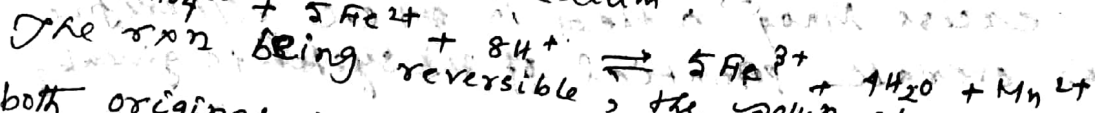


indicators used are called redox indicators.

Let us consider, the titration of Fe^{2+} ion by $KMnO_4$ soln in 1 (M) acid medium.



both original ions and the ions form in course of titration. Therefore the soln containing two redox systems, Fe^{3+}/Fe^{2+} and MnO_4^-/Mn^{2+} . Any of them may be used to calculate the potential at any stage of titration. i.e;

$$E = 0.77 + \frac{0.059}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$or, E = 1.51 + \frac{0.059}{5} \log \frac{[MnO_4^-]}{[Mn^{2+}]}$$

0.99
E° values of Fe^{3+}/Fe^{2+} and MnO_4^-/Mn^{2+} couples in 1 (M) H_2SO_4 medium at 25°C are +0.77V and +1.51V respectively. Find the redox potential at the eq. pt. in the titration of 0.1 (N) Fe^{2+} with 0.1 (N) $KMnO_4$ in 1 (M) H_2SO_4 medium. $\therefore [H^+] = 1$

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calculate the potential at the eq. pt. in titration of 0.1 (N) Fe^{2+} with 0.1 (N) $KMnO_4$ in 1 (M) H_2SO_4 medium.

Suppose 100 c.c ($\frac{N}{10}$) $FeSO_4$ soln is titrated with $\frac{N}{10}$ $KMnO_4$ soln at 25°C.

Case-I: When 50 c.c permanganate soln is added, then the overall potential of the system is given by

$$E = 0.77 + \frac{0.059}{1} \log \frac{50}{50} = 0.77 \text{ volt.}$$

Case-II: When 91 c.c permanganate soln is added, then the overall potential of the system is given by

$$E = 0.77 + \frac{0.059}{1} \log \frac{91}{9} = 0.829 \text{ volt.}$$

Case-III: When 99 c.c permanganate soln is added, then the overall potential of the system is given by

$$E = 0.77 + \frac{0.059}{1} \log \frac{99}{0.1} = 0.887 \text{ volt.}$$

Case-IV: When 99.9 c.c permanganate solution is added, then the overall potential of the system is given by

$$E = 0.77 + \frac{0.059}{1} \log \frac{99.9}{0.1} = 0.947 \text{ volt.}$$

Case-V: When 100.1 c.c MnO_4^- is added, the endpoint of titration is already attained and amount of excess MnO_4^- added is 0.1 c.c. Therefore the overall potential of the system is given by

$$E = 1.51 + \frac{0.059}{5} \log \frac{0.1}{100} = 1.475 \text{ volt.}$$

Case - VI

When 101 c.c. MnO_4^- is added, the end point of titration is already attained and amount of excess MnO_4^- added is 1 c.c. Therefore the overall potential of the system is given by

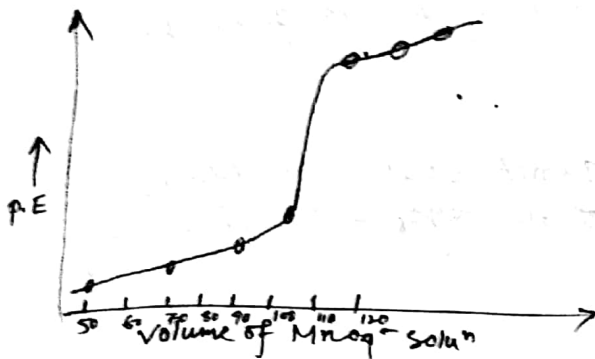
$$E = 1.51 + \frac{0.059}{5} \log \frac{1}{100} \\ = 1.486 \text{ volt.}$$

Case - VII:

When 110 c.c. MnO_4^- is added, the end point of titration is already attained and amount of excess MnO_4^- added is 10 c.c. Therefore the overall potential of the system is given by

$$E = 1.51 + \frac{0.059}{5} \log \frac{10}{100} \\ = 1.498 \text{ volt.}$$

From the above values we get the following curve by plotting Potential vs volume of MnO_4^-



Calculate the potential of the solution at the equivalence point

Let E is the potential at the equivalence point. Now, from $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple we can write,

$$E = 0.77 + \frac{0.059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \dots \dots \dots (1)$$

On case of $\text{MnO}_4^-/\text{Mn}^{2+}$ couple, we can write

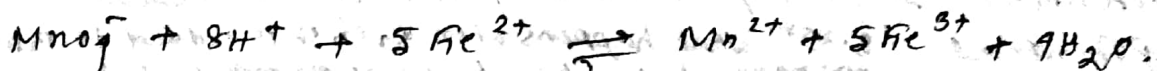
$$E = 1.51 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \quad [\because [\text{H}^+] = 1]$$

$$\text{or, } 5E = 5 \times 1.51 + 0.059 \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]} \dots \dots \dots (2)$$

Adding equⁿ (1) and (2), we get,

$$6E = (0.77 + 5 \times 1.51) + 0.059 \log \frac{[\text{MnO}_4^-][\text{Fe}^{3+}]}{[\text{Mn}^{2+}][\text{Fe}^{2+}]}$$

Now at the equivalence point, the overall eqnⁿ is



At the equivalence point, we can write,

$$[\text{Fe}^{2+}] = 5 \times [\text{MnO}_4^-]$$

and $[\text{Fe}^{3+}] = 5 \times [\text{Mn}^{2+}]$

putting the values of $[\text{Fe}^{2+}]$ and $[\text{Fe}^{3+}]$ in eqnⁿ (3), we get,

$$GE = (0.77 + 5 \times 1.51) + 0.059 \log \frac{[\text{MnO}_4^-] \times 5 \times [\text{Mn}^{2+}]}{[\text{Mn}^{2+}] \times 5 \times [\text{MnO}_4^-]}$$

∴ $E = \frac{1 \times 0.77 + 5 \times 1.51}{5+1} = 1.39 \text{ volt}$.

⊗⊗⊗ 9th general for a rxn

$a\text{ox}_1 + b\text{red}_2 \rightleftharpoons a\text{red}_1 + b\text{ox}_2$, the potential at the equivalence point is given by,

$$E = \frac{b \times E_1^\circ + a \times E_2^\circ}{a+b}$$

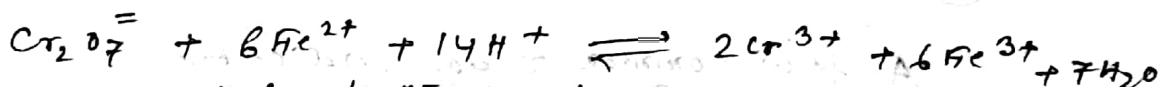
where E_1° and E_2° are the potentials of oxidising and reducing agent, 'a' and 'b' are their stoichiometric co-efficients.

Question: Calculate the potential at the equivalence point of a redox titration betⁿ manganate salt and dichromate salt,

given $E^\circ_{\text{Cr}_2\text{O}_7/\text{Cr}^{3+}} = 1.33 \text{ volt}$ and $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ volt}$.

⊗ (Manganate salt): — ($\text{FeSO}_4, \text{NH}_4\text{SO}_4, 5\text{H}_2\text{O}$)

Ans: At the equivalence point the overall rxn is



The potential at the equivalence point (E) is, given by

$$E = \frac{6 \times 1.33 + 1 \times 0.77}{6+1} = 1.25 \text{ volt}$$

Choice of redox indicator:

A redox indicator undergoes a detectable colour change in the vicinity of its standard redox potential. For every redox indicator there is a narrow potential range at which it changes colour. The choice of redox indicator should be such that its range of potential (E) for colour change falls within the limits of sharp change of

Potential at the equivalence point of a redox potential. ^{0.205} what happens when $K_2Cr_2O_7$ is added to BDS? exhibit colour change used as an indicator? In what range of potential does E° of BDS _{= 0.76V} Thus in the titration of Fe^{2+} ion by di-

chromate solution, the change of potential extends from 0.947 volt to 1.302 volt at the equivalence point. Therefore di-phenyl amine is unsuitable as an indicator.

In fact if used its colour will change when only about 70% Fe^{2+} is oxidised, since the potential then becomes 0.792 volts.

In presence of PO_4^{3-} or F^{-} ions, its potential range for colour change (0.73 volt to 0.79 volt) falls within the potential break of the titration curve (0.712V to 1.302V). Therefore di-phenyl amine is quite suitable as an indicator.

A redox indicator having a higher value of E° (e.g; N-phenyl anthranilic acid, $E^{\circ} = 1.08V$) Fe^{2+} ion can be titrated with dichromate solution even without the presence of H_2PO_4 or F^{-} ion, as 1.08 volt is already within the potential break (0.946 v to 1.302 v) in the titration curve.

A few common redox indicator

Indicator	Colour in		E° (volt) at pH=0
	reduced form	oxidised form	
1. Methylene blue	Colourless	Blue	0.52
2. Di-phenyl amine	Colourless	Blue violet	0.76
BDS Barium Diphenyl amine Sulphonate	Green	Red violet	0.83
3. Di-phenyl amine Sulphonic acid	Colourless	Red violet	0.85
4. N-phenyl anthranilic acid	Colourless	Red violet	1.08
5. Ferroin	Red	pale blue	1.19