## 19.2 Acid-Base Titration Curves

- **Titration curves** – plots of *pH* versus the volume of titrant added during titration
- **Equivalence point (E)** – a point along the course of the titration at which the acid and the base are present in equivalent (stoichiometric) amounts and consume each other completely
  - Typically, the *pH* **changes sharply at the E-point** and this fact is used in the detection of the **E-point**
  - The titration is actually stopped at the **end point**
  - Ideally, the end point should be at the equivalence point, but in practice they can differ slightly due to imperfect detection of the **E**-point

Acid-Base Indicators

- **Indicators** – used to estimate the *pH* of solutions and to detect the **E**-point in titrations
  - Weak organic acids with general formula **HIn**
  - Exhibit different colors at different *pH* values
  - The colors are quite intense so only small amounts are needed for detection
- **Indicator rage** – a relatively narrow *pH* range over which the indicator changes color
  - If the **E**-point is within (or close to) the indicator range, the indicator changes color very close to **E**
  - $\Rightarrow$ The *pH* at the **E**-point must be known for the proper selection of an indicator

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➤ The indicator is a weak B-L acid

$$HIn + H_2O \leftrightarrow H_3O^+ + In^-$$
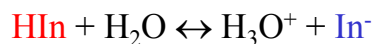
- The acid form of the indicator, **HIn**, and its conjugate base, **In⁻**, **have different colors**
- If **[HIn]/[In⁻] > 10**, the solution has the color of the acid form, HIn
- If **[HIn]/[In⁻] < 0.1**, the solution has the color of the base form, In⁻

$\Rightarrow$ The color change is within **0.1 < [HIn]/[In⁻] < 10**

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]} \quad \Rightarrow \quad \frac{[HIn]}{[In^-]} = \frac{[H_3O^+]}{K_{In}}$$

$\Rightarrow$ The ratio **[HIn]/[In⁻]** depends on **[H₃O⁺]**

$$[H_3O^+] = K_{In}\frac{[HIn]}{[In^-]} \quad \Rightarrow \quad pH = pK_{In} - \log\frac{[HIn]}{[In^-]}$$

$\rightarrow \log(0.1) = -1 \qquad \rightarrow \log(10) = +1$

$\Rightarrow$ The indicator range is: $\boxed{pH(range) \approx pK_{In} \pm 1}$
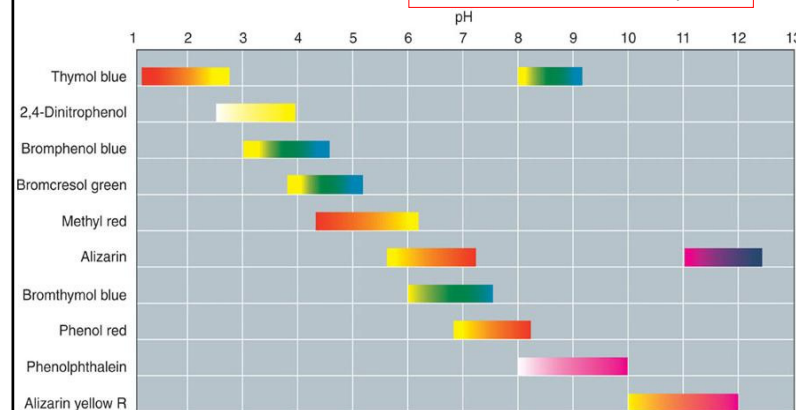
Strong Acid-Strong Base Titration Curves

➤ Strong acids and bases are completely converted to H_3O^+ and OH^- in water solns.

⇒ The net ionic equation of the titration is:

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

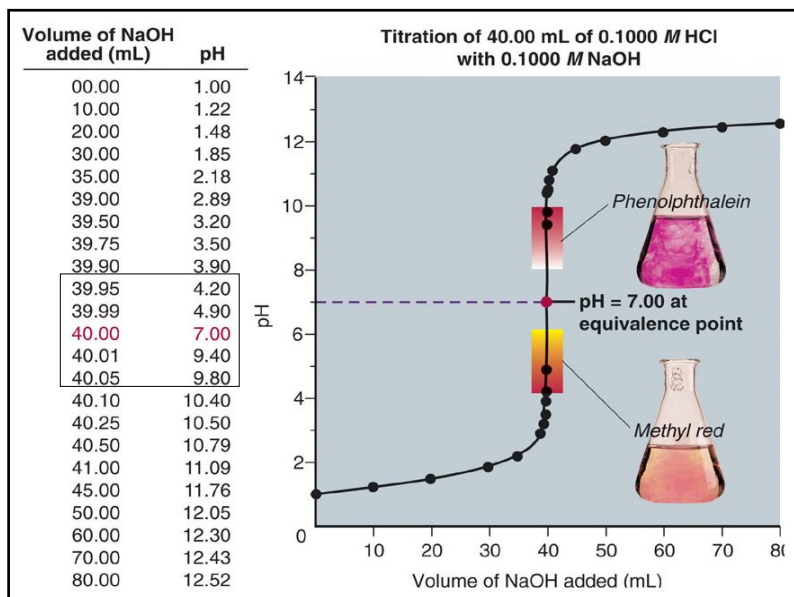⇒ At the **E**-point, **pH = 7.00** (neutral)

➤ To calculate the **pH** during the titration:

1. Calculate the **mmol of H_3O^+** from the acid
2. Calculate the **mmol of OH^-** from the base
3. Calculate the **excess mmol of H_3O^+ or OH^-** from the difference between (1) and (2)
4. Calculate **[H_3O^+]** or **[OH^-]** from the excess and the total volume of the solution (V_{tot}) → convert to **pH**

Example: Calculate the **pH** during the titration of **40.0 mL 0.100 M** HCl with **0.100 M** NaOH after the addition of **25.0 mL** NaOH.

0.100 M HCl → 0.100 M H_3O^+ = 0.100 mmol/mL

0.100 M NaOH → 0.100 M OH^- = 0.100 mmol/mL

1. **H_3O^+** → 40.0 mL × 0.100 mmol/mL = **4.00 mmol**
2. **OH^-** → 25.0 mL × 0.100 mmol/mL = **2.50 mmol**
3. **Excess acid** = 4.00 − 2.50 = **1.50 mmol H_3O^+**
4. V_{tot} = 40.0 + 25.0 = **65.0 mL**

   1.50 mmol / 65.0 mL = **0.0231 M H_3O^+**

   pH = -log(0.0231) = **1.64** (acidic, before **E**-point)

Volume of NaOH added (mL)	pH
00.00	1.00
10.00	1.22
20.00	1.48
30.00	1.85
35.00	2.18
39.00	2.89
39.50	3.20
39.75	3.50
39.90	3.90
39.95	4.20
39.99	4.90
40.00	7.00
40.01	9.40
40.05	9.80
40.10	10.40
40.25	10.50
40.50	10.79
41.00	11.09
45.00	11.76
50.00	12.05
60.00	12.30
70.00	12.43
80.00	12.52

Titration of 40.00 mL of 0.1000 *M* HCl with 0.1000 *M* NaOH

Phenolphthalein

pH = 7.00 at equivalence point

Methyl red

➤ A titration curve for the titration of a strong base with a strong acid looks like a mirror image of that for the titration of a strong acid with a strong base

• **Characteristics** of strong acid-strong base **t**-curves

  – Slow **pH** changes before and after the **E**-point

  – A sharp **pH** change at the **E**-point (**pH** = 7.00) → 1-2 drops cause a **pH** change of 5-6 pH units)

  – The **vertical region** of the **t**-curve is quite long (from $pH \approx 4$ to $pH \approx 10$)

  – Any indicator having a range within the vertical region of the **t**-curve can be used (the indicator range does not have to be at 7.00)

⇒ Phenolphthalein (8.3-10), Methyl red (4.3-6.2), Phenol red (6.8-8.3), … can all be used

Example: Calculate the *pH* during the titration of **20.0 mL 0.500 M** HCl with **0.250 M** Ba(OH)$_2$ after the addition of **21.0 mL** Ba(OH)$_2$

0.500 M HCl $\rightarrow$ 0.500 M H$_3$O$^+$

0.250 M Ba(OH)$_2$ $\rightarrow$ 0.500 M OH$^-$!!!
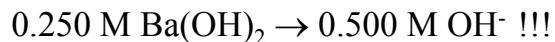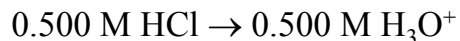
1. **H$_3$O$^+$** $\rightarrow$ 20.0 mL $\times$ 0.500 mmol/mL = **10.0 mmol**
2. **OH$^-$** $\rightarrow$ 21.0 mL $\times$ 0.500 mmol/mL = **10.5 mmol**
3. **Excess base** = 10.5 – 10.0 = **0.50 mmol OH$^-$**
4. V_{tot} = 20.0 + 21.0 = **41.0 mL**

   0.50 mmol / 41.0 mL = **0.012 M OH$^-$**

   pOH = -log(0.012) = **1.91**

   pH = 14.00 – 1.91 = $\boxed{12.09}$ (basic, after **E**-point)

Weak Acid-Strong Base Titration Curves

➤ The strong base is completely converted to OH$^-$ in water solution
  ⇒ The net ionic equation of the titration is:
  $$HA + OH^- \rightarrow H_2O + A^-$$
  ⇒ At the **E**-point, *pH* > **7.00** (basic) due to the presence of **A$^-$** which is a weak base
➤ **Regions** of the titration curve:
1. **Initial point** $\rightarrow$ solution of the **weak acid HA**
2. **Before the E-point** $\rightarrow$ **buffer solution** of the weak acid, HA, and its conjugate base, A$^-$ (buffer region)
3. **At the E-point** $\rightarrow$ solution of the **weak base A$^-$**
4. **After the E-point** $\rightarrow$ **excess of OH$^-$** from base

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Example: Calculate the *pH* during the titration of **20.0 mL 0.500 M** HCOOH with **0.500 M** NaOH after the addition of **0.0**, **10.0**, **19.0**, **20.0** and **21.0 mL** NaOH

1) 0.0 mL NaOH added **(Initial point):**
$\rightarrow$ A 0.500 M solution of the **weak acid** HCOOH

HCOOH + H$_2$O $\leftrightarrow$ H$_3$O$^+$ + HCOO$^-$		
i 0.500	0	0
c -x	+x	+x
e 0.500 - x	x	x

$K_a = \dfrac{[H_3O^+][HCOO^-]}{[HCOOH]}$

$K_a = \dfrac{x^2}{0.500 - x} \approx \dfrac{x^2}{0.500}$
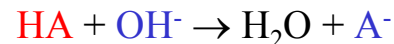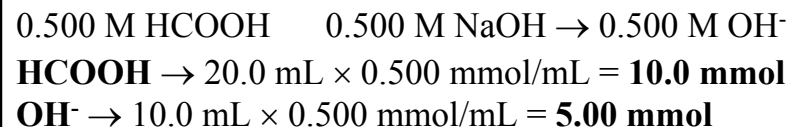
$x = (0.500K_a)^{1/2} = (1.8\times10^{-4}\times0.500)^{1/2} = 9.5\times10^{-3} = [H_3O^+]$

$\Rightarrow$ *pH* = -log[H$_3$O$^+$] = -log(9.5$\times$10^{-3}) = $\boxed{2.02}$

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2) 10.0 mL NaOH added **(Half-way to the E-point):**

0.500 M HCOOH   0.500 M NaOH $\rightarrow$ 0.500 M OH$^-$

HCOOH $\rightarrow$ 20.0 mL $\times$ 0.500 mmol/mL = **10.0 mmol**
OH$^-$ $\rightarrow$ 10.0 mL $\times$ 0.500 mmol/mL = **5.00 mmol**

	HCOOH	+ OH$^-$	$\rightarrow$ H$_2$O	+ HCOO$^-$
s	10.0	5.00	–	0.00
r	-5.00	-5.00	–	+5.00
f	5.00	0.00	–	5.00

(left label: *mmol*)

$\rightarrow$ The system is a **buffer** (HCOOH $\rightarrow$ *a*, HCOO$^-$ $\rightarrow$ *b*)

pH = *pK$_a$* + log(*n$_b$*/*n$_a$*) = *pK$_a$* + log(5.00/5.00) = *pK$_a$* + 0

$\Rightarrow$ *pH* = *pK$_a$* = -log(1.8$\times$10^{-4}) = $\boxed{3.74}$

$\Rightarrow$ Half-way to the **E**-point $\rightarrow$ *pH* = *pK$_a$* !!!