


Equilibrium & Further Aspects of Equilibria.

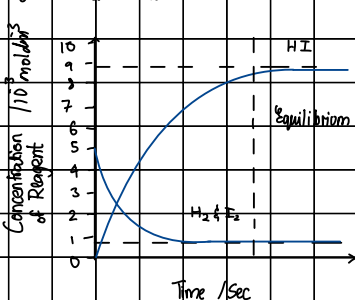
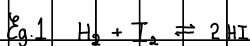


Equilibrium & Further Aspects of Equilibria

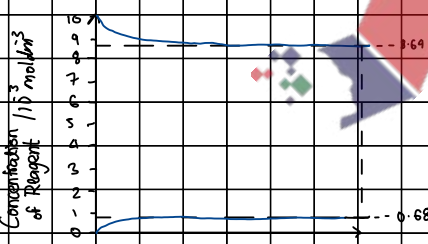
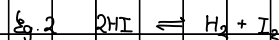
Reversible Reaction: A reaction in which the products can react to reform the original reactants is called a reversible reaction.

Equilibrium: A stage where the rate of forward reaction is equal to the rate of backward reaction. In a closed system:

- Closed system is one in which none of the reactants or products escape from the system. (Reaction mixture)
- Concentration of Products & Reactants remain constant.
- It is dynamic i.e.
 - Reactants & products are continuously reacting.
 - Where rate of forward reaction is equal to rate of backward reaction.
 - & concentration of products & reactants remain constant.
 - in a closed system.



	H_2	I_2	HI
Initial Conc.	5	5	0
	-4.32	-4.32	
Equilibrium	0.68	0.68	$4.32 \times 2 = 8.64$



	Initial Conc	H_2	I_2
	10	0	0
	$[-1.36]$	$1.36/2$	$1.36/2$
Equilibrium	8.64	$= 0.68$	$= 0.68$

Le Chatelier's Principle

If one or more factors that affect equilibrium are changed the system will oppose the change to restore equilibrium.

Equilibrium Shifts to Right

Yield of Products Increase

Equilibrium Shifts to Left

Conc./Yield of Reactants Increases

FACTORS AFFECTING EQUILIBRIUM

① Temperature

Exothermic
(doesn't like heat)

↑ Temp	↓ Product
↓ Temp	↑ Product

Endothermic
(likes heat)

↑ Temp	↑ Product
↓ Temp	↓ Product

② Pressure

$R_{\text{mole}} > P_{\text{mole}}$	↑ Pressure	↑ Product
$R_{\text{mole}} < P_{\text{mole}}$	↑ Pressure	↓ Product
$R_{\text{mole}} = P_{\text{mole}}$	NO EFFECT OF PRESSURE AT EQUILIBRIUM	

③ Concentration

Product

↓ Concentration	↑ Yield
↑ Concentration	↓ Yield

Reactant

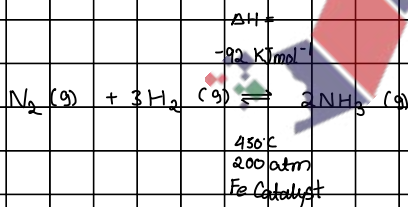
↑ Concentration	↑ Yield
↓ Concentration	↓ Yield

④ Catalyst eg. $\text{Fe}_2\text{O}_3, \text{V}_2\text{O}_5$

Helps achieve equilibrium faster, but doesn't affect equilibrium because it speeds up both backward & forward reaction equally.
Doesn't affect yield.

Equilibrium & Industry

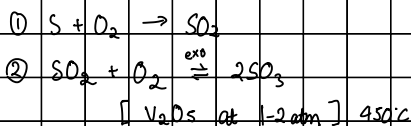
→ Haber's Process (NH_3)



Increasing Yield:

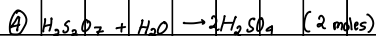
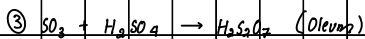
- 1) decrease temperature
- 2) Increase Pressure
- 3) Condense & Remove NH_3 as soon as it is formed

→ Contact Process (H_2SO_4)



To Increase Yield:

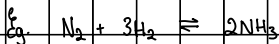
- 1) ↓ temperature
- 2) ↑ Pressure, although unnecessary as yield is enough at 2 atm (expensive)



EQUILIBRIUM CONSTANT (K_c)

c = concentration

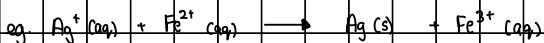
A relationship that links K_c to equilibrium concentration & stoichiometry of reactants & products is called Equilibrium expression.



Equilibrium expression $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$ "[]" equilibrium concentration (mol dm⁻³)

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^4} = \frac{1}{(\text{mol dm}^{-3})^2} = \text{mol}^{-2} \text{ dm}^6$$

In equilibrium expression, we ignore solid because its concentration remains constant.

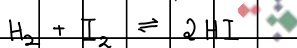


Solid is not included whether in reactant or product.

$$K_c = \frac{[Fe^{3+}(aq)]}{[Ag^+(aq)][Fe^{2+}(aq)]}$$

• Effect of change in concentration, pressure & temperature on K_c.

Concentration & Pressure



$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 0$$

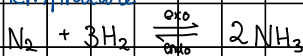
∴ K_c = no-unit

∴ Concentration does not affect K_c.

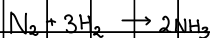
∴ Pressure doesn't affect K_c

Concentration of [HI] ↑ -
equilibrium shifts to RHS

Temperature



↓ temp - equilibrium to RHS

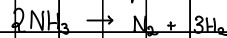


conc ↓ conc ↑

To restore temp

K_c increases

↑ temp - equilibrium to LHS



conc ↓ conc ↑

To restore temp

K_c Decreases

∴ ONLY TEMPERATURE AFFECTS K_c

↳ As change in conc & pressure forces the reaction to reverse to its original state, only temperature causes change.

EQUILIBRIUM CONSTANT (K_p)

P - Pressure

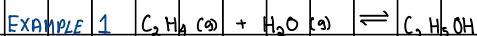
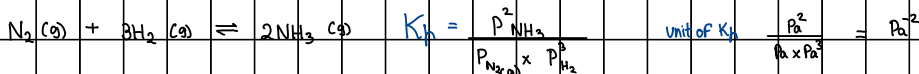
Partial Pressure: The pressure exerted by any one gas in the mixture is called its partial pressure

Pressure: The total pressure of a gas equals to the sum of the partial pressures of the individual gases

$$P_{\text{total}} = P_a + P_b + P_c$$

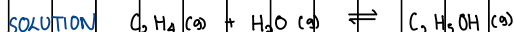
Equilibrium expression involving partial pressures

EXAMPLE



Initial mol 2.0 2.0 0.0

Equilibrium mol ? ? 1.0 Total pressure at equilibrium is 40 kPa Calculate K_p



initial mol 2.0 2.0 0.0
 Equilibrium mol 1.0 1.0 1.0
mol left mol left formed

Calculate Eq. moles

calculate Mole Fraction (x)

$$x_{\text{C}_2\text{H}_4} = \frac{n_{\text{C}_2\text{H}_4}}{n_{\text{total}}} = \frac{1}{1+1+1} = \frac{1}{3}$$

$$x_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{total}}} = \frac{1}{3}$$

$$x_{\text{C}_2\text{H}_5\text{OH}} = \frac{n_{\text{C}_2\text{H}_5\text{OH}}}{n_{\text{total}}} = \frac{1}{3}$$

Use moles to Calculate mole fraction

Calculate Partial Pressures

$$P_{\text{C}_2\text{H}_4} = x_{\text{C}_2\text{H}_4} \times P_{\text{total}} = \frac{1}{3} \times 40 = 13.33 \text{ kPa}$$

$$P_{\text{H}_2\text{O}} = x_{\text{H}_2\text{O}} \times P_{\text{total}} = \frac{1}{3} \times 40 = 13.33 \text{ kPa}$$

$$P_{\text{C}_2\text{H}_5\text{OH}} = x_{\text{C}_2\text{H}_5\text{OH}} \times P_{\text{total}} = \frac{1}{3} \times 40 = 13.33 \text{ kPa}$$

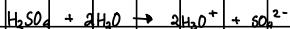
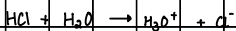
Calculate Partial Pressure

$$K_p = \frac{P_{\text{C}_2\text{H}_5\text{OH}}}{P_{\text{C}_2\text{H}_4} \times P_{\text{H}_2\text{O}}} = \frac{13.33}{13.33 \times 13.33} = \frac{1}{13.33} = 0.0750 \text{ Pa}^{-1}$$

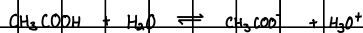
Find K_p

Acids & Bases

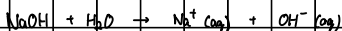
Strong Acid - An Acid which completely dissociates into ions when added to water.



Weak Acid - An Acid which partially dissociates into ions.



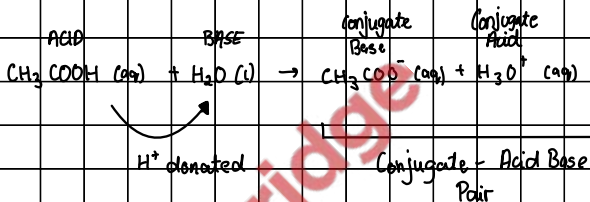
Strong Base - A Base which completely dissociates into ions.



Bronsted-Lowry Acids and Bases

Acid An acid is a proton donor (H^+)

Base: Is a proton acceptor (H^+)



Measuring pH

The pH scale can be used to indicate whether a solution is acidic, alkali, or neutral. At 25°C (or 298 K) a solution with pH lower than 7 is acidic, a solution with pH 7 is neutral, a solution with pH greater than 7 is alkali.

We can use a pH meter or universal indicator.

R	O	Y	G	B	I	V								
0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

pH is the negative logarithm to base 10 of the hydrogen ion concentration in an aqueous solution.

$$\text{pH} = -\log_{10} [\text{H}^+(\text{aq})] \quad \text{it has no units.}$$

→ The Dissociation of Water



$$\text{Equilibrium Constant } K_w = \frac{[\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O}(\text{l})]}$$

Degree of dissociation is very small so $[\text{H}_2\text{O}(\text{l})]$ remains constant.

$$\therefore K_w (\text{Ionic Product}) = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$$

K_w has a value of 1.0×10^{-14} at 298 K

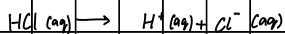
In pure water the concentrations of H^+ & OH^- ions are equal so

$$[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$$

Calculating the pH of Strong Bases, Strong Acids, Weak Bases & Weak Acids

Strong acids are completely ionised in solution so concentration of H^+ ions is approximately the same as the concentration of acid. (For monobasic acids / monoprotic acids which contain only one replaceable H^+ ion per molecule like HCl)

eg. pH of HCl (0.1 mol dm^{-3})

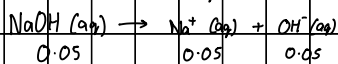


$$[\text{HCl}] = [\text{H}^+] = 0.1 \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log_{10} (0.1) = 1$$

Strong bases:

eg. Calculate the pH of a solution of NaOH of concentration $0.0500 \text{ mol dm}^{-3}$



$$K_w = [\text{H}^+][\text{OH}^-]$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.05} = 2 \times 10^{-13} \text{ mol dm}^{-3}$$

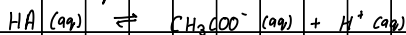
$$\text{pH} = -\log_{10} [\text{H}^+] \\ = -\log_{10} [2 \times 10^{-13}] = 12.7$$

Weak Acids

Weak Acids dissociate only partially in aq. solution. Examples: Carbonic Acid (H_2CO_3), Ethanoic Acid (CH_3COOH)



Dissociation of a weak Acid is represented by:



$$K_a = \frac{[\text{H}^+ \text{ (aq)}][\text{A}^- \text{ (aq)}]}{[\text{HA (aq)}]} = \frac{[\text{H}^+ \text{ (aq)}]^2}{[\text{HA (aq)}]}$$

(Acid Dissociation) constant

(Equilibrium Expression for monoprotic acid)

The value of K_a indicates the extent of dissociation of the acid.

$pK_a \rightarrow$ Acid dissociation constants can be expressed in a more convenient form by taking the negative logarithm to base 10 of K_a .

$$pK_a = -\log_{10} K_a$$

The higher the value of K_a , the stronger the acid.

The lower the value of pK_a , the stronger the acid.

Eg. Calculate the value of K_a for ethanoic acid. A solution of $0.010 \text{ mol dm}^{-3}$ ethanoic acid, has a pH of 2.90.

Solⁿ $\text{pH} = -\log_{10} [\text{H}^+(\text{aq})]$
 $2.9 = -\log_{10} [\text{H}^+(\text{aq})]$
 $[\text{H}^+] = 10^{-2.9}$
 $= 1.26 \times 10^{-3} \text{ mol dm}^{-3}$

$$K_a = \frac{[\text{H}^+]^2}{[\text{HA}]} = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]} = \frac{(1.26 \times 10^{-3})^2}{0.010} = 1.59 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\therefore K_a = 1.59 \times 10^{-4} \text{ mol dm}^{-3}$$

Eg. Calculate the pH of $0.100 \text{ mol dm}^{-3}$ methanoic acid. ($K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$)

Solⁿ $[\text{HCOOH}] = 0.100 \text{ mol dm}^{-3}$ $[\text{H}^+] = 1.32 \times 10^{-3} \text{ mol dm}^{-3}$
 $K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$
 $1.74 \times 10^{-5} = \frac{[\text{H}^+]^2}{0.100}$
 $\text{pH} = -\log_{10} [\text{H}^+]$
 $= -\log_{10} [1.32 \times 10^{-3}]$
 $= 2.88$

Buffer Solution

A Buffer solution is one that resists changes in pH when small amounts of acid & alkali are added.

There are two types of Buffer Solutions :-

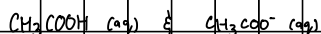
1) Acidic Buffer Solution

It is commonly made from a weak acid & its conjugate base (salt)

It has a pH < 7

Example: Ethanoic acid & Sodium Ethanoate $\text{CH}_3\text{COOH (aq)}$ & $\text{CH}_3\text{COO}^- \text{Na}^+ \text{(aq)}$.

↳ Conjugate base (Ethanoate ion)

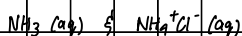


2) Alkaline Buffer Solution

It is commonly made from a weak base & its conjugate acid (its salt)

It has a pH > 7

Example: Ammonium Chloride solution of Ammonia Solution

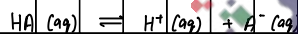


* Equal Molar Proportions are added *

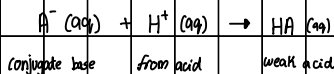
How A Buffer Solution Works

Consider a general acidic buffer containing HA (weak acid) and its conjugate base A^- .

The equilibrium that exists in this solution is -

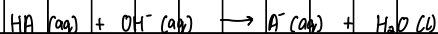


If some HCl is added to this solution, extra H^+ reacts with A^- (conjugate base) in the solution.



That means equilibrium shifts to LHS. The H^+ added is "mopped up" by reaction with the conjugate base and also because HA formed is a weak acid, the pH doesn't change it remains stable.

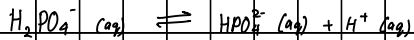
If some NaOH is added to the solution, the extra OH^- reacts with HA (weak acid) in the solution



Equilibrium shifts to R.H.S

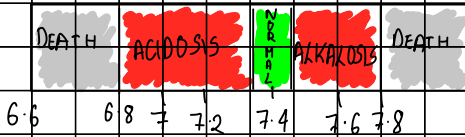
The OH^- added is "mopped up" by reaction with the weak acid & once again pH doesn't change, remains stable.

A common buffer used in the study of biochemical reactions is a phosphate buffer containing dihydrogen phosphate ions (H_2PO_4^-), the acid. And HPO_4^{2-} ions acts as a conjugate base.

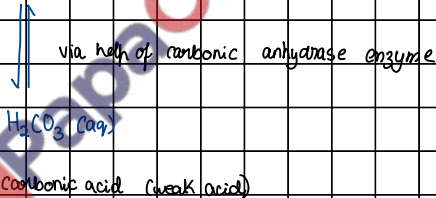
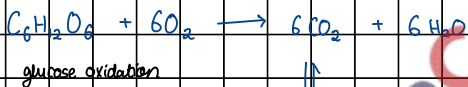


Blood pH

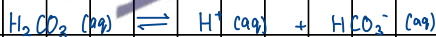
* In order for the human body to function properly, the human body needs to maintain a pH between 7.35 & 7.45. Values greater than 7.8 or less than 6.8 often result in death.



To prevent acidosis or alkalosis the body relies on the interaction of a chemical buffer system in the blood. The cells in our body produce CO_2 .



In blood,



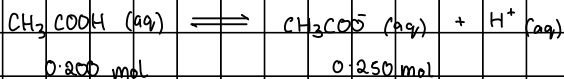
Now if $[\text{H}^+]$ increases, equilibrium shifts to LHS and pH remains constant.

if $[\text{H}^+]$ decreases, equilibrium shifts to RHS and keeps the pH constant.

Calculating the pH of a Buffer Solution.

Ex. 1 Calculate the pH of a solution containing $0.200 \text{ mol dm}^{-3}$ ethanoic acid ($K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$) and $0.250 \text{ mol dm}^{-3}$ sodium ethanoate

Solution



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{1.74 \times 10^{-5} \times 0.250}{0.200} = 1.39 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{pH} &= -\log_{10} [\text{H}^+] \\ &= -\log_{10} [1.39 \times 10^{-5}] = 4.86 \end{aligned}$$

\therefore pH of this buffer system is 4.86

* The Henderson-Hasselbalch Equation:

$$\text{pH} = \text{p}K_a + \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) \quad \text{p}K_a + \log_{10} \left(\frac{[\text{conjugate base or salt}]}{[\text{weak acid}]} \right)$$

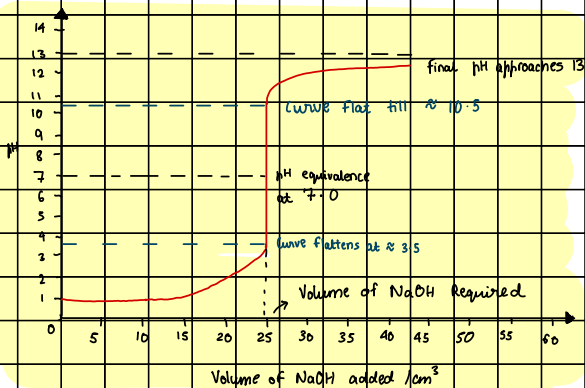
So for the same question above we can use this formula as follows:

$$\begin{aligned} \text{pH} &= -\log_{10} K_a + \log_{10} \left(\frac{0.250}{0.200} \right) \\ &= -\log_{10} (1.74 \times 10^{-5}) + \log_{10} \left(\frac{0.250}{0.200} \right) = 4.86 \end{aligned}$$

Titration Curves & Indicators

① Calculate initial pH using concentration whenever possible: eg. Concentration H^+ is $0.100 \text{ mol dm}^{-3}$, $pH = -\log_{10}(0.1) = 1$

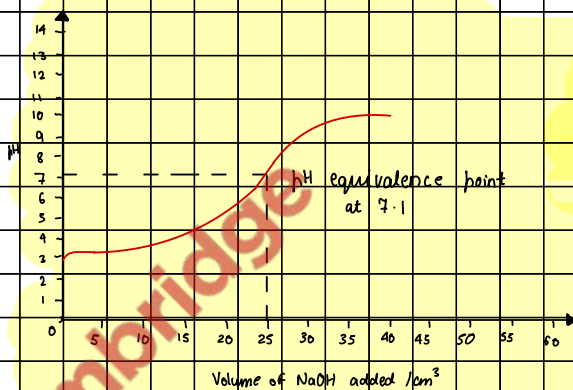
Strong Acid - Strong base Titration Curve



★ Sharp fall at 3.5 - 10.5

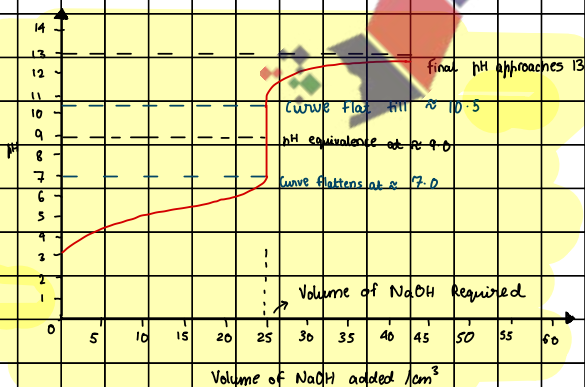
★ Graph is inverted vertically when strong acid's added to base instead.

Weak acid - Weak base Titration Curve



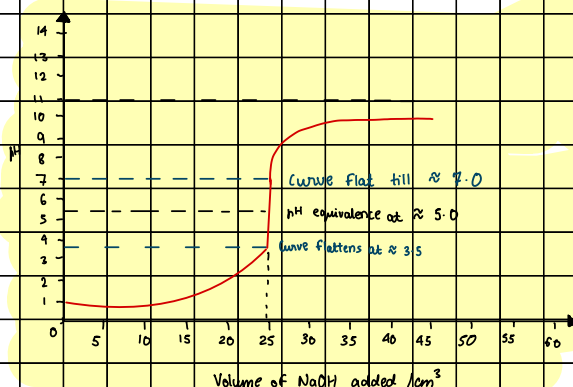
★ No Sharp Fall, Gradual Change, No Indicator suitable

Weak Acid - Strong Base Titration Curve



★ Sharp fall from 7.0 - 10.5

Strong Acid - Weak Base Titration Curve



★ Sharp Fall 3.5 - 7.0

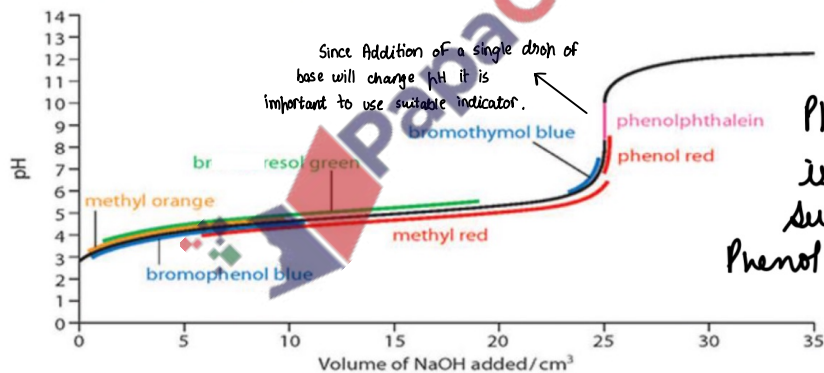
Indicators

Equivalence Point : The equivalence point of a titration is the point at which equivalent numbers of moles of acid & alkali have been added. The end point of a titration is the point at which the indicator changes colour - these are not necessarily the same.

pH Range : The pH range of an indicator is the pH values between which the indicator has intermediate colours, because comparable amounts of un-ionised & ionised forms are present.

Indicator	pH Range	Acid Color	Alkali Color
methyl orange	3.1 - 4.4	Red	Yellow
bromothymol blue	6.0 - 7.6	Yellow	Blue
methyl red	4.2 - 6.3	Red	Yellow
phenol red	6.8 - 8.4	Yellow	Red
Phenolphthalein	8.2 - 10.0	colorless	Pink

Example : Weak Acid - Strong Base titration



Phenolphthalein is the most suitable one. Phenol red is also suitable.

Figure 4 The ranges of various indicators superimposed on a weak acid-strong base titration curve.

Because only strong acid-strong base titrations have $\text{pH} = 7.0$ at the end point, it is important to remember that the indicator is being used to determine the point at which equivalent numbers of moles of acid and alkali have been added, and not the point at which $\text{pH} = 7$.