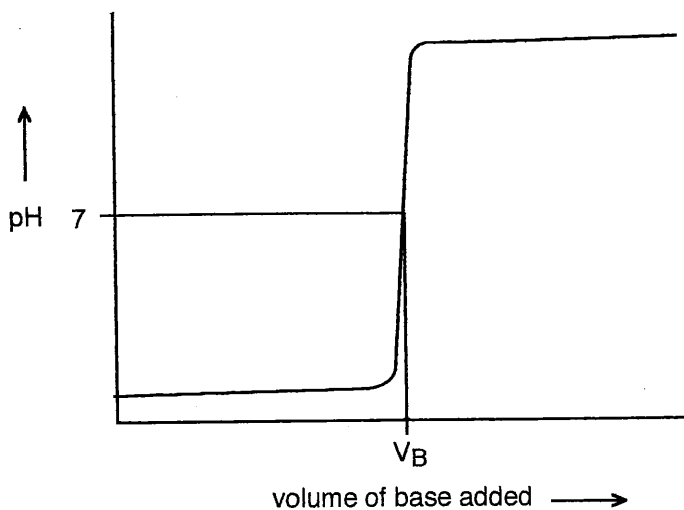


In general, the pH behaviour observed when titrating a **STRONG ACID** with a **STRONG BASE** resembles the graph below.



Special features of the curve:

- V_B is the volume of base required to get to the equivalence point.
- The pH rises almost vertically around the value of V_B .

Choosing an indicator:

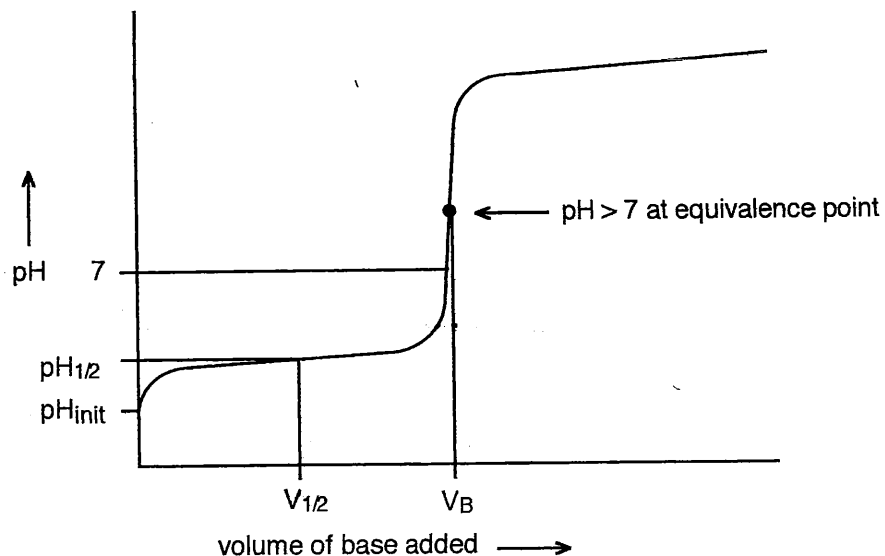
- The **SALT** of a **STRONG ACID** and a **STRONG BASE** is **NEUTRAL** in solution.

For example: $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$; $\text{NaCl}(\text{aq})$ has a pH of 7.

- The titration requires an indicator which changes colour around $\text{pH} = 7$; that is, has $\text{p}K_a = 7$.

B. THE TITRATION OF A *weak acid* WITH A *STRONG BASE*

In general, the pH behaviour observed when titrating a weak acid with a strong base resembles the graph below.



Special features of the curve:

- There is an initial upswing in the pH at the start of the titration.
- V_B is the volume of base required to get to the equivalence point, and $V_{1/2} = \frac{1}{2} V_B$; that is, $V_{1/2}$ is the point on the graph which is half the value of V_B .
- The equivalence point occurs above $\text{pH} = 7$.

Calculating The Concentration of the Acid from the Volume of NaOH at the Equivalence Point

In the titration of a monoprotic acid (CH_3COOH) with NaOH, three out of four of the following pieces of data are available.

$$\begin{array}{ll} V_A = \text{the volume of the acid used} & V_B = \text{the volume of the base added} \\ [\text{HA}] = \text{the concentration of acid used} & [\text{OH}^-] = \text{the concentration of base added.} \end{array}$$

The normal titration calculation will then be used. For example, if $[\text{HA}]$ was unknown

$$\begin{array}{l} \text{then} \quad \text{moles OH}^- \text{ added} = [\text{OH}^-] \times V_B \\ \quad \quad \text{moles HA used} = \text{moles OH}^- \text{ added} \end{array}$$

$$\text{and} \quad [\text{HA}] = \frac{\text{moles HA used}}{V_A}$$

Calculating K_a and the Concentration of the Weak Acid

Although the acid concentration can be found using the volume of NaOH added at the equivalence point, it is also possible to find the acid concentration when the base concentration is *not known*.

Assume NaOH is being added to CH_3COOH and that the above graph has been plotted to show the "pH-vs-volume of NaOH added" behaviour which occurs during the titration.

On the above graph two special pH's can be defined:

- $\text{pH}_{1/2}$ = the pH at which the volume equals $V_{1/2}$.
- pH_{init} = the initial pH of the weak acid solution (before any NaOH is added).

Step 1: Use $\text{pH}_{1/2}$ to determine the K_a value for the weak acid

The K_a expression relates $[\text{H}_3\text{O}^+]$, $[\text{CH}_3\text{COO}^-]$ and $[\text{CH}_3\text{COOH}]$. Assume you start with 0.100 mol of CH_3COOH in 1.00 L of solution. At the equivalence point 0.100 mol of NaOH is added, and at the "half-volume" point (where $V = V_{1/2}$ and $\text{pH} = \text{pH}_{1/2}$ on the graph) 0.050 mol of NaOH is added. The "ST, Δ , EQ" table below shows the situation existing at the half-volume point. Since CH_3COOH is in excess, all the added NaOH is used up.

	CH_3COOH	+	OH^-	\longrightarrow	$\text{CH}_3\text{COO}^- + \text{H}_2\text{O}$
ST	0.100		0.050		0
+ Δ	-0.050		-0.050		+0.050
= EQ	0.050		≈ 0		0.050

As can be seen from the table, at exactly halfway to the equivalence point half of the initial CH_3COOH is neutralized and converted to CH_3COO^- .

Therefore $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$ (see the EQ-line in the above table)

and
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = [\text{H}_3\text{O}^+]_{1/2}$$

so that $\boxed{\text{p}K_a = \text{pH}_{1/2}}$, at the point $\text{pH}_{1/2}$ on the above graph.

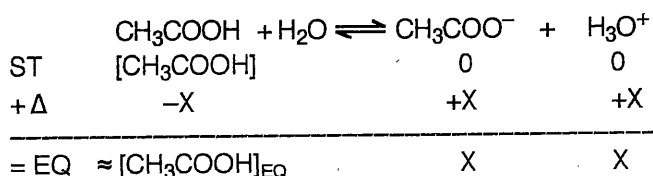
Therefore, the value of K_a can be determined by using the pH value at point $\text{pH}_{1/2}$.

Step 2: Combine the K_a value with pH_{init} to determine the concentration of the weak acid

Let $[\text{CH}_3\text{COOH}]$ = the initial concentration of CH_3COOH which is introduced into a solution.

X = the amount of CH_3COOH which dissociates

$[\text{CH}_3\text{COOH}]_{\text{EQ}}$ = the concentration of CH_3COOH which exists at equilibrium



The initial pH (" pH_{init} ") is measured before any base is added to the initial solution, allowing calculation of the initial $[\text{H}_3\text{O}^+]$ in solution. As the table shows, the ionization of CH_3COOH produces a solution having

$$X = [\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-]$$

so that
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]_{\text{EQ}}} = \frac{[\text{H}_3\text{O}^+]^2}{[\text{CH}_3\text{COOH}]_{\text{EQ}}}$$

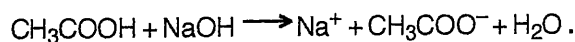
which rearranges to
$$[\text{CH}_3\text{COOH}]_{\text{EQ}} = \frac{[\text{H}_3\text{O}^+]^2}{K_a}$$

Since the value of K_a has previously been found from " $\text{pH}_{1/2}$ " and the value of $[\text{H}_3\text{O}^+]$ can be found from " pH_{init} ", the value for $[\text{CH}_3\text{COOH}]_{\text{EQ}}$ can be calculated. Finally, the initial molarity of the CH_3COOH , $[\text{CH}_3\text{COOH}]$, can be calculated from the equation

$$[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COOH}]_{\text{EQ}} + X.$$

Choosing an indicator

- The salt of a **weak acid** and a **STRONG BASE** is **BASIC** in solution, as can be seen from the pH at the equivalence point on the graph. (The fact that the resulting salt produces a basic solution also can be seen from the reaction equation:



The Na^+ is a spectator and CH_3COO^- is a weak base which produces a basic solution in water.)²⁴

- An indicator is required which changes colour in the basic range. If the acid being titrated is very weak, the $\text{p}K_a$ of the indicator should be several pH units above 7; the stronger the acid, the closer to 7 the $\text{p}K_a$ value should be. For most situations in Chem 12, an indicator with a $\text{p}K_a$ value in the range 8–10 suffices.