LECTURE TOPICS:

TODAY'S CLASS: start Ch.18

NEXT CLASS: continue Ch.18

(1)

Chapter 18: OTHER ASPECTS OF AQUEOUS EQUILIBRIA

▪ **Application of eqm concepts to control of pH (buffers), analysis of solutions (titrations), & understanding of solubility**

Outline (but not in this order here)
18.3 Acid-base titrations

18.1 The Common ion effect
18.2 Controlling pH: buffer solutions

18.4 Solubility of salts
18.5 Precipitation reactions

(Not responsible for 18.6 & 18.7)

Chapter Goals

▪ Understand the common ion effect

▪ Understand the control of pH in aqueous solutions with buffers

▪ Evaluate the pH in the course of acid-base titrations

▪ Apply chemical equilibrium concepts to the solubility of ionic compounds

(2)

18.3 Titrations & titration curves

TITRATION = volumetric analysis
- Exploits known chemical rxn

*e.g.,* acids & bases: $H_3O^+ + OH^- \rightarrow 2\ H_2O$

NOTE: This reaction goes to completion
i.e., K is large (= $1/K_w = 10^{14}$)
so we often forget that it's an eqm…

- Typical titration reactions:
  $HA + NaOH \rightarrow H_2O + NaA$ (a salt)
  $B + HCl \rightarrow H_2O + HBCl$ (a salt)

Titrant →
known [ ]

sample of
unknown [ ]
Analyte →

+ a way to
monitor rxn
progress…

PROCEDURE: Titrant + Analyte → Rxn…
Measure volume of titrant required to reach
perfect stoichiometric completion of rxn
= "equivalence point"

(3)
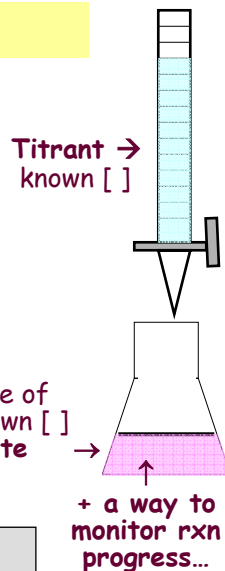
Titrations & eqm knowledge: *e.g.,* weak HA with NaOH…

1.) Initially: have a solution of weak acid in water…

Equilibrium: $HA + H_2O \xrightleftharpoons{K_a} A^- + H_3O^+$
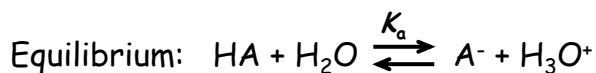
*If [HA]$_o$ is known,
could calculate
solution's initial pH…*

2.) Then, start disturbing this eqm:
    Titration: $HA + NaOH \rightarrow H_2O + NaA$

*Draws HA dissociation
fwd by consuming H_3O^+
⇒ net effect same as
if deprotonates HA.*

3.) At equiv. point: enough titrant added to consume all HA
now have a solution of the acid's salt…
…whose rxn with water comes to eqm:

Equilibration: $NaA + H_2O \xrightleftharpoons{K_b} HA + NaOH$
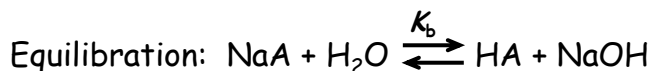
*Could calculate
solution's pH…*

FOR QUANTITATIVE PURPOSES, IT IS VERY IMPORTANT
(4) THAT WE KNOW EXACTLY WHEN EQUIV. PT. IS REACHED.

Titration calculations
(assuming we can accurately determine the equivalence point)

Dealing with a Strong Acid - Strong Base Titration

Simple: **A stoichiometry problem** (review from Chem 205; see Ch.5)
- assume rxn goes to completion
- remaining solution is neutral (pH = 7)
- no need to think much about eqm, since reaction is so <u>very</u> product favoured!

Dealing with a Weak - Strong Titration (either way)

Step 1: **A stoichiometry problem**
- assume titration rxn goes to completion
- then determine species (salt!) remaining in solution at equivalence point
- will include a weak acid's (or base's) conjugate!

Step 2: **An equilibrium problem: salt equilibrates with water**
- salt will equilibrate with water (A/B chemistry)
- calculate pH of this weak A/B solution!

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Ex.: How much lactic acid is in our sample?

You titrate a 25.0 mL sample of lactic acid ($HC_3H_5O_3$, $K_a=1.4\times10^{-4}$) with 8.00×10^{-2} M NaOH. It requires 31.35 mL of titrant.
(a) What mass of lactic acid was in the sample?
(b) What is the pH of the sample at the equivalence point?

(a) STEP 1: Deal with stoichiometric rxn of acid & base:

$$HC_3H_5O_3(aq) + NaOH(aq) \longrightarrow NaC_3H_5O_3(aq) + H_2O(aq)$$
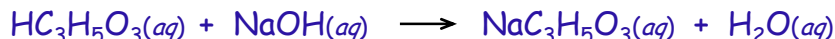
V = 0.0250 L   V = 0.03135 L
C = ?   C = 8.00×10^{-2} M
n = ?   n = (0.03135 L)$\times$(8.00×10^{-2} mol/L)
                    = 2.5080×10^{-3} mol *note: kept extra SFs...*

At the equivalence point: perfect stoichiometric ratio (1:1)
    # moles acid initially present = # moles base added
                    = 2.508×10^{-3} mol

In original sample:
Mass $HC_3H_5O_3$ = MM $\times$ n
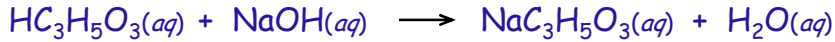   = (90.079 g/mol) $\times$ (2.508×10^{-3} mol)
    = 0.226 g was present in the 25.0 mL sample
        note: 3 SF in data...

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STEP 2: EQUILIBRIUM…
(b) Calculate the pH of the solution at the equiv. point….

$$HC_3H_5O_3(aq) + NaOH(aq) \longrightarrow NaC_3H_5O_3(aq) + H_2O(aq)$$

After this product-favoured acid-base rxn:
what is the dominant species present in the solution?

Lactate equilibrates with water: how much is initially present?
- All lactic acid converted to lactate: $\#n_{lactate} = 2.508 \times 10^{-3}$ mol

- Total volume of solution at equiv.pt: $V = V_{sample} + V_{titrant}$
  $= 0.0250$ L $+ 0.03135$ L
  $= 0.05635$ L

- Thus: concentration of lactate initially: $C = 0.04451$ M

Lactate equilibrates with water: how basic is lactate?
- K_a for lactic acid $= 1.4 \times 10^{-4}$
- K_b for lactate (conjugate base) $= K_w / K_a$
  $= 1 \times 10^{-14} / 1.4 \times 10^{-4}$
  (7) $= 7.143 \times 10^{-11}$ *1 extra SF…*

(b) Calculate the pH of the solution at the equiv. point….
Lactate equilibrates with water:

$$C_3H_5O_3^- + H_2O \underset{\rightleftharpoons}{\overset{K_b}{}} HC_3H_5O_3 + OH^-$$

	$C_3H_5O_3^-$	H_2O	$HC_3H_5O_3$	OH^-
Initial	0.04451 M	solvent…	0	0
Change	- x	---	+ x	+ x
Eqm	0.04551-x	---	+ x	+ x

$$K_b = \frac{[C_3H_5O_3^-][OH^-]}{[HC_3H_5O_3]} \implies 7.143 \times 10^{-11} = \frac{x^2}{0.04451-x}$$

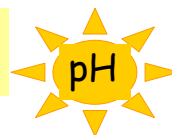Note that K << 1000x smaller than initial [ ]
…therefore CAN use approximation

$$7.143 \times 10^{-11} \approx \frac{x^2}{0.04451}$$

$$x = \sqrt{(0.04451 \times 7.143 \times 10^{-11})}$$

$$x = 1.78 \times 10^{-6} \text{ M} \quad = [OH^-]$$

pH = 14 – pOH
   = 14 – [-log(1.78×10⁻⁶)]
   = 8.251 *mildly basic*

(8)

1.) <u>using a chemical "indicator"</u>
= a substance whose colour depends on pH
- cheap, easy…but must be careful (& know pH at eq.pt….)
CHEMISTRY BEHIND THIS → end of 18.3

2.) <u>using a pH meter</u>
- electrode: H^+ passes through thin glass membrane
- a redox rxn of H^+ creates current proportional to $[H_3O^+]$
→ costs a little more… & a bit more time-consuming...
but: can be automated!
AND reveals information about species

⇩
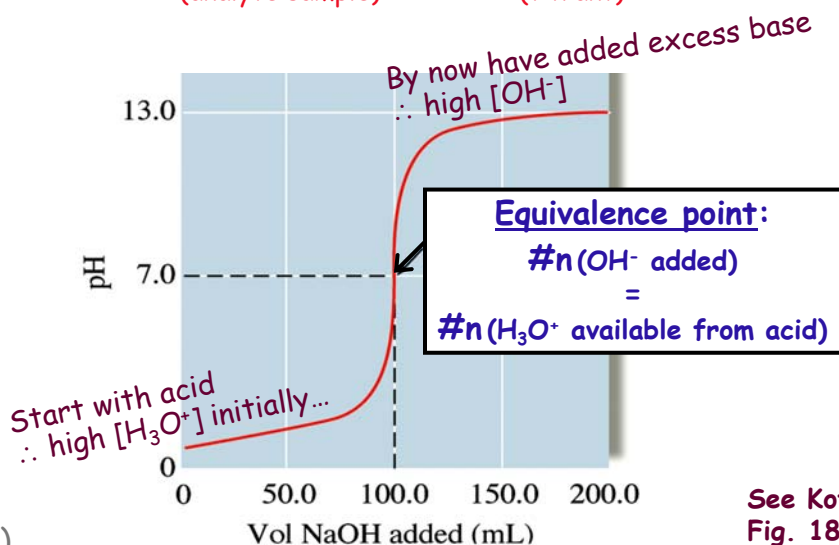
Titration curve (or pH curve)
= plot of pH of solution being analyzed
versus amount of titrant added

(9)

A1) TITRATION of "STRONG" with "STRONG"
Z.'s Figure 15.1: Titration curve for the titration of
50.0mL of 0.200*M* HNO_3 with 0.100*M* NaOH
(analyte sample)   (titrant)

By now have added excess base
∴ high $[OH^-]$

13.0

pH   7.0

Equivalence point:
#n(OH⁻ added)
=
#n(H_3O^+ available from acid)

Start with acid
∴ high $[H_3O^+]$ initially…

0

0   50.0   100.0   150.0   200.0
Vol NaOH added (mL)

See Kotz
Fig. 18.4

(10)

GENERAL SHAPES OF TITRATION CURVES:
  indicative of strengths of acids/bases involved
  → helpful when your sample is an <u>unknown</u> acid/base

**See Kotz
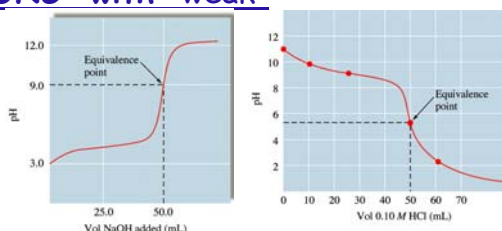Fig.18.x
x=4,5,7**

A) TITRATION of "STRONG" with "STRONG"

• pH curves are sharp
      & symmetric

• at equiv. pt.: pH = 7
   because have soln of
   "very weak" conjugate
   acid (or base)
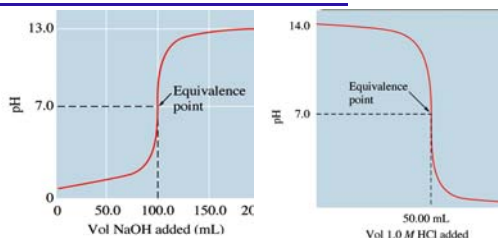
B) TITRATION of "STRONG" with "weak"

• pH curves not symmetric...

• at equiv. pt.:
  = soln of conjugate
    weak acid or weak base
    ⇨ pH ≠ 7

(11)

Why is the titration curve's shape different when a weak acid or base is involved?

Because of the ACID-BASE PROPERTIES of the "SALT" formed
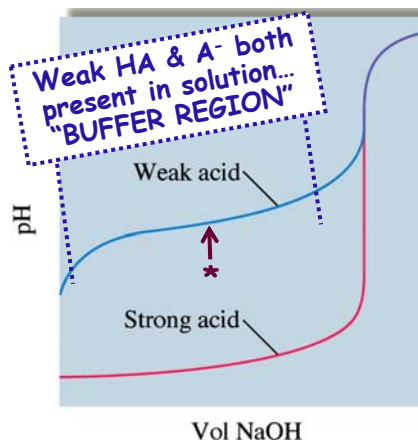during titration's rxn: acid + base → salt + water

strong acid strong base	Smooth pH ↑ due to consumption of H_3O^+. Salt too weak to influence pH.
weak acid strong base	Anion is a weak base. ⇨pH ↑ quickly at 1st due to action of A^-. ⇨later: buffered
strong acid weak base	Cation is a weak acid... (see Fig.18.7)

Weak HA & A^- both present in solution... "BUFFER REGION"

Halfway to equivalence point (∗), ½ of analyte is "neutralized"
• at that moment: [HA] = [A^-] ⇨ **therefore pH = acid's pK_a**
• implication: can use titrations to help identify unknown species too!

Acid-Base Indicators = colourful weak acids/bases

An INDICATOR is: a weak acid "H-In" *OR* a weak base "In⁻"
whose conj. base/acid is a different colour

$$\text{H-In}_{(aq)} + H_2O_{(l)} \rightleftharpoons \text{In}^-_{(aq)} + H_3O^+_{(aq)}$$

STRATEGY: once analyte completely consumed by titrant (**equiv.point**),
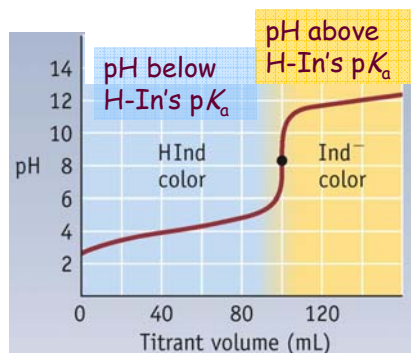next drop of titrant causes indicator to change colour (**end point**)

Indicator error = difference between volume of titrant used (end pt.)
vs. should have used (equiv.pt.)
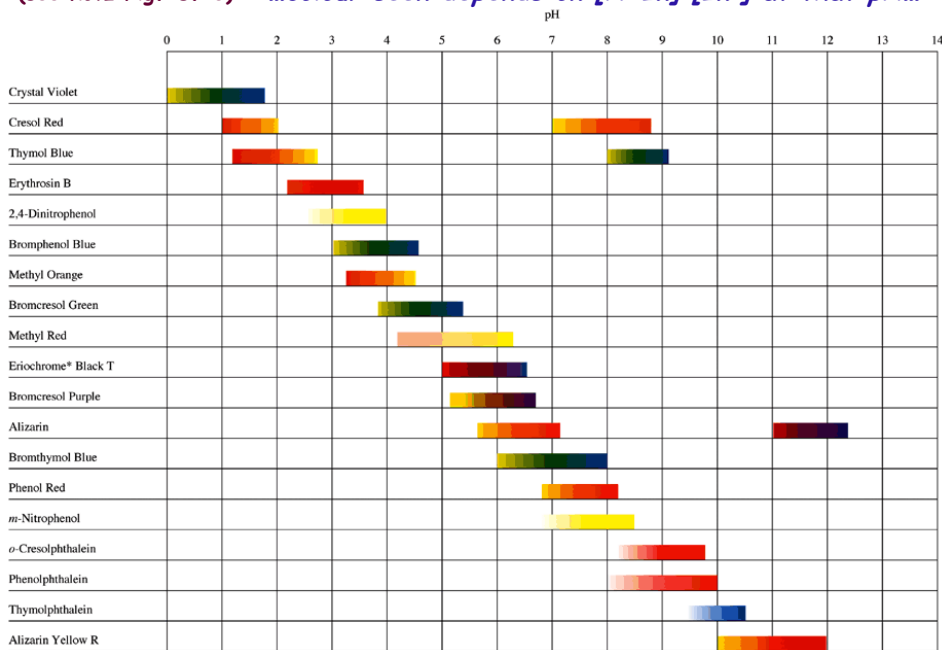
**TO MINIMIZE INDICATOR ERROR,
CHOOSE INDICATOR WITH…**

- H-In with pK_a = pH of equiv. pt.
- THUS: Colour change occurs
as close as possible to
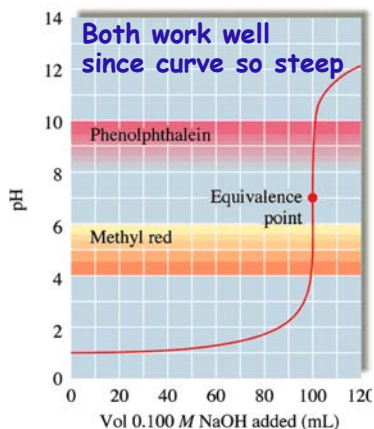pH of equivalence point

see Fig.18.9 →

(13)

Z.'s Figure 15.8: **pHs of colour change for common A/B indicators**
(see Kotz Fig.18.10)   *…colour seen depends on [H-In]:[In⁻] at that pH…*

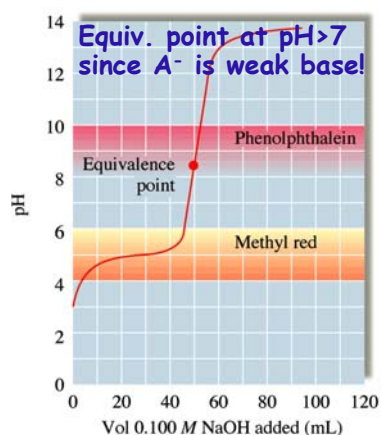Z.'s Fig. 15.9: Titration of strong acid with strong base 100.0 mL of 0.10 M HCl with 0.10 M NaOH.

Both work well since curve so steep

Z.'s Fig. 15.10: Titration of weak acid with strong base 50 mL of 0.1 M $HC_2H_3O_2$ with 0.1 M NaOH.

Equiv. point at pH>7 since A^- is weak base!

Homework: which indicator would be most appropriate?

Suggestion: solve this on your own & compare with your classmates

Imagine you are required to do repeated analyses of samples containing sodium benzoate (NaC_6H_5COO), which is used as a preservative. You are planning to manually perform titrations with HCl using a pH indicator (not a pH meter). Based on the expected pH at the equivalence point, which indicators (from Z.Fig.15.8 list) would be suitable choices? *If more than one indicator would be suitable, please explain which one would be easiest to use, and why.*

Relevant details:
- Your samples will be 20.0 mL, with [NaC_6H_5COO] ≈ 0.04 M.
- You are planning to use a titrant solution of [HCl] = 0.03755 M.

ASSIGNED READINGS:

BEFORE NEXT CLASS:

Read: section 18.3

Practice: A/B & titration calculations & concepts
using pK_a to identify speciation at different pHs

+ WORK ON Problems from Ch.17 & 18.3