

ACID-BASE Indicators: What they are and how they are used.

Read the following statements and consider whether they are true or false

- Indicators are used to indicate the pH of a solution.
- Indicators exhibit one colour in acidic solutions and another colour in alkaline solution.

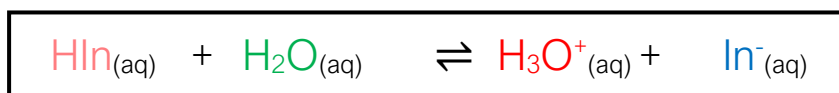
In fact, the answer to both questions is **false**.

Many students think that the answer to these questions is true. This misunderstanding results from their early exposure to the chemistry of acids and alkalis. The indicator that most students come across, earlier in school, is Universal indicator. This is actually a mixture of several indicators chosen to give a range of colours (all colours of the rainbow). We can all recall the colour of Universal Indicator in water as being green. Most people have heard of the very common indicator known as litmus. This indicator can either be found impregnated into paper or as a solution. This is one rare example of an indicator that has essentially one colour in acidic solution (**red**) and another colour in alkali (**blue**).

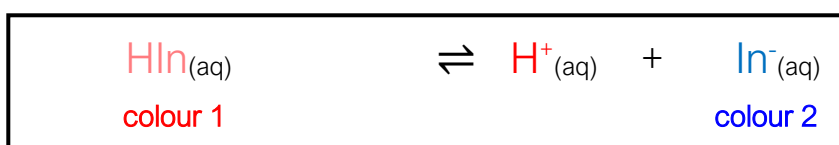
In this topic, explanations will be given which should lead you to understand why the above statements are false.

Indicators are **Weak Acids**

Indicators are molecules that partially dissociate to yield a proton and therefore are weak acids. We can represent an indicator using the general formula $\text{HIn}_{(\text{aq})}$. Indicators must also have a K_a (so $\text{p}K_a$)



Now let's imagine that HIn exhibits **colour 1** and In^- exhibits **colour 2**. We can now write;



and;

$$K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

n.b. It is common to write K_a for an indicator as K_{In}

Putting this in the form of the Henderson-Hasselbalch equation gives;

$$\text{pH} = \text{p}K_{\text{In}} + \log_{10} \left(\frac{[\text{In}^-]}{[\text{HIn}]} \right)$$

both of these factors are controlled by relatively large volume of solution into which the indicator is placed and **not by the dissociation of the indicator!**

If a **small amount of these molecules** (just enough to see the colour) are added to a solution, the colour that is observed will depend upon the ratio:



It has been consistently shown that, to the human eye, if the ratio of any pairs of colours is roughly **10:1** or greater, we see one colour with no hint of the other. In this example we would see **red**. If the ratio shifted the other way to **1:10** then only **blue** would be observed. Of course, a ratio of **1:1** would be seen as **purple**.

If a small amount of indicator molecules are added to a large amount of solution then the pH will be controlled by the solution into which the molecules have been placed. The small amount of indicator (a **weak acid** solution!) will have only a tiny effect on the pH of the solution. We could consider the pH of the solution to control the ratio of **HIn:In⁻**. It will not be the indicator's dissociation that affects the pH!

Looking at the equation above, for an indicator with a **pKa of 4.7** can you predict the pH of the solution that would cause the indicator to exhibit the colour **purple**? (Hint: This is the point when the **weak acid** and **conjugate base** are in equal proportions.)

pH=____

How large would the **smallest change in pH** need to be to alter the **purple** appearance to **red**?

change in pH=____

From the pH that causes the indicator to exhibit the **purple** colour, how large would the **smallest change in pH** need to be to alter the **purple** appearance to **blue**?

change in pH=____

Given these two pHs, over a range of how many pH units will an indicator change its colour from **red** to **blue**?

____pH units.

So, we can now see that most indicators exhibit two colours and that the change in colour occurs over a narrow pH range. Furthermore, this range is rarely in the region of **pH7**.

The **mid-point colour** exhibited by any indicator (**purple** in our example) occurs when:








$$\text{pH} = \text{pKa} \quad (\text{or } \text{pK}_{\text{In}})$$

Some typical Indicators

Two very common acid/base indicators are **methyl orange** and **phenolphthalein**.

- **METHYL ORANGE** has a pK_a of 3.7 so the range over which it changes colour is typically quoted as 3.0-4.3
- **PHENOLPHTHALEIN** has a pK_a of 9.3 so the range over which it changes colour is typically quoted as 8.6-10.0

Some other indicators are given below:

Indicator	pK_a	pH range and colour change
Alizarin yellow	11.2	10.1  12.0
Phenolphthalein	9.3	8.3  10.0
Bromothymol blue	7.3	6.0  7.6
Litmus	6.5	5.0  8.0
Bromocresol green	4.7	3.8  5.4
Methyl orange	3.7	3.1  4.4
Thymol blue	1.7	1.2  2.8

We can see that some indicators (with pK_a less than 6) can actually exhibit both colours in acid conditions and many others (with pK_a greater than 8) can exhibit both colours in alkaline conditions. Litmus has a pK_a of 6.5 which essentially means that it is blue in all alkaline conditions and red in acidic conditions.

Choice of Indicator

As long as the indicator's range ($pK_a \pm 1$ pH unit) falls on the very steep (nearly vertical) part of a titration curve, then the indicator will be suitable. This means that, upon the addition of one drop of solution just before the end-point (the smallest addition) the **equivalence point** and the **colour change** (which we use to indicate the end-point) will both coincide.

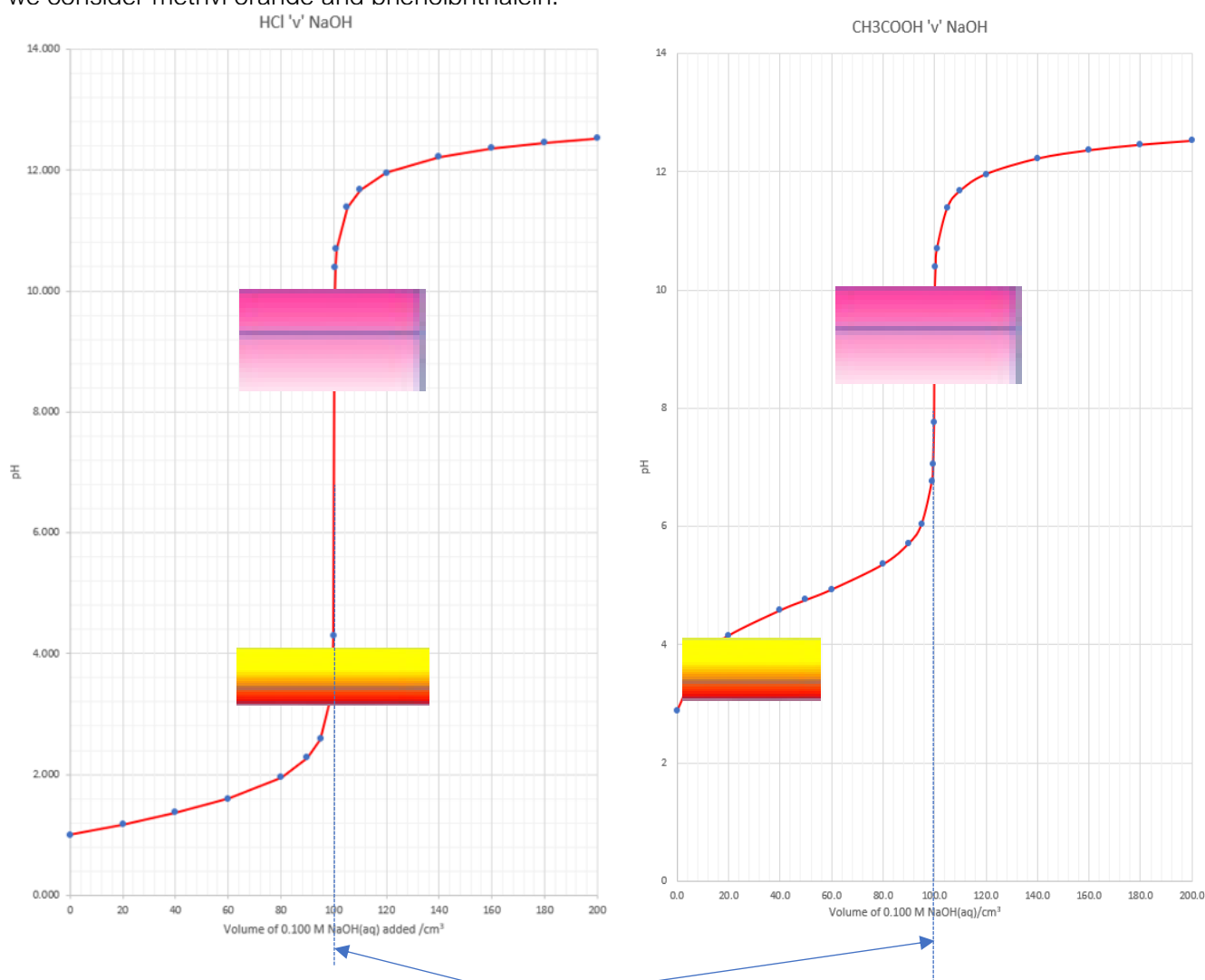
For a **STRONG ACID** 'v' **STRONG BASE**, both **methyl orange** and **phenolphthalein** are suitable.

For a **WEAK ACID** 'v' **STRONG BASE**, only **phenolphthalein** is suitable.

For a **STRONG ACID** 'v' **WEAK BASE**, only **methyl orange** is suitable.

For a **WEAK ACID** 'v' **WEAK BASE**, no indicator is suitable.

If we consider methyl orange and phenolphthalein:



volume of $0.100 \text{ mol dm}^{-3}$ NaOH required to fully neutralise the acid (the equivalence point)
This is what a titration is attempting to find by the indicator colour change.