffer. The conjugate base is there in large amounts to react with any H_3O^+ added to the buffer.

Remember that pH is dependent on only two substances: H_3O^+ and OH^-. A buffer reacts with and depletes any added H_3O^+ and OH^-, thereby keeping the pH close to the original value.

If H_3O^+ is added to our HSO_3^- / SO_3^{2-} buffer, it will react with SO_3^{2-}, causing a shift to the left:

$$HSO_3^- + H_2O \Leftrightarrow SO_3^{2-} + H_3O^+$$

$[H_3O^+] \uparrow \underset{\text{buffer (shift)}}{\downarrow} = \uparrow$; $[HSO_3^-] \downarrow$; $[SO_3^{2-}] \uparrow$ pH ↓ slightly.

* not a 'perfect'
buffer anymore

Not all of the H_3O^+ added will directly affect pH (LeChatelier), so the pH will only *slightly* lower. If too much H_3O^+ is added, the buffer will eventually ***collapse*** as all moles of the SO_3^{2-} (which is the source of OH^-) will be used up.

If OH^- is added to our buffer, we can view its effect in two ways (each of which producing the same result => a *slight* increase in pH)

$$SO_3^{2-} + H_2O \Leftrightarrow HSO_3^- + OH^- \text{ (base hydrolysis equation)}$$

$[OH^-] \uparrow \underset{\text{buffer (shift)}}{\downarrow} = \uparrow$; $[SO_3^{2-}] \uparrow$; $[HSO_3^-] \downarrow$ pH ↑ slightly

TITRATION CURVES
EXPLANATION

Key

① 10 mL of 0.1 M (∴ pH 1) HCl in flask. 0.1 M NaOH in burette.

VOLUME NaOH added	Moles of Greater Quantity Ion (H_3O^+ / OH^-)	pH of substance in flask
0 mL	0.0010 mol H_3O^+	1
1 mL	0.0009 mol H_3O^+	1.09
2 mL	0.0008 mol H_3O^+	1.18
3 mL	0.0007 mol H_3O^+	1.27
4 mL	0.0006 mol H_3O^+	1.37
5 mL	0.0005 mol H_3O^+	1.48
6 mL	0.0004 mol H_3O^+	1.60
7 mL	0.0003 mol H_3O^+	1.75
8 mL	0.0002 mol H_3O^+	1.95
9 mL	0.0001 mol H_3O^+	2.28
10 mL	0 mol H_3O^+/OH^-	7
11 mL	0.0001 mol OH^-	11.68
12 mL	0.0002 mol OH^-	11.96
13 mL	0.0003 mol OH^-	12.12
14 mL	0.0004 mol OH^-	12.22
15 mL	0.0005 mol OH^-	12.30
⋮		
20 mL	0.0010 mol OH^-	12.52

Think about an analogy using money. It is more difficult to pay a $10 000 loan down to $1 000 than it would be to pay a $10 loan down to $1.

Therefore, pH can move from approximately pH 5 to pH 9 with only drops of OH^- from the burette. This accounts for the sharp vertical rise characteristic of titration curves.

A strong acid/strong base titration curve has an equivalence point of pH 7 due to the fact that the resulting salt will not hydrolyze acidically or basically:

$$HCl + NaOH \Rightarrow H_2O + NaCl$$

$NaCl \longrightarrow Na^+ + Cl^-$

neither ion will hydrolyze.

An ideal indicator for a strong acid/strong base titration would be one that has a pH colour change range at or around pH 7. What indicators would be ideal?

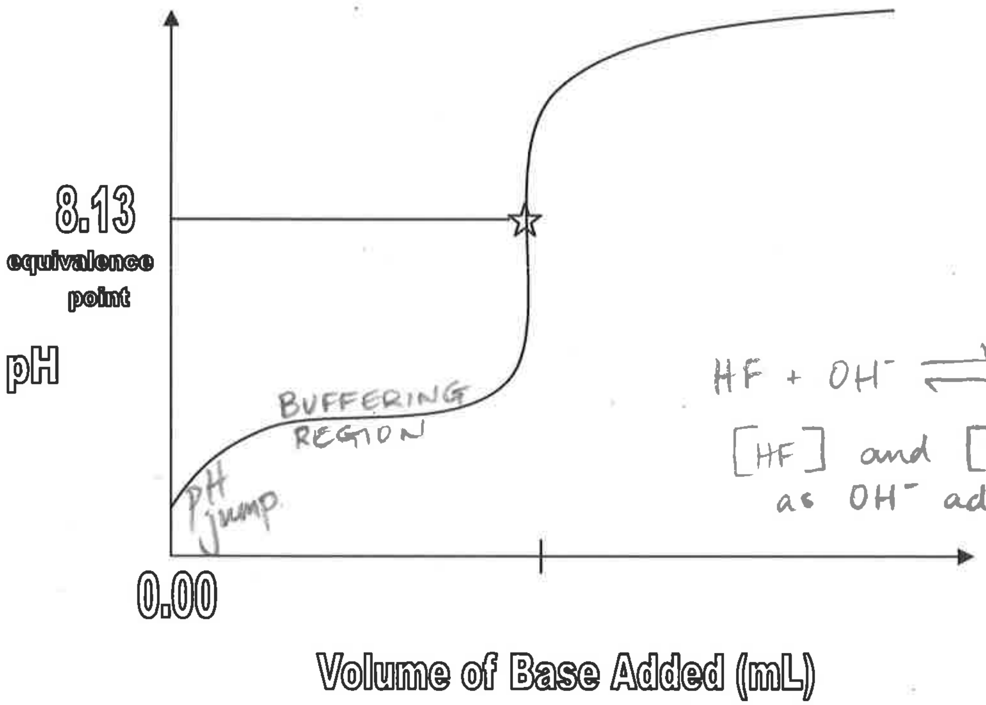
BROMTHYMOL BLUE, PHENOL RED, NEUTRAL RED

However, PHENOLPHTHALEIN is most commonly used as it is inexpensive and still gives acceptable results. Why will it still give acceptable results?

Colour change range (8.2-10.0) is on the 'vertical' of the strong-strong titration curve. Thus, the difference between the equiv. point (pH 7) and the endpoint is only 1-2 drops of base.

Some titrations involve titrating a weak acid with a strong base, or titrating a weak base with a strong acid. Let's look at each one individually.

Weak Acid/Strong Base Titration (strong base is in the burette)



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

$[HF]$ and $[F^-]$ get closer as OH^- added ⇒ better buffer.

Though two parts of this curve are different than the strong acid/strong base curve, the sharp vertical rise is still present.

Notice the small pH jump at the beginning of this curve. That is characteristic of any weak/strong titration. Also, the equivalence point is at a pH of 8-10. This is because the salt produced from a weak acid/strong base titration will hydrolyze basically:

$$HF + NaOH \Rightarrow H_2O + NaF \qquad NaF \longrightarrow Na^+ + F^-$$

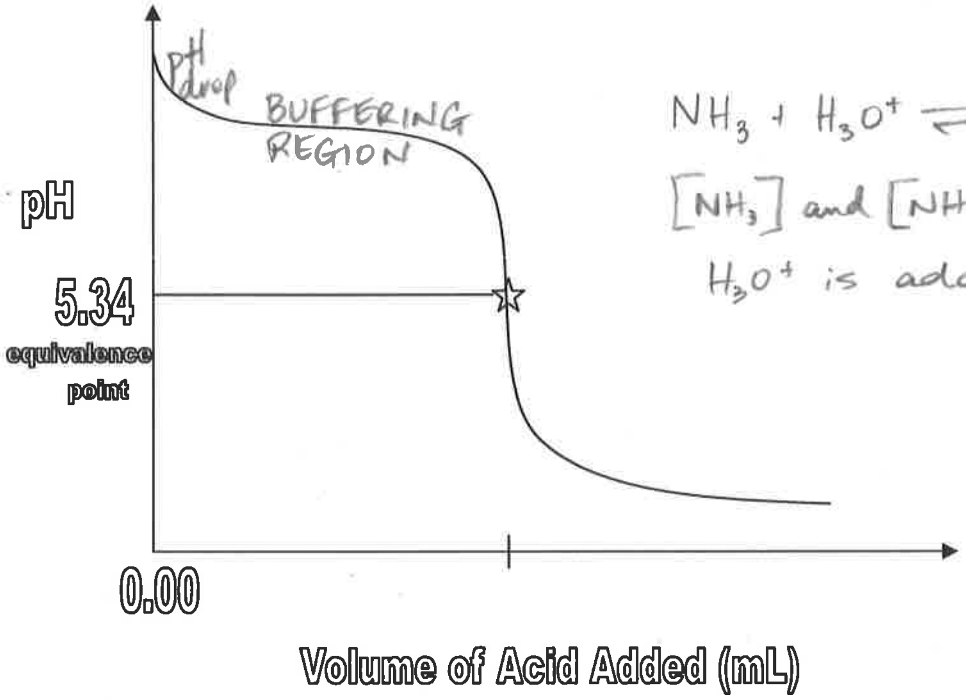
F^- from NaF will hydrolyze basically to produce OH^-, thereby increasing the pH at the equivalence point!

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

Which indicators would be ideal for a weak acid/strong base titration?

Thymol Blue
Phenolphthalein
Thymolphthalein

Weak Base/Strong Acid Titration (strong acid is in the burette)



$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$

$[NH_3]$ and $[NH_4^+]$ get closer as H_3O^+ is added ⇒ better buffer.

Why does this curve start at a high pH and end at a low pH?

Weak base in flask to begin titration, thus relatively high pH to start. As acid is added, pH decreases.

Characteristics include an initial dip in pH and an equivalence point pH of 4-6. This is because the salt produced will hydrolyze acidically:

$HCl + NH_3 \Rightarrow NH_4Cl$ $NH_4Cl \longrightarrow NH_4^+ + Cl^-$

NH_4^+ from NH_4Cl hydrolyzes acidically, thereby decreasing the pH at the equivalence point. $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$

Which indicators would be ideal for a weak base/strong acid titration?

Methyl Orange, Bromcresol Green, Methyl Red, Chlorophenol Red.

Do question 125 p.176 Hebden (omit (e)), and Assignment 10 #1.

Quantitative Titration Questions – Determination of K_a

1. The following data is obtained when a solution of FUROIC ACID ($(C_4H_3O)COOH$) is titrated with NaOH:

[NaOH] = 0.125 M; Volume Furoic Acid = 25.0 mL
Volume NaOH required to reach equiv. pt. = 28.8 mL
Initial pH of Furoic Acid = 2.021.

- i. Calculate the K_a of Furoic Acid
- ii. Find [Furoic Acid]$_i$
- iii. Is the resulting titration mixture acidic, basic, or neutral at the equivalence point?
- iv. Suggest suitable indicators for this titration.

$$(C_4H_3O)COOH + H_2O \rightleftharpoons H_3O^+ + (C_4H_3O)COO^-$$

I FROM TITR^N DATA: $\boxed{0.144\ M}$ $\quad$ 0 M $\quad$ 0 M

C -0.009528 $\quad$ + $\quad$ +

FROM pH$_i$: $\boxed{9.528 \times 10^{-3}\ M}$

E 0.1345 M

$$[H_3O^+]_{eq} = \text{invlog}(-2.021) = 9.528 \times 10^{-3}\ M$$

$$NaOH \longrightarrow Na^+ + OH^-$$

mol NaOH added = mol. OH^- added = mol. H_3O^+ in flask =
mol furoic acid in flask = $MV = (0.125\ M)(0.0288\ L)$
$= 0.00360$ mol

$$[\text{furoic acid}]_i = \frac{\text{mol}}{V_i} = \frac{0.00360\ \text{mol}}{0.0250\ L} = 0.144\ M$$

$$K_a = \frac{[H_3O^+][(C_4H_3O)COO^-]}{[(C_4H_3O)COOH]} = \frac{(9.528 \times 10^{-3})^2}{0.1345} = \boxed{6.75 \times 10^{-4}}$$

iii) BASIC (weak base in products)

iv) Thymol Blue, Phenolphthalein, Thymolphthalein, Neutral Red

2. The following data is obtained when ethylamine (a monoprotic weak base – $C_2H_5NH_2$) is titrated with HCl:

[HCl] used = 0.113 M; Volume of ethylamine = 25.00 mL

Volume of HCl added from buret = 19.22 mL

pH_i of ethylamine = 11.855.

- i. Calculate the K_b of ethylamine
- ii. Find $[\text{ethylamine}]_i$
- iii. Is the resulting titration mixture acidic, basic, or neutral at the equivalence point?
- iv. Suggest suitable indicators for this titration.

$$C_2H_5NH_2 + H_2O \rightleftharpoons OH^- + C_2H_5NH_3^+$$

I	TITRATION DATA: $\boxed{0.086\underline{8}744\text{ M}}$		0 M	0 M
C	$-0.0071\underline{6}14$ M		+	+
E	$0.079\underline{7}13$ M		pHi: $\boxed{\underline{7}.1614 \times 10^{-3}\text{ M}}$	

$$[H_3O^+]_{eq} = \text{invlog}(-pH) = \text{invlog}(-11.855) = 1.39\underline{6}4 \times 10^{-12}\text{ M}$$

$$[OH^-]_{eq} = \frac{K_w}{[H_3O^+]_{eq}} = \frac{1 \times 10^{-14}}{1.39\underline{6}4 \times 10^{-12}} = 7.1\underline{6}14 \times 10^{-3}\text{ M}$$

TITRATION: $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

mol HCl added = mol H_3O^+ added = mol OH^- in flask = mol $C_2H_5NH_2$ in flask = $MV = (0.113\text{ M})(0.01922\text{ L})$

$= 0.0021\underline{7}186$ mol

$$[C_2H_5NH_2]_i = \frac{\text{mol}}{V_i} = \frac{0.0021\underline{7}186\text{ mol}}{0.02500\text{ L}} = 0.086\underline{8}744\text{ M}$$

$$K_b = \frac{[OH^-][C_2H_5NH_3^+]}{[C_2H_5NH_2]} = \frac{(7.1\underline{6}14 \times 10^{-3})^2}{0.079\underline{7}13} = \boxed{6.43 \times 10^{-4}}$$

iii) ACIDIC (weak acid in products)

iv) Methyl Orange, Bromcresol Green, Methyl Red, Chlorophenol Red

Assignment 10: Titration Curve Exercises

1. A student titrated a 25.00mL sample of 0.20M HX acid with 0.20M NaOH. The following data was collected.

Volume of NaOH added (mL)	pH
0.00	2.72
10.00	4.57
24.90	7.14
24.99	8.14
25.00	8.88
25.01	9.60
26.00	11.59
35.00	12.52

a) Is HX weak or strong? Support with two observations from the table.

HX is weak

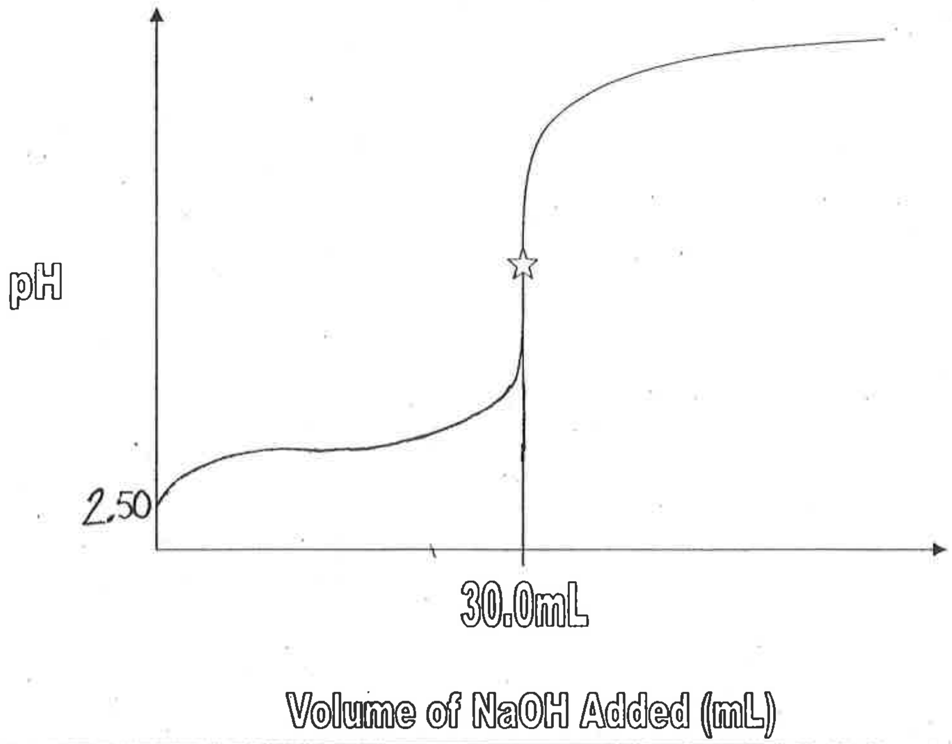
① pH jump @ beginning of titration

② pH @ Equiv. pt. (25.00 mL NaOH added) = 8.88

b) Select an indicator, and give the colour at the equivalence point.

Thymol Blue → Green

2. Given the following titration curve:



A 32.0mL sample of HA was titrated with 0.20M NaOH, and the titration curve shown was obtained. Calculate the Ka of HA.

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

I	0.1875 M	0	0
C	−0.003162		
E	0.184338 M	0.003162 →	

$[H_3O^+]_{eq} = \text{invlog}(-2.50)$

$= 0.003162$

$[HA]_i$: $HA + NaOH \longrightarrow H_2O + NaA$

mol NaOH = MV = (0.20 M)(0.0300L) = 0.0060 mol = mol OH

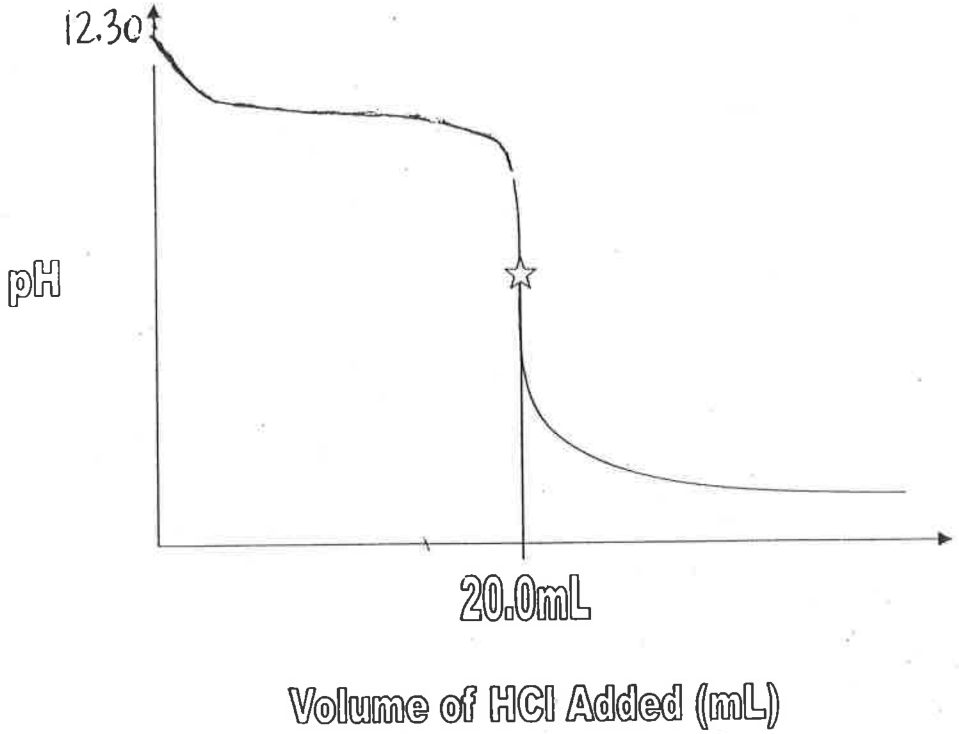
∴ mol H_3O^+ = 0.0060 mol = mol HA

$$[HA]_i = \frac{mol}{V} = \frac{0.0060\ mol}{0.0320\ L} = 0.1875\ M$$

$$K_a = \frac{[H_3O^+]^2}{[HA]} = \frac{(0.003162)^2}{0.184338} = \boxed{5.4 \times 10^{-5}}$$

HA is weak but it completely dissociates because NaOH is a strong base. ∴ mol HA = mol H_3O^+.

3. Given the following titration curve.



A 30.0mL sample of the base B^- was titrated with 0.200M HCl, and the titration curve above was obtained. Calculate the K_b of B^- .

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

I 0.1333 | 0 | 0

C -1.9953×10^{-2}

E 0.11338 M

$\leftarrow 1.9953\times10^{-2}$

$[OH^-]_{eq} = \text{inv}\log(-pOH) = \text{inv}\log(-1.70)$

$= 1.9953\times10^{-2}$ M

$[B^-]_i$: $NaB + HCl \longrightarrow HB + NaCl$

weak acid

mol HCl = MV = (0.200 M)(0.0200 L) = 0.00400 mol

= mol H_3O^+ = mol OH^- = mol B^- = 0.00400 mol

$[B^-] = \frac{\text{mol}}{V} = \frac{0.00400 \text{ mol}}{0.0300 \text{ L}} = 0.1333$ M

$$K_b = \frac{[OH^-]^2}{[B^-]} = \frac{(0.019953)^2}{0.11338} = \boxed{3.5\times10^{-3}}$$

* mol OH^- = mol B^- b/c HCl is a strong acid. Base completely dissociates

Assignment 11: *Take Home Quiz* & Hebden p. 176 #125-126, 130

VIII) Acidic and Basic Anhydrides

When **non-metal oxides** react with water, an ACID is formed. **Non-metal oxides** are called ACIDIC ANHYDRIDES.

$SO_2 + H_2O \Rightarrow H_2SO_3$
$SO_3 + H_2O \Rightarrow H_2SO_4$
$CO_2 + H_2O \Rightarrow H_2CO_3$

Notice that these are SYNTHESIS reactions.

When **metal oxides** react with water, a BASE is formed. **Metal oxides** are called BASIC ANHYDRIDES.

$Na_2O + H_2O \Rightarrow 2\,NaOH$
$MgO + H_2O \Rightarrow Mg(OH)_2$
$CaO + H_2O \Rightarrow Ca(OH)_2$

Notice that these too are **synthesis** reactions.

Assignment 12: Hebden p. 185 #144-145

IX) Acid Rain

Fuels that contain sulfur undergo combustion (typically in lead smelters) to form sulfur dioxide (SO_2). Sulfur dioxide then reacts with oxygen in the air to produce sulfur trioxide (SO_3). Combustion in cars causes N_2 from the air to react with oxygen, forming nitrogen dioxide (NO_2), which is then released as exhaust. All of the above gases will react with water vapour to form **Acid Rain.**

$SO_2 + H_2O \Rightarrow H_2SO_3$
$SO_3 + H_2O \Rightarrow H_2SO_4$
$2NO_2 + H_2O \Rightarrow HNO_2 + HNO_3$

It is important to note that even "normal" rain is slightly acidic (pH 5.6) due to dissolved CO_2 in water vapour to produce carbonic acid.

$$CO_2 + H_2O \Rightarrow H_2CO_3$$

Acid Rain is defined as rain having a pH < 5.6.

Environmental Problems of acid rain: see Hebden p. 187-188

1. Fish and plant growth seriously affected.
2. Leaches minerals out of rocks/soils.
3. Metal, stone, and limestone structures damaged.
4. Who cleans up?
5. Water contamination affects human health
6. Food crops destroyed.

Protection Against Acid Rain:

1. Most lakes have a natural H_2CO_3/HCO_3^- buffer system due to dissolved CO_2. *see below
2. Spraying powdered $CaCO_3$ into lakes:

$$CaCO_3 \Rightarrow CaO + CO_2$$

$$CaO + H_2O \Rightarrow Ca(OH)_2$$

or

$$H_2SO_4 + CaCO_3 \Rightarrow CaSO_{4(s)} + CO_2 + H_2O \text{ (weak acid)}$$

Lakes with limestone ($CaCO_3$) are self neutralizing.

* once acid rain stops, CO_2 from ambient air reacts with lake water to form more carbonic acid which helps increase [bicarbonate ion]. Thus, to a point, the bicarbonate ion can help to correct the acidic conditions of the lake. If too much acid rain fell, however, it may be too late to save the wildlife!

Assignment 13: Read Hebden p. 186-188 Do Questions 146-147