9.06 REDOX INDICATOR

It has been discussed in the acid-base titration section that the indicators undergo sharp colour change at the pH near the equivalence point of an acid-base titration. Likewise, a redox indicator indicates by its sudden colour change in the redox potential of a redox titration near the equivalence point. E_0 value of the indicators will be intermediate between the E_0 value of the solution to be titrated and that of the titrant.

Thus, redox indicators are mostly organic compounds capable of undergoing reversible oxidation or reduction in the titration medium, having distinct and sharp colour change between the oxidised or reduced form with slight variation of the potential.

Indicators are of two types: (a) internal indicator and (b) external indicator. Again, some redox titration can be done without adding indicator, e.g., titration with $KMnO_4$ and I_2. In permanganometric titration, as long as reducing agent is present in the titrating solution, $KMnO_4$ will not impart any colour, but when all reducing agents are removed, addition of single drop imparts purple colour. So, $KMnO_4$ may be called self- or auto-indicator.

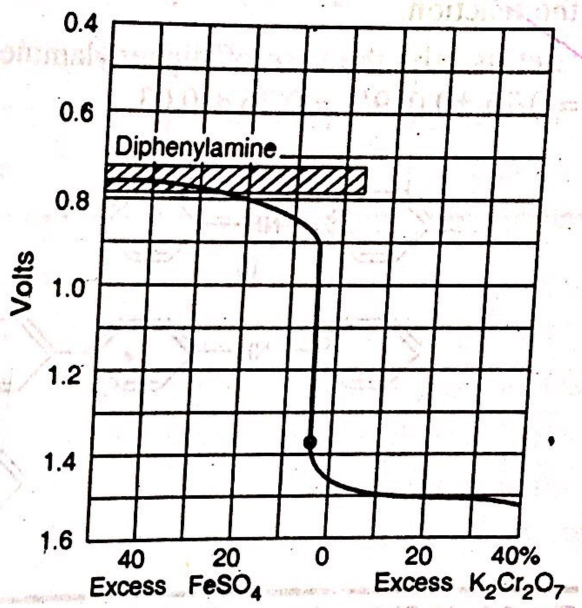

Fig. 9.2 Curve for titration of $FeSO_4$ solution with dichromate (at $[H^+] = 1$).

Similarly, reducing agents can be titrated with I_2 solution when dark brown iodine solution becomes colourless due to the change, $I_2 + 2e^- \rightleftharpoons 2I^-$. Towards the end point, dark brown colour becomes fade and so starch solution is used to form a deep blue adsorption complex with iodine. Titration is complete when this deep blue colour disappears with single drop. (Care must be taken at this stage, starch is to be added when concentration of iodine is low in solution, otherwise drifted end point is obtained.)

Internal indicators are added in the solution to be titrated. As for example, diphenylamine, barium diphenylamine sulphonate, etc., are used during the titration of Fe^{2+} with $K_2Cr_2O_7$ solution in 1.5 N acid medium. Here, solution changes from light greenish to bluish violet colour with slight variation of potential.

External redox indicators are not added in the solution to be titrated, e.g., titration of Fe^{2+} with $K_2Cr_2O_7$ as stated above. Freshly prepared potassium ferricyanide solution, taken as an external indicator, is taken on the spot plate. Towards the end point of titration, one drop of the solution is added to ferricyanide solution on the spot plate when blue colour does not appear, titration is complete. External indicators now are not in use as satisfactory internal indicators are available.

Choice of indicator:

The indicators will behave as a reversible redox system indicated by the reaction,

$In_{Ox} + ne^- \rightleftharpoons In_{Red}$

The Nernst equation at potential E can be written as,

$$E = E_{0\,In} + \frac{0.0591}{n}\log\frac{[In_{Ox}]}{[In_{Red}]}$$ where $E_{0\,In}$ is the standard potential of the indicator.

The colour of the solution depends upon the ratio $[In_{Ox}]/[In_{Red}]$. It has been found that if the oxidised form is coloured, then intensity of colour of the solution depends when $[In_{Ox}] \approx 10[In_{Red}]$. So, the equation of $E = E_{0In} + \frac{0.0591}{n}\log 10 = E_{0In} + \frac{0.0591}{n}$(colour of In_{Ox}) when the reduced form is coloured, the E will be $E = E_{0In} + \frac{0.0591}{n}\log\frac{1}{10} = E_{0In} - \frac{0.0591}{n}$(colour of In_{Red}). Consequently, the range of potential over which sharp change in colour will be obtained is $E = E_{0In} \pm 0.0591/n$.

If both the oxidised and reduced forms are coloured, and their intensities differ considerably, the intermediate colour of the solution will be obtained when $E = E_0 \pm 0.06$ volt. For sharp change in colour $E = E_0 \pm 0.15$ volt, i.e., 0.15 volt from the formal potential of the other systems present in the reaction.

Let us take the case of diphenylamine indicator (E_0= 0.76). So, the potential range will be $E = 0.76 \pm 0.059/2 = 0.76 \pm 0.03$.

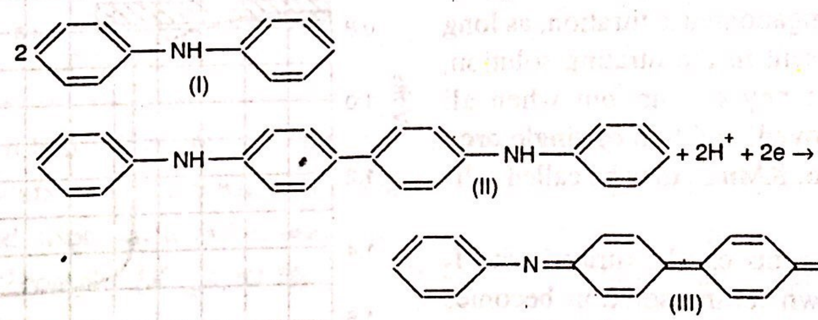

Fig. 9.3 (I) Diphenylamine, (II) Diphenyl benzidine (colourless), (III) Diphenyl benzidine (violet).

Therefore, at $E = 0.73$ the reduced form, i.e., colourless form predominates and at $E = 0.79$, i.e., the oxidised form (bluish-violet form) predominates. In the section—change of potential with concentration—it has been shown that when 91cc of the Fe^{2+} has been oxidised then potential of the redox solution becomes 0.828volt, i.e., before theoretical end point, indicator gives colour and that will give erroneous result. To avoid this, NaF or H_3PO_4 is added to the solution. This F^- or PO_4^{3-} will form complex with the Fe^{3+} and reduces the active concentration of Fe^{3+} in solution. So, potential will not increase and colour of the reduced form of the indicator predominates. When all the Fe^{2+} are consumed by $K_2Cr_2O_7$, then addition of one drop of $K_2Cr_2O_7$ increases the potential at 1.475 volt, the oxidised form of the indicator predominates and colour becomes bluish-violet. The titration curve of Fe^{3+}/Fe^{2+} system with $K_2Cr_2O_7$ is given above. A sharp break in the curve indicates the end point.