Equivalence point

In chemistry, the equivalence point refers to the end of the titration - the point at which the amount of the titrant (its concentration multiplied by the volume consumed in the titration) is equivalent to the amount of the substance being determined.

Methods of equivalence point indication

- **Visual indication** - subjectively observable change in the titrated sample solution, colour change, precipitate formation, fluorescence. Most often it is a change in colour of a suitable dye, indicator, added to the titrated solution, which occurs just when the equivalence point is reached.
- **Instrumental indication** - measured by an instrument, where one of the physical quantities of the titrated solution (e.g. conductivity of the solution, pH, etc.) is measured as a function of the volume of titrant added - again, the titration curve. The quantity is chosen so that at the equivalence point there is a significant change in this curve (e.g. a break), so that from some point in this change we determine the consumption of titrant.

Indicators are substances that react either with the substance to be determined or with excess titrant, and the reacted and unreacted forms are different colours. At the equivalence point, one form is then converted to the other. These are substances of a similar nature to the titrant or the titrated substance. According to the nature of the titrations, there are a number of different kinds of indicators.

Acid-base indicators (for acid-base titrations). These are weak organic acids or bases. The acidic form (HInd), which exists at a higher H+ concentration (lower pH), has a different color than the basic form (Ind-). The indicator acid and base form a conjugated pair with an ionization constant K_{HInd}.

$$HInd \rightleftharpoons H^+ + Ind^-$$

According to the concentration of ions in the titrated solution, the ratio of the concentrations of the two forms is established - protolytic equilibrium

$$K_{HInd} = \frac{[H^+] \cdot [Ind^-]}{[HInd]} \qquad \frac{[Ind^-]}{[HInd]} = \frac{K_{HInd}}{H^+}$$

By mathematical modification (negative logarithm of these relations) we get the expression

$$pH = pK_{HInd} - log\frac{[HInd]}{[Ind^-]}$$

In a titration determination, e.g. of an acid by a volumetric alkaline solution, the acidic form is present in the titrated solution. In fact, both forms are present directly at the equivalence point. Just beyond the equivalence point, the acidic form disappears completely (reacts with the excess of basic titrant into the basic form). This shows that the colour of the indicator usually changes gradually over a small range around the equivalence point. The log HInd/Ind- ratio can take values from approximately -1 to +1 during the titration, therefore the pH range of the colour transitions of acid-base indicators (functional range) is usually within 2 pH units.

Examples of acid-base indicators:

- **Methyl orange, pH functional range 3.0-4.4; red - orange;**

    Sodium 4-[4-(dimethylamino)phenylazo]benzene sulphonate

- **Methyl red, functional pH range 4.4-6.2; red - yellow;**

    2-(4-Dimethylaminophenylazo)benzoic acid

- **Phenolic red, functional pH range 6.8-8.4; yellow - red;**

    Phenolsulfophthalein, 3,3-bis(4-hydoxyphenyl)-sulfophthalide

- **Phenolphthalein, functional pH range 8.2-10.0; colourless - reddish-purple;**

    3,3-bis(4-hydroxyphenyl)-1(3H)-isobenzofuranone

Indicators of complexometric titrations - **metallochromic**, are substances forming a complex with the metal ion to be determined. The complex with the metal is coloured differently from the free form of the indicator. Only the metal complex form is present before the equivalence point. Just before the equivalence point, when free ions of the metal to be determined are no longer present in the solution, the complexing titrant begins to react with the metal ion that has been bound into the complex with the indicator, thereby displacing the free form indicator.

Examples of metallochromic indicators: **eriochromic black T** (going from purple to blue), **xylenol orange** (from red or purple to yellow), **murexide** (from yellow or red to purple).

Precipitation titration indicators form coloured precipitates or soluble coloured complexes just after the equivalence point with the first excess of titrant, or may cause a change in colour of the precipitate or solution at the equivalence point as a result of adsorption on the precipitate particles or, conversely, desorption (see argentometry, solubility product).

Indicators of redox reactions. Substances whose reduced form is different in colour from the oxidized form are very often used. The first excess of oxidizing titrant just beyond the equivalence point converts the reduced form to the oxidized form, (examples **benzidine** or **diphenylamine** - they go from colourless to blue). A number of redox indicators work irreversibly, like some of the coloured substances (e.g. **methyl red**), which become oxidised by the first excess of oxidising agent, resulting in decomposition of the substance, manifested by decolouration. However, the reduced colour form cannot be recovered by reduction.

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