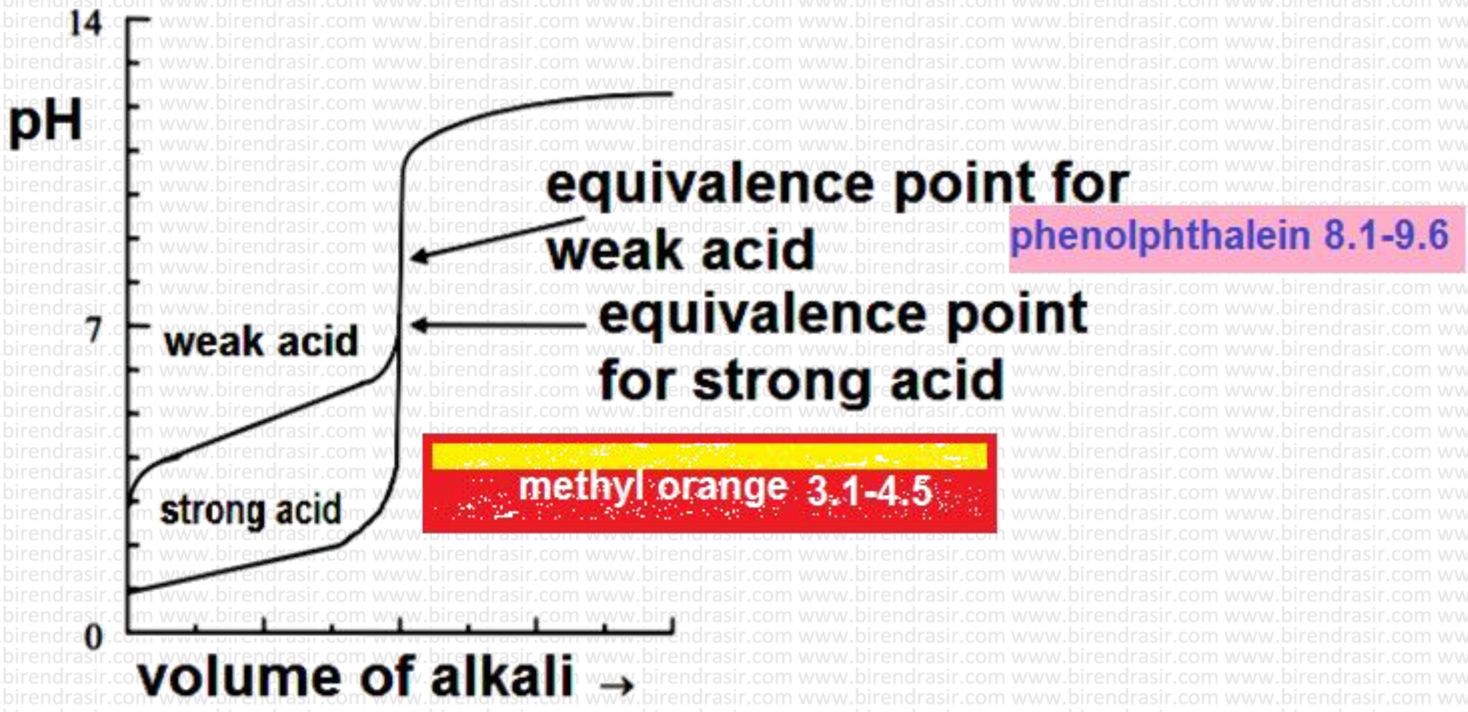
pH GRAPH / TITRATION CURVE

If the pH of an acid solution is plotted against the amount of base added during a titration, the shape of the graph is called a titration curve of pH graph. Titration is a technique used in analytical chemistry used to find the concentration of any acid or base. Titration involves the gradual addition of one solution whose concentration is known (from burette) to another solution of known volume, whose concentration is to be found (into flask).

Acid base titration is accompanied by change in pH. Indicators are frequently employed in detecting the end points in acid-base titrations. Due to hydrolysis, the pH at the end point depends upon the relative strengths of acid and the base being titrated and since different indicators have different pH ranges within which they can be used so the selection of proper indicator is very important for a given titration.

Methyl orange	3.1 - 4.5	Red	Yellow
Phenolphthalein	8.0 - 9.8	Colourless	Pink

pH titration curve of weak acid like CH_3COOH and strong acid like HCl with strong base like NaOH

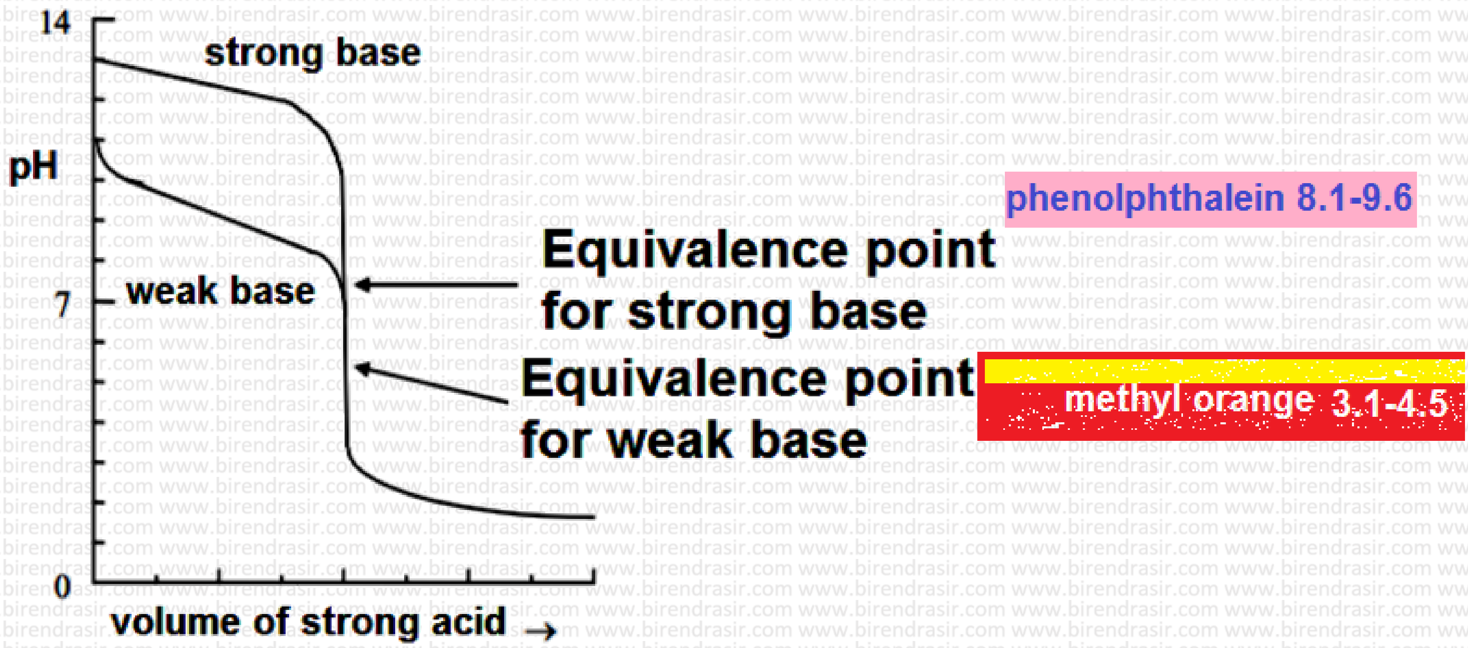


For titration of strong acid like HCl with strong alkali we can use indicators like methyl orange (range 3.1 to 4.4), methyl red (range 4.2 to 6.3), bromothymol blue (range 6 to 7.6) and phenolphthalein (range 8 to 9.8). Near the end point the titration curve is almost vertical and there is rapid change of pH may be from 4 to 10.

For titration of weak acid like CH_3COOH with strong alkali like NaOH we can use phenolphthalein indicator (range 8 to 9.8) but we cannot use indicators like methyl orange (range 3.1 to 4.4), methyl red (range 4.2 to 6.3), bromothymol blue (range 6 to 7.6). Here vertical portion does not start until beyond pH 7 and the end point lies somewhere between pH 8 to 10. This is due to hydrolysis of sodium acetate (salt of weak acid and strong base, $pH = \frac{1}{2}pK_w - \frac{1}{2}\log C - \frac{1}{2}pK_a$). To find the pH in between we can use formula of buffer solution of weak acid and its conjugate $pH = pK_a + \log_{10}\frac{[\text{conjugate base}]}{[\text{weak acid}]}$).

If we use very weak acid H_3BO_3 ($K_a = 6.0 \times 10^{-10}$) then titration curve does not show any sharp rise in pH this is because boric acid is so weak that its salt with sodium gets largely hydrolysed and giving alkaline solution, therefore pH goes on rising continuously and no sharp rise at equivalence point so weak acids with K_a less than 10^{-7} cannot be titrated successfully.

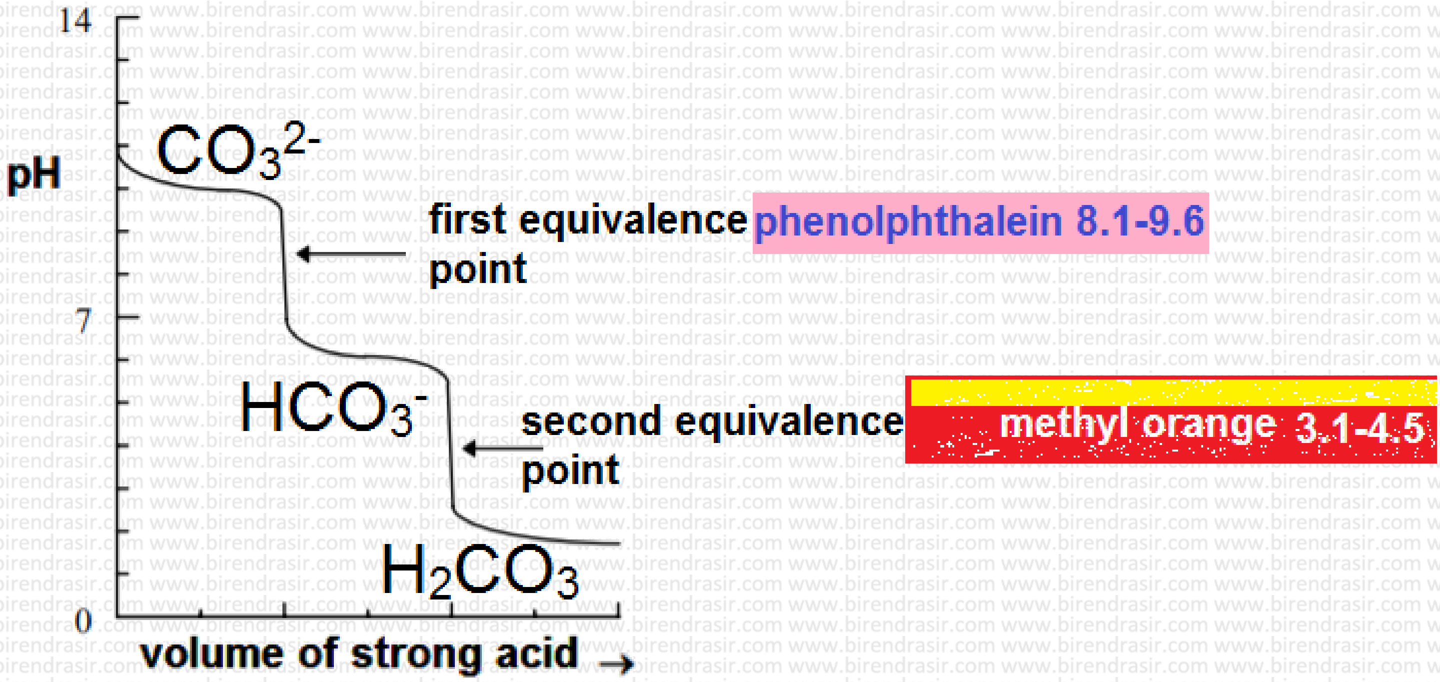
pH titration curve of weak base like NH_4OH and strong base like NaOH with strong acid like HCl



For titration of strong base like NaOH with strong acid we can use indicators like methyl orange (range 3.1 to 4.4), methyl red (range 4.2 to 6.3), phenolphthalein (range 8 to 9.8). Near the end point the titration curve is almost vertical and there is rapid change of pH may be from 10 to 4.

For titration of weak base like NH_4OH with strong acid like NaOH we can use indicators like methyl orange (range 3.1 to 4.4), methyl red (range 4.2 to 6.3) but phenolphthalein indicator (range 8 to 9.8) is useless indicator. Here pH change at the equivalence point lies in the range of 6 to 4. This is due to hydrolysis of NH_4^+ (salt of weak base and strong acid, $pH = \frac{1}{2}pK_w + \frac{1}{2}\log C + \frac{1}{2}pK_b$). To find the pH in between we can use formula of buffer solution of weak base and its conjugate acid $pOH = pK_b + \log_{10}\frac{[\text{conjugate acid}]}{[\text{weak base}]}$).

pH titration curve of sodium carbonate Na_2CO_3 with HCl



This curve shows two reflection points. One reflection indicates conversion of sodium carbonate into bicarbonate

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl.$$

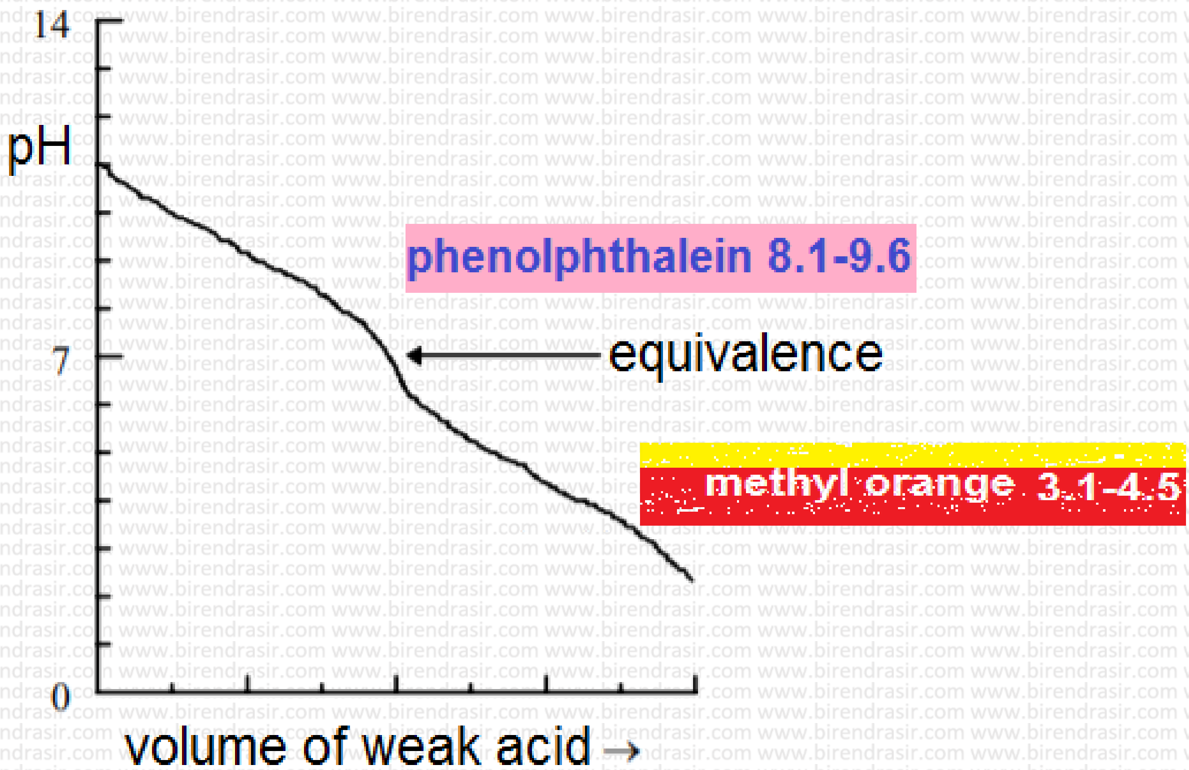
This reaction gets completed at about pH 8.5 so here phenolphthalein can be used to detect the end point.

The second point of inflection indicates the neutralisation of sodium bicarbonate

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O.$$

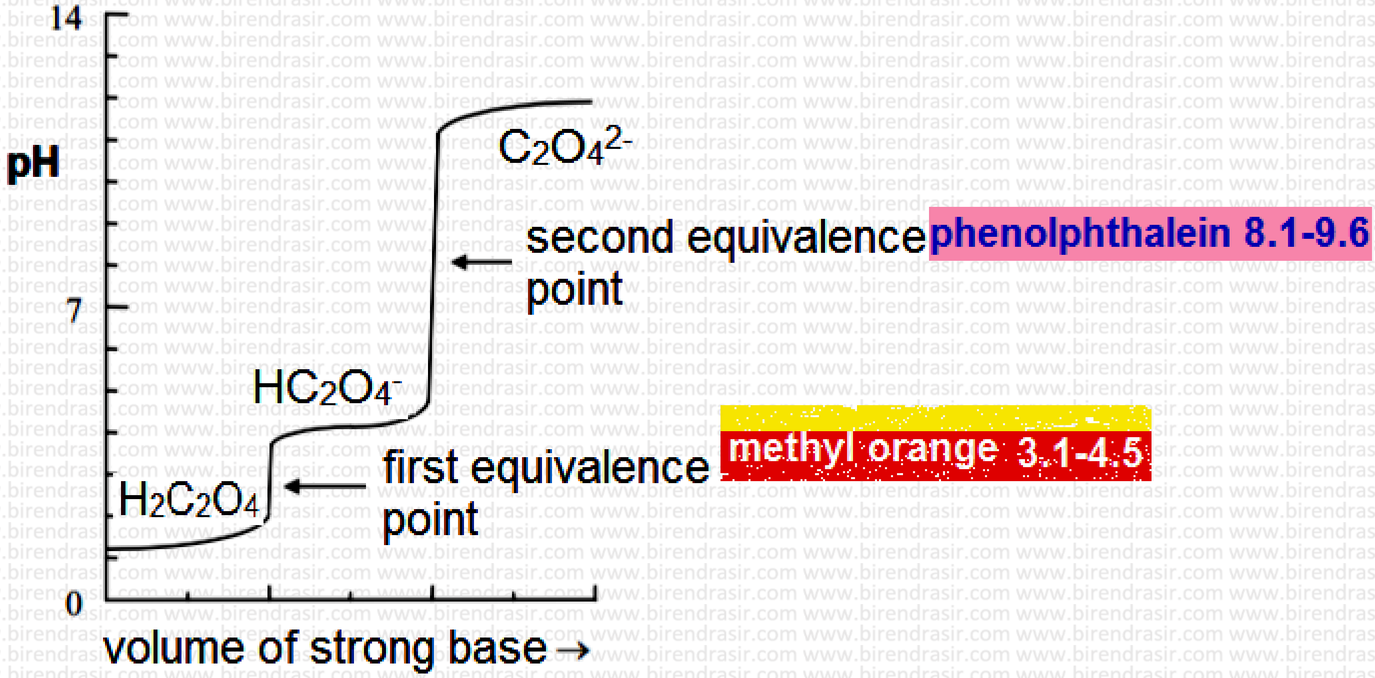
This reaction gets completed at pH 4.3 so methyl orange is suitable indicator here not phenolphthalein.

pH titration curve of weak base with weak acid



Here neither phenolphthalein is useful nor methyl orange.

pH titration curve of oxalic acid HOOC-COOH with strong base NaOH



This curve shows two reflection points. One reflection indicates conversion of $H_2C_2O_4$ into $NaHC_2O_4$.

$$HOOC\text{-}COOH + NaOH \longrightarrow NaOOC\text{-}COOH + H_2O.$$

This reaction gets completed at about pH 2.71 so here methyl orange can be used to detect the end point.

The second point of inflection indicates the neutralisation of $NaHC_2O_4$

$$NaOOC\text{-}COOH + NaOH \longrightarrow NaOOC\text{-}COONa + H_2O.$$

This reaction gets completed at pH 8.36 so phenolphthalein is suitable indicator.

ACID	BASE	pH CHANGE	CHOICE OF INDICATOR
HCl	NaOH	4 to 10	Methyl orange or phenolphthalein (pH range is wide)
CH_3COOH	NaOH	8 to 10	Phenolphthalein
NaOH	HCl	10 to 4	Methyl orange or phenolphthalein (pH range is wide)
CH_3COOH	NH_3	No sharp change	No indicator is suitable
NH_4OH	HCl	6 to 3	Methyl orange
HCl	NH_4OH	3 to 6	Methyl orange
Na_2CO_3	HCl	9.5 to 6.5 (first equivalence point) 5.5 to 2.5 (second equivalence point)	Phenolphthalein for first equivalence point (8.5) and methyl orange for second equivalence point (4.3)
$H_2C_2O_4$	NaOH	1.5 to 3.5 (first equivalence point) 5 to 11 (second equivalence point)	Methyl orange for first equivalence point (2.71) and phenolphthalein for second equivalence point (8.36)