

SUBJECT - CHEMISTRY

CLASS - B.Sc (Hons) PART - III

PAPER - V

TOPIC - Redox indicators.

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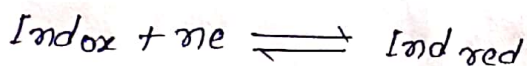
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Q write a note on Redox indicators.

Ans. Redox indicator

certain organic dyes have the ability to undergo oxidation or reduction followed by change in colour, as such they can act as redox indicators. They exist in oxidised and reduced forms which have different colours -



A redox indicator detects the sudden change in the oxidation potential in the neighbourhood of the end-point in the redox titration. The oxidation potential (E) is given as -

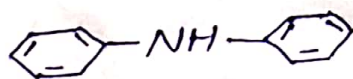
$$E = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Ind}_{\text{ox}}]}{[\text{Ind}_{\text{red}}]}$$

where terms have usual meanings. The colour of the solution depends upon the oxidation potential. The indicator changes colour at the end-point in redox titrations due to the change in its oxidation potential. At the end point, oxidation potential of the solution changes rapidly, hence the potential of indicator will also rapidly change because it has the property to adjust itself to acquire the same potential as that of the system in which it is placed. Hence a redox potential has an oxidation potential intermediate between that of the solution titrated and that of the titrant.

Diphenyl amine is used as internal redox indicator in the estimation of  $Fe(II)$  by dichromate method. Since this indicator is slightly soluble hence 0.2% aqueous  $\beta$ -diphenylamine Sulphonate is used. These indicators are themselves colourless but when oxidised by a slight excess of  $Cr_2O_7^{2-}$ , they give intensely blue-violet compounds. The titrating mixture always contains two systems:  $Fe^{3+}/Fe^{2+}$  and  $Cr_2O_7^{2-}/Cr^{3+}$  having  $E^0$  values 0.77 and 1.33 volts respectively. Though this indicator has  $E^0$  value 0.76 volt only, still it is used because this titration is carried out in presence of phosphoric acid which removes most of  $Fe^{3+}$  as stable colourless  $[Fe(HPO_4)]^+$  complex. This reduces  $[Fe^{3+}]$  and hence potential decreases

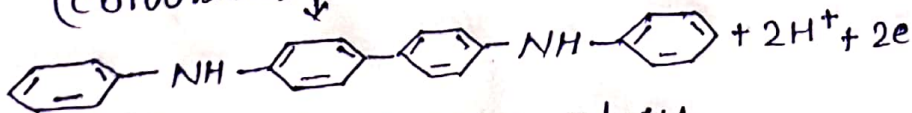
$$E = 0.77 + \frac{0.0591}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

At potential below 0.73 volt, the reduced form (I) of the indicator is predominant and the solution remains colourless. At potential above 0.79 volt, the oxidised form (II) is predominant and the solution has intense blue-violet colour.



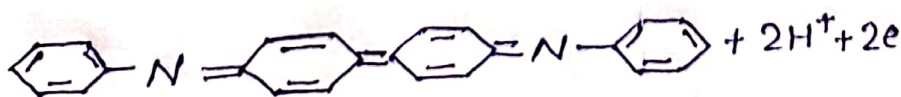
Diphenylamine (I)

(Colourless) ↓



Diphenyl benzidine (Colourless)

↓↑



Diphenyl benzidine (Colourless)