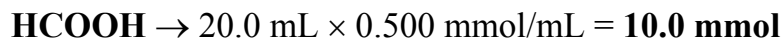


Cont: Titration of 20.0 mL 0.500 M HCOOH with 0.500 M NaOH

3) 19.0 mL NaOH added (Before the E-point):



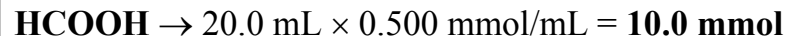
		HCOOH + OH ⁻ → H ₂ O + HCOO ⁻			
mmol	<i>s</i>	10.0	9.50	-	0.00
	<i>r</i>	-9.50	-9.50	-	+9.50
	<i>f</i>	0.50	0.00	-	9.50

→The system is a **buffer** (HCOOH → *a*, HCOO⁻ → *b*)

$$pH = pK_a + \log(n_b/n_a) = -\log(1.8 \times 10^{-4}) + \log(9.50/0.50)$$

$$\Rightarrow pH = 3.74 + 1.28 = \boxed{5.02}$$

4) 20.0 mL NaOH added (E-point):



		HCOOH + OH ⁻ → H ₂ O + HCOO ⁻			
mmol	<i>s</i>	10.0	10.0	-	0.00
	<i>r</i>	-10.0	-10.0	-	+10.0
	<i>f</i>	0.00	0.00	-	10.0

→A solution of the **weak base** HCOO⁻

$$V_{tot} = 20.0 + 20.0 = \mathbf{40.0 \text{ mL}}$$

$$10.0 \text{ mmol} / 40.0 \text{ mL} = \mathbf{0.250 \text{ M HCOO}^-}$$

		HCOO ⁻ + H ₂ O ↔ OH ⁻ + HCOOH		
<i>i</i>	0.250	0	0	$K_b = \frac{[\text{OH}^-][\text{HCOOH}]}{[\text{HCOO}^-]}$ $K_b = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250}$
<i>c</i>	-x	+x	+x	
<i>e</i>	0.250 - x	x	x	

$$K_b(\text{HCOO}^-) = K_w/K_a(\text{HCOOH}) = 1.0 \times 10^{-14} / 1.8 \times 10^{-4}$$

$$K_b(\text{HCOO}^-) = 5.6 \times 10^{-11}$$

$$x = (K_b \times 0.250)^{1/2} = (5.6 \times 10^{-11} \times 0.250)^{1/2} = 3.7 \times 10^{-6} = [\text{OH}^-]$$

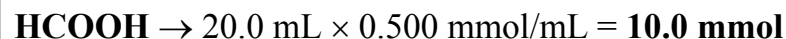
[Check assumption: $(3.7 \times 10^{-6} / 0.250) \times 100 = 0.0015\% < 5\%$]

$$\Rightarrow pOH = -\log[\text{OH}^-] = -\log(3.7 \times 10^{-6}) = 5.43$$

$$\Rightarrow pH = 14.00 - pOH = 14.00 - 5.43 = \boxed{8.57}$$

⇒ At the E-point → **pH > 7 (basic solution!!!)**

5) 21.0 mL NaOH added (After the E-point):



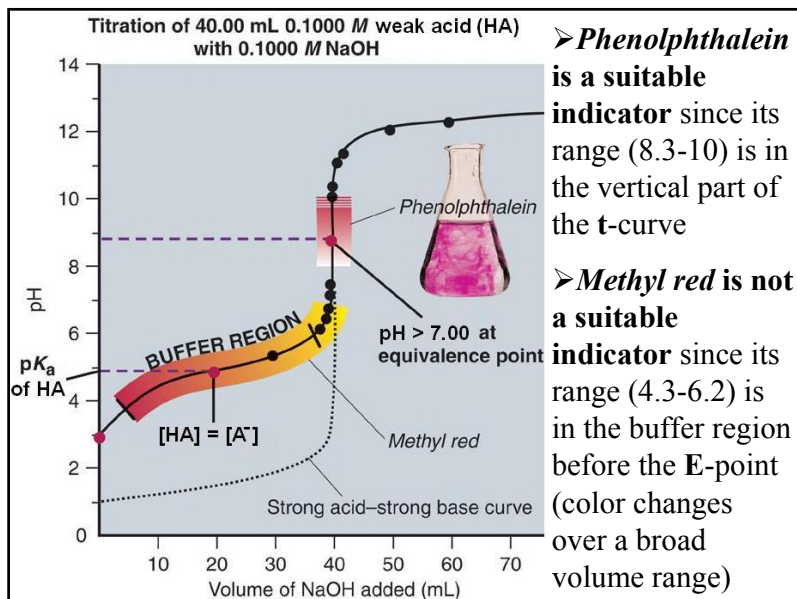
		HCOOH + OH ⁻ → H ₂ O + HCOO ⁻			
mmol	<i>s</i>	10.0	10.5	-	0.00
	<i>r</i>	-10.0	-10.0	-	+10.0
	<i>f</i>	0.00	0.50	-	10.0

→A solution of the **excess strong base** (OH⁻) and the weak base (HCOO⁻) → the weak base is neglected

$$V_{tot} = 20.0 + 21.0 = \mathbf{41.0 \text{ mL}}$$

$$0.50 \text{ mmol} / 41.0 \text{ mL} = \mathbf{0.012 \text{ M OH}^-}$$

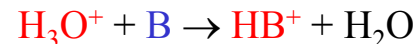
$$pOH = -\log(0.012) = 1.91 \Rightarrow pH = 14.00 - 1.91 = \boxed{12.09}$$



Weak base-Strong Acid Titration Curves

➤ The strong acid is completely converted to H_3O^+ in water solution

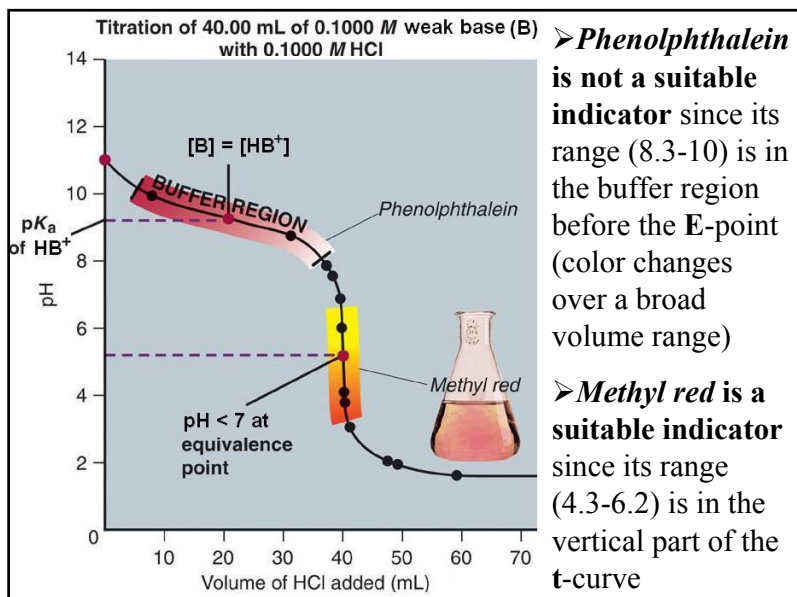
⇒ The net ionic equation of the titration is:



⇒ At the E-point, $\text{pH} < 7.00$ (acidic) due to the presence of HB^+ which is a weak acid

➤ **Regions of the titration curve:**

1. **Initial point** → solution of the **weak base B**
2. **Before the E-point** → **buffer solution** of the weak base, B, and its conjugate acid, HB^+ (buffer region)
3. **At the E-point** → solution of the **weak acid HB^+**
4. **After the E-point** → **excess of H_3O^+** from acid



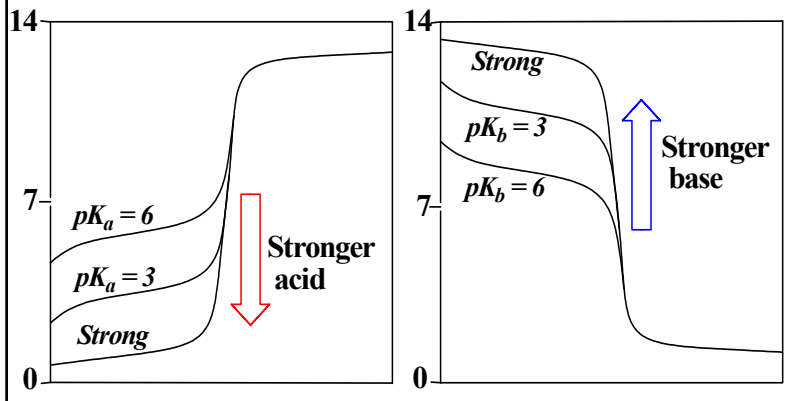
➤ A titration curve for the titration of a weak base with a strong acid looks like a mirror image of that for the titration of a weak acid with a strong base

• **Characteristics of t-curves involving weak acids/bases**

- Slow pH changes before and after the E-point and a sharp pH change at the E-point
- At the E-point
 - $\text{pH} > 7.00$ for titration of weak acids
 - $\text{pH} < 7.00$ for titration of weak bases
- Half-way to the E-point, pH equals pK_a of the weak acid (or the conjugate acid of the weak base)
- The **vertical region** of the t-curve is shorter than the vertical region for strong acid-strong base titrations
- A careful selection of the indicator is necessary

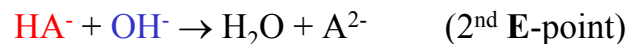
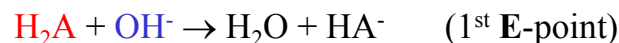
Dependence of the Titration Curve on the Strength of the Acid or Base

- Weaker acids and bases have shorter vertical pH ranges at the E-point (more difficult to detect)



Titration Curves for Polyprotic Acids

- The loss of each proton results in a separate E-point and a separate buffer region
- For a diprotic acid, H_2A , titrated with a strong base there are two E-points and two buffer regions
- The net ionic equations of the titration are:



Example: Titration of H_2SO_3 (a diprotic acid with $pK_{a1} = 1.85$ and $pK_{a2} = 7.19$) with NaOH

