18.3 pH Curves

Buffers: acts to reduce impact of one thing on another
- resistant to changes in pH on additions of small amts of acid/alkalis

$$1\,dm^3\ H_2O\ \text{at}\ 298K \begin{cases} \rightarrow pH\,4 + 0.1\,cm^3\ 1.0\,mol\,dm^{-3}\ HCl \\ \rightarrow pH\,10 + 0.1\,cm^3\ 1.0\,mol\,dm^{-3}\ NaOH \end{cases}$$

pH 7

How Buffers work:

mixture of 2 solns, contain 2 A/B pairs

1) Acidic buffers (maintain pH < 7)

composition of buffer soln

Mix: weak acid + salt of weak acid/strong alkali

★ CH_3COOH $NaCH_3COO$

★ eq: $\boxed{CH_3COOH} \rightleftharpoons CH_3COO^- + H^+$

$NaCH_3COO \longrightarrow Na^+ + \boxed{CH_3COO^-}$

↑ salts fully dissociate

★ reservoirs: ready to react w/ H^+/OH^-

soln contain high [ ] of conj. A/B pair

Response to A/B

★ Add H^+: $CH_3COO^- + H^+ \rightleftharpoons \boxed{CH_3COOH}$ ↳ make more of other

Add OH^-: $CH_3COOH + OH^- \rightleftharpoons \boxed{CH_3COO^-} + H_2O_{(l)}$

H^+ & OH^- do not persist ∴ no pH change

2) Basic Buffers (maintain pH > 7)

Composition of buffer soln

mix: weak base w/ salt of weak base w/ strong acid

NH_3 NH_4Cl

★ eq: $\boxed{NH_3} + H_2O \rightleftharpoons NH_4^+ + OH^-$ } reservoirs: conj A/B pair

$NH_4Cl \rightarrow \boxed{NH_4^+} + Cl^-$

↑ salt = full dissociation

Response:

★ Add H^+ : $NH_3 + H^+ \rightleftharpoons \boxed{NH_4^+}$ remake pair

Add OH^- : $NH_4^+ + OH^- \rightleftharpoons \boxed{NH_3} + Cl^-$

↳ do not persist ∴ no pH change

Determining pH of buffer soln (D.4)

assumptions: 1) dissociation of weak acid is small →

$[HA]_i \approx [HA]_{eqm}$

2) Salt is considered fully dissociated

$[MA]_i \approx [A^-]_{eqm}$

★ common ion effect (due to eqm): presence of common ion (A^-) suppresses ionization of weak A/B or reduces solubility of salt (error in calcs)

★ $HA \rightleftharpoons H^+ + A^-$ $MA \rightarrow M^+ + A^-$

★ $$K_a = \frac{[H^+][A^-]}{[HA]} \longrightarrow [H^+] = \frac{K_a\,[HA] \approx [HA]_i}{[A^-] \approx [MA]_i}$$

$$[H^+] = K_a \frac{[\text{acid}]}{[\text{salt}]} \longrightarrow pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

★ examples: pg 890-892

Making Buffer Solns

- start w/ weak A/B close to wanted pH/pOH
  $\downarrow$ pka/pk$_b$ value
- mix w/ soln of salt w/ conj A/B or partially neutralize w/ strong A/B (to make salt)

★ R	CH_3COOH +	$NaOH$ $\longrightarrow$	$NaCH_3COO$ +	H_2O
I	2	1	0	0
C	-1	-1	+1	+1
E	$\boxed{1}$	0	$\boxed{1}$	1

buffer soln

ex pg 382

Influencing Buffers

Dilution: K_a & K_b not changed
ratio of A/B & salt not changed
☆ pH not changed
buffering capacity affected (how much buffer can hold)

Temperature: affects K_a & K_b ∴ pH

SAlt Hydrolysis

No hydrolysis: SA + SB
☆ $HCl + NaOH \rightarrow \underset{\downarrow}{Na}\underset{\downarrow}{Cl} + H_2O$ pH 7
weak conjugates

Anion hydrolysis
A^- is conj. base for parent acid
Weak acid → strong conj. base → hydrolyze H_2O

☆ $\overset{\text{Anion}}{\boxed{A^-}} + H_2O \rightleftharpoons HA + \overset{\text{Anion}}{\boxed{OH^-}}$ $pH > 7$
$(Na)CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

Cation hydrolysis
M^+ is conj acid for parent base

☆ $\overset{\text{Cation}}{\boxed{M^+}} + H_2O \rightleftharpoons MOH + \overset{\text{cation}}{\boxed{H^+}}$ $pH < 7$
$NH_4(Cl) + H_2O \rightleftharpoons NH_4OH + H^+$

metal ion (cation): outcome depends on its charge density (small ions w/ 2+/3+ charge)
like: Al^{3+} + Fe^{3+} → release H^+ (through formation of complex ion)

Table 385 - Summary

Acid / Base Titrations

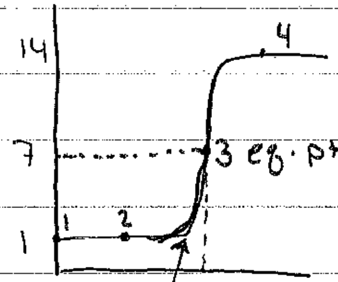
- Technique for controlling neutralization rxns quantitatively
- Reaction continues untile equivalence (stoichiometric) pt.
  ↓
  * exact neutralization (salt + H_2O)
- Used in process of standardization in industry → calc of the exact conc of 1 soln when other is known

Titration Curves → plotted values during titration of change in pH (not linear → pH curve)

examples use: 1. 0.10 mol dm^3 soln
2. initial vol 50.0 cm^3 acid in flask, base in burrett
3. A + B in 1:1 ratio = eq. pt. is at equal volume

1) Strong acid / strong base ★ $HCl + NaOH \rightarrow NaCl + H_2O$

pH equivalence 7 (no hydrolysis)

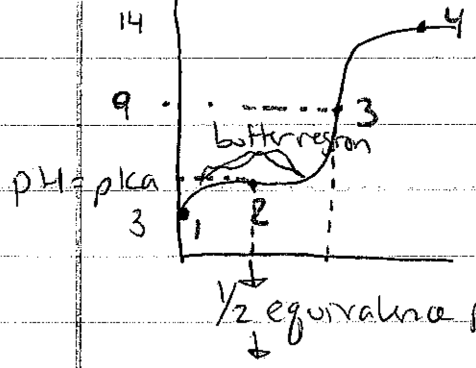


point of inflection ½ way up → eq. pt.

1) initial pH low (strong A)
2) pH gradually changes until equivalence
3) sharp jump at equivalence (3-11)
4) after equivalence, flattens at high (strong B)

2) weak acid / strong base ★ $CH_3COOH + NaOH \rightleftharpoons NaCH_3COO^- + H_2O$

pH equivalence > 7 (anion hydrolysis)



1) initial pH high (weak A)
2) pH stays relatively constant (buffer) until equivalence
3) jump in pH 7-11
4) After equivalence, flattens at high (strong B)

★ represents ½ acid neutralized into salt, ½ acid ⇒ buffer made

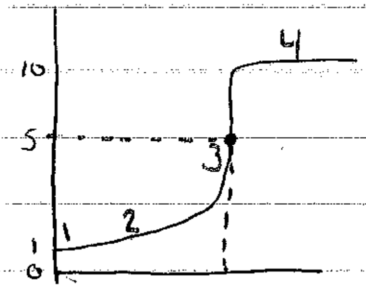
Calculate pka b/c [acid] = [salt]

$\therefore pH = pka + \log \frac{[salt]}{[acid]}$ > same #

$\therefore pH = pka$ at ½ eq pt.

3) strong acid / weak base $HCl + NH_3 \rightleftharpoons NH_4Cl$

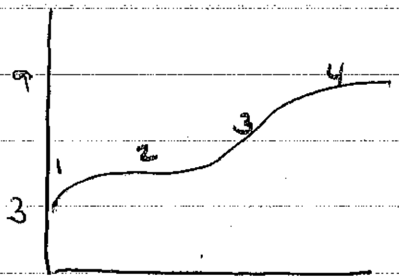
pH equivalence < 7 (cation hydrolysis)



1) initial pH low (SA)
2) pH stays relatively constant (buffer)
3) jump in pH 3-7
4) After equivalence, flattens low pH (WB)

4) weak acid / weak base $CH_3COOH + NH_3 \rightleftharpoons CH_3COO^-NH_4$

pH equivalence difficult to define



1) inital pH high (WA)
2) addition of base causes pH to rise steadily
3) pH change c equivalence less sharp
4) After equivalence, flattens at low pH (WB)

☆ * acid into base (inverse graph)
start high pH - end low → same rules apply (just reverse)

Indicators

- color signal for change in pH

indicators are weak acids / bases

associated + dissociated have dift. colors

★ WA → $HIn \rightleftharpoons H^+ + In^-$

color A   color B

Apply Le Chatelier's Principle

$\uparrow [H^+]$: shift to reactants (HIn) ~~$\downarrow$pH~~

$\downarrow [H^+]$: shift to products (In^-) ~~$\uparrow$pH~~

Change in color

★ $Ka = \frac{[H^+][In^-]}{[HIn]}$ at eqm $[In^-] = [HIn]$

$Ka = [H^+]$ or $pKa = pH$

$\downarrow$

change / end point → additson of small amt A/B

shift eqm

$\downarrow$ change color

$\downarrow$

diff In, diff pka,

diff end pt

Indicators can be used to signal equivalence pt in titration

when end point coincides w/ eq. point

proper indicator?

1) determine combination of A/B reacting
2) deduce pH of salt soln at equivalence
3) choose appropriate indicator

pg 393 list of examples