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Subject: Chemistry
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Paper: C3T: Inorganic Chemistry
Topic: Redox and Precipitation Reaction
PART 5

Comments: Go through the whole lesson thoroughly.

[N.B.- Acknowledgement of indebtedness to Mr. Sibshankar Das, my respected Teacher regarding collection of study materials in Inorganic Chemistry**]**

Find out The standard electronpotential for MnO_4^-/MnO_2 redox couple in acid medium. Given $E^\circ_{MnO_4^-/Mn^{2+}} =$ 1.51 volt and $E^\circ_{MnO_2/Mn^{2+}} = 1.23$ volt at 298 K.

$$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$$

Thus The process may occure in two possible pathways

$$\begin{tikzcd} MnO_4^- \arrow[r, "E^\circ", "n=3"'] \arrow[rr, bend right, "1.51V"', "n=5"] & MnO_2 \arrow[r, "1.23V", "n=2"'] & Mn^{2+} \end{tikzcd}$$

As ΔG° for both the pathways are the same, we can write,

$$-5 \times F \times 1.51 = -F(3E^\circ + 2 \times 1.23)$$

$$\Rightarrow 5 \times 1.51 = 3E^\circ + 2 \times 1.23$$

$$\Rightarrow 3E^\circ = 7.55 - 2.46$$

$$\Rightarrow E^\circ = \frac{5.09}{3} = 1.696$$

$$\Rightarrow E^\circ \simeq 1.70 \text{ volt}$$

The standard electrode potential for MnO_4^-/MnO_2 redox couple in acid medium is 1.70 volt (Ans).

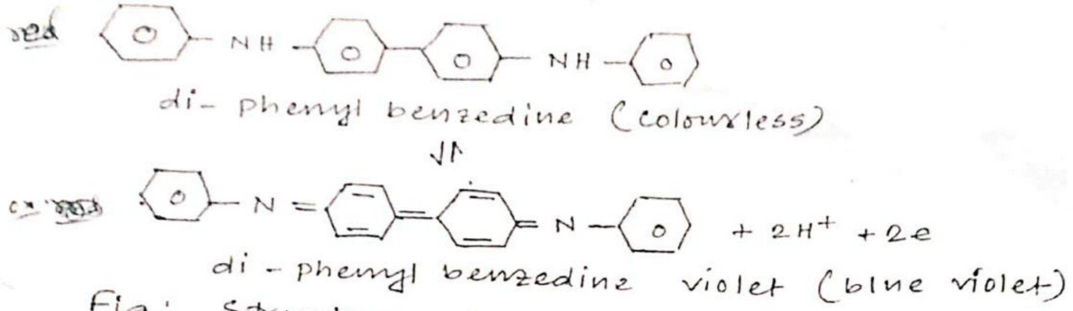
- Redox Indicators

The indicators that change colour at a definite potential of the titrated solⁿ in redox titration are called redox indicators.

Redox indicators are mostly organic dyes which can undergo reversible oxidation or reduction in the titration medium giving different colours. Usually the reduced form is colourless and the oxidised form is different colour. The redox indicator for any titration is so chosen that it gets oxidised very near the equivalence points of the titration e.g; colourless di-phenyl amine is oxidise to diphenyl benzedine violet (blue-violet) via diphenyl benzedine (colourless).

Di-phenyl amine (Colourless)

↓



Fig; Structure of di- phenyl amine, di - phenyl benzedine, di- phenyl benzedine violet.

Di-phenyl amine ($E° = 0.76V$ at $1M_{H^+}$) is a good redox indicator. Establish its working potential range.

The oxidised and reduced forms of a redox indicator establish a redox system with a characteristic electrode potential. If the two forms are expressed as In_{ox} and In_{red} respectively, we may write

$$\underset{\text{Coloured}}{In_{ox}} + ne \rightleftharpoons \underset{\text{Colourless.}}{In_{red}}$$

According to Nernst equation we can write

$$E_{In} = E^{\circ}_{In} + \frac{0.059}{n} \log \frac{[In_{ox}]}{[In_{red}]} \text{ at } 25°C.$$

It may be assumed that the colour of the oxidised form predominates when its concentration is ten times that of the colourless form. So for an appreciable colour of the oxidised form we have the condition,

$$E_{In} = E^{\circ}_{In} + \frac{0.059}{n} \log \frac{10}{1}$$
$$= E^{\circ}_{In} + \frac{0.059}{n}$$

Again the solution may be consider colourless when the reduced form has at least ten times greater concentration than the oxidised form. we may then write,

$$E_{In} = E^{\circ}_{In} + \frac{0.059}{n} \log \frac{1}{10}$$
$$= E^{\circ}_{In} - \frac{0.059}{n}.$$

Thus the range of potential values across which an indicator exhibits sharp contrast of colour will be,

$$\boxed{E_{In} = E^{\circ}_{In} \pm \frac{0.059}{n}}$$

The value of E° for di-phenylamine is 0.76 volt, while n=2 The range Therefore lies from 0.73 volt to 0.79 volt. Below 0.73 V The reduced form predominates and The solⁿ is colourless. As The potential increases more and more indicators are oxidise and at or above 0.79 volt The indicator will assume intense blue violet colour which is The colour of The oxidise form.

- **Redox titration and it's curve in a redox system.**

The EMF of a half cell depends upon The Conc. of different Chemical species present in The system. In any titration process, The relative amount of The two reacting species are gradually varied so That The solution being titrated acquires different potentials at different stages of The titration. This fact may be utilysed to locate The equivalents points of a titration.

Except when The titrant is itself Coloured, one may use a suitable indicator which would get oxidised at The potential of The equivalence point (or very close to it). This procedure is more suitable for redox titrations and The indicators used are called redox indicators.

Let us consider, The titration of Fe^{2+} ion by $KMnO_4$ solution in 1M acid medium. The rxn is -

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftharpoons 5Fe^{3+} + 4H_2O + Mn^{2+}$$

The rxn being reversible, The solution always Contains both original ions and The ions formed in course of titration. Therefore The solution Contains 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; $$E = 0.77 + \frac{0.059}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \qquad [H^+] = 1 \text{ at } 25^\circ C$$

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

Suppose 100 cc (N/10) $FeSO_4$ solution is titrated against (N/10) $KMnO_4$ solution.

Case - 1

When 50 cc permanganate has been 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 - 2

When 91 c.c MnO_4^- is added, Then the overall potential of the system is given below,

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

Case - 3.

When 99 c.c MnO_4^- has been added, Then

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

Case - 4

When 99.9 c.c MnO_4^- has been added, Then

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

Case - 5

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 - 6

When 101 C.C MnO_4^- is added, Then The overall potential of The system is given by

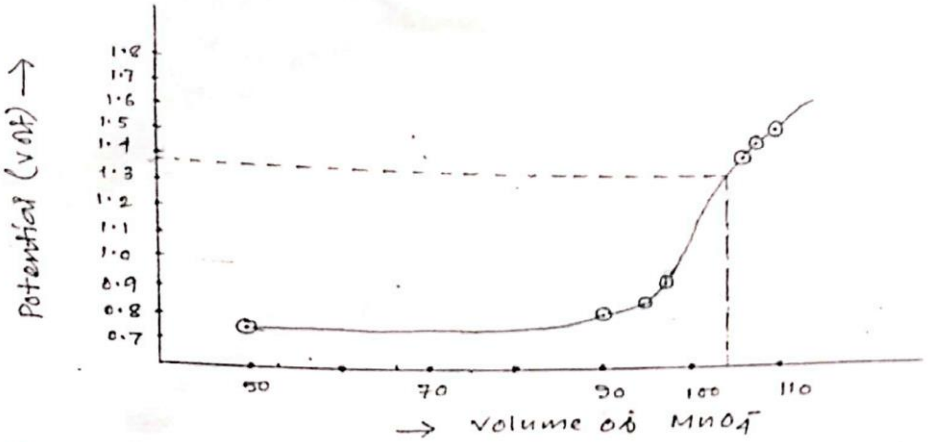
$$E = 1.51 + \frac{0.059}{5} \log \frac{1}{100}$$
$$= 1.487 \text{ volt.}$$

Case - 7

When 110 C.C MnO_4^- is added, Then 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 versus volume of MnO_4^- solution.



- Calculate the potential of the solution at the equivalence point.

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

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

In case of MnO_4^-/Mn^{2+} couple we can write

$$E = 1.51 + \frac{0.059}{5} \log \frac{[MnO_4^-]}{[Mn^{2+}]} \quad [C_{H^+} = 1]$$

$$\Rightarrow 5E = 5 \times 1.51 + 0.059 \log \frac{[MnO_4^-]}{[Mn^{2+}]} \quad \text{——} ②$$

Adding equation ① and ② we get,

$$6E = (0.77 + 5 \times 1.51) + 0.059 \log \frac{[Fe^{3+}][MnO_4^-]}{[Fe^{2+}][Mn^{2+}]} \quad \text{——} ③$$

Now at the equivalence point the overall equation is

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightleftharpoons 5Fe^{3+} + Mn^{2+} + 4H_2O$$

At the equivalence point, we can write

$$[Fe^{2+}] = 5[MnO_4^-] \text{ and } [Fe^{3+}] = 5[Mn^{2+}]$$

Putting the values of $[Fe^{2+}]$ and $[Fe^{3+}]$ in equ^n ③, we get,

$$6E = (0.77 + 5 \times 1.51) + 0.059 \log \frac{5[Mn^{2+}][MnO_4^-]}{5[MnO_4^-][Mn^{2+}]}$$

$$= (0.77 + 5 \times 1.51) + 0.059 \log 1$$

$$E = \frac{(0.77 \times 1 + 5 \times 1.51)}{1+5}$$

$$= 1.39 \text{ volt.}$$

In general for a rxn $a\,ox_1 + b\,red_2 \rightleftharpoons a\,red_1 + b\,ox_2$ The potential at equivalence point is given by

$$E = \frac{bE_1^\circ + aE_2^\circ}{b+a}$$

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

A Q) Calculate the potential at the equivalence point of the redox titration between Mohr's salt and $Cr_2O_7^{=}$ solution. Mohr's salt = $FeSO_4, (NH_4)_2SO_4, 6H_2O$.

Given $E^\circ_{Cr_2O_7^{=}/Cr^{3+}} = 1.33$ volt

$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$ volt

At the equivalence point the overall rxn is,

$$Cr_2O_7^{=} + 6Fe^{2+} + 14H^+ \rightleftharpoons 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

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

$$= \frac{8.75}{7} = 1.25 \text{ volt.}$$

- **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 E (Potential) for colour change falls within the limits of sharp change of potential at the equivalence point of a redox titration".

Thus in the titration of Fe^{2+} ion by permanganate, the change of potential extends from 0.947 volt to 1.475 volt at the equivalence point. Therefore di-phenyl amine is unsuitable as an indicator. In fact if used it's colour will change when only about 80% Fe^{2+} is oxidised, since the potential then becomes 0.80 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 (0.85 volt to 1.475 volt). for F⁻ ion Therefore di-phenyl amine is then quite suitable as an Indicator.

In the titration of Fe^{2+} by $Cr_2O_7^{=}$ ion, the extend of break in the titration curve is from 0.917 volt to 1.30 volt. Hence the titration to be carried out in presence of H_3PO_4 or F^- ions, using di-phenyl amine indicator, in order to extend the break in the titration curve from 0.65 volt to 1.30 volt. In this case the potential range of the indicator (0.73 volt to 0.79 volt) for colour change may fall within the limits of potential change at the equivalence point.

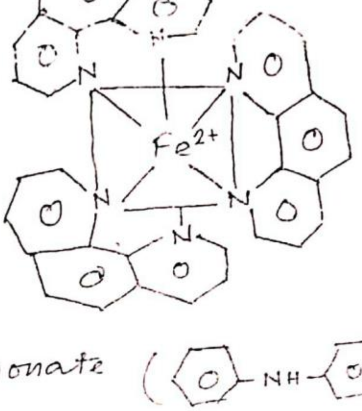
A redox indicator having a higher value of E° (e.g: N-phenyl anthranilic acid, $E^\circ = 1.08$ volt), Fe^{2+} ion can be titrated with di-chromate even without the presence of H_3PO_4 or F^- ions, as 1.08 volt is already within potential break (0.947 volt to 1.30 volt) in the titration curve.

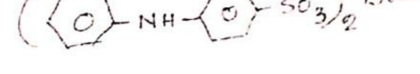
- A few common redox indicator.

Indicator	Colour in Reduced form	Colour in Oxidising form	E° (volt) at $pH = 0$
a) Methylene blue	a) Colourless	a) Blue	a) 0.52
b) Di-phenyl amine	b) Colourless	b) Blue violet	b) 0.76
c) Di-phenyl amine sulphonic acid BDS	c) Colourless	c) Red violet	c) 0.85 0.83
d) N-phenyl anthranilic acid	d) Colourless	d) Red violet	d) 1.08
e) Ferroin	e) Red	e) Pale blue	e) 1.14

* Ferroin: A complex of ortho phenanthroline with Fe^{2+}

$[Fe(o\text{-}Phen)_3]^{2+}$



BDS = Barium diphenyl amine sulphonate


W9 ⊕ Redox potential of an aqueous soln containg Fe^{3+} and Fe^{2+} at 25°C is 0.70 volt. Calculate the ratio of $[Fe^{2+}]/[Fe^{3+}]$ in the sol^n. Given $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$ V

The Nernst equation for cell emf is

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

$$\Rightarrow 0.70 = 0.77 + 0.059 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$\Rightarrow \log_{10} \frac{[Fe^{3+}]}{[Fe^{2+}]} = -0.07/0.059$$

$$\Rightarrow \frac{[Fe^{3+}]}{[Fe^{2+}]} = \frac{13}{200}$$

$$\Rightarrow [Fe^{2+}] : [Fe^{3+}] = 200 : 13$$

* • Brass can be electrodeposited in presence of KCN sol^n – explain.

The standard reduction potential of the system Cu^{2+}/Cu is much higher (0.34 volt) than that of the system Zn^{2+}/Zn (−0.763 volt) both in aqueous solution. So, when an aqueous solution containing Zn and Cu salts is electrolysed, Cu deposits earlier. In presence of excess KCN or NaCN both Zn^{2+} and Cu^{2+} form complexes, $Zn(CN)_4^{2-}$ and $Cu(CN)_4^{3-}$ respectively. The later ion has a much higher formation constant and hence the concentration of free Cu^{2+} ion in sol^n is reduced to much greater extended than for the Zn^{2+} ion. Therefore the potentials of the two couples are brought close to one another. Thus the simultaneous deposition of both Cu and Zn can be achieved. Thus Brass can be electrodeposited in Presence of KCN sol^n.

$$Cu^{2+} + e \rightleftharpoons Cu^+$$

$$Cu^+ + 4CN^- \rightleftharpoons Cu(CN)_4^{3-} \quad Zn^{2+} + 4CN^- \rightleftharpoons Zn(CN)_4^{2-}$$

• 1(N) $KMnO_4$ solution may mean 0.33 (M) or 0.20 (M) $KMnO_4$ solution – comment

The equivalent weight of an oxidant can be calculated from the change in oxidation no. of the reduced element in a reaction. In the reduction of $KMnO_4$ to a manganous salt in an acid medium ($MnO_4^- \longrightarrow Mn^{2+}$) the change in oxidation number of

$+7 - 2 = 5$.

Therefore the equivalent weight of $KMnO_4$ is 1/5 of the molecular weight in acid medium i.e $1(N)\ KMnO_4 = \frac{1(M)\ KMnO_4}{5} = 0.20$ molar $KMnO_4$.

In alkaline slightly or nutral medium $KMnO_4$ is reduced to MnO_2. The change of oxidation no of $Mn = +7 - 4 = +3$ i.e in ~~alkaline~~ this medium, The equivalent weight of $KMnO_4$ is 1/3 of the molecular weight. Therefore $1(N)\ KMnO_4 = \frac{1(M)\ KMnO_4}{3}$

$= 0.33$ molar $KMnO_4$.

- Frost Diagram.

Let us consider an element 'x' capable of forming a number of species with varying oxidation number 'N'. For each species we have a couple $x(N)/x(0)$ with a characteristic potential $E°$.

$$x(N) + Ne \xrightarrow{E^\circ} x(0)$$

Frost diagram of an element is a plot of $NE°$ against 'N'. For different couples $x(N)/x(0)$, since N electrons are involved in the reduction we have $-\Delta G^\circ = NFE^\circ$ i.e $NE^\circ = \frac{-\Delta G^\circ}{F}$. Where $\Delta G°$ is the Gibb's free energy change for the half rxn. So Frost diagram is a plot of Gibb's free energy change against oxidation number. The species representing the most stable oxidation state of an element will have the lowest $-\Delta G°$ i.e The lowest $NE°$. therefore The most stable oxidation state of an element will lie lowest in its Frost diagram. All frost diagrams will have an $NE° = 0$ and $N = 0$ plot for the elementary state.

The slope of the line joining any two points in a Frost diagram is equal to the standard reduction Potential of the couple represented by the two points.

Let us consider the following Latimer diagram

$$\begin{tikzcd}
\underset{(0)}{O_2} \arrow[r, "+0.70V"] \arrow[rr, bend right, "1.23\ volt"'] & \underset{(-I)}{H_2O_2} \arrow[r, "+1.76V"] & \underset{(-II)}{H_2O.}
\end{tikzcd}$$

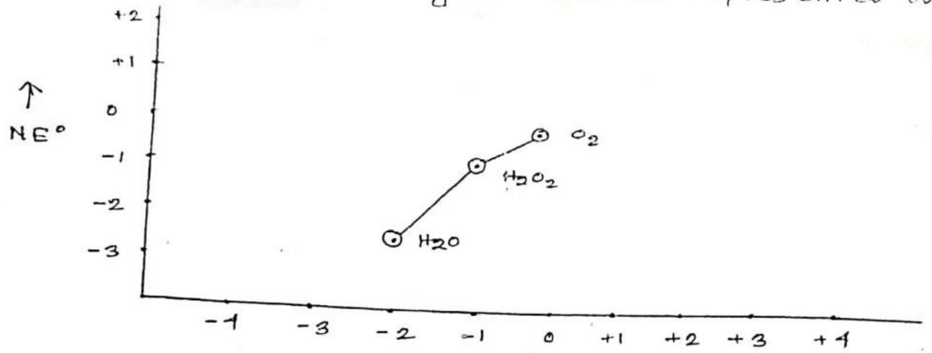
In case of H_2O_2, oxidation number of oxygen $= -1$

$\therefore\ NE^\circ = -1 \times 0.70 = -0.70$ volt

In case of H_2O, oxidation number of oxygen $= -2$

$NE^\circ = -2 \times 1.23 = -2.4$ volt

Hence the Frost diagram can be represented as :



The difference between two NE° values is $\{-0.70-(-2.46)\} = 1.76$ volt. The change in oxidation number of oxygen $= -1-(-2) = +1$. Hence,

$$\text{Slop} = \frac{\text{change in } NE^\circ \text{ values}}{\text{change in oxidation no.}} = \frac{1.76}{1} = 1.76 \text{ volt}$$

Therefore standard reduction potential can be calculated from the Frost diagram.

- Constract the Frost diagram from the following Latimer diagram,

$$\begin{tikzcd}
MnO_4^- \arrow[r, "0.56V"] & MnO_4^{2-} \arrow[r, "2.26V"] & MnO_2 \arrow[r, "0.95V"] & Mn^{3+} \arrow[d, "1.51V"] \\
 & & Mn & Mn^{2+} \arrow[l, "-1.18V"']
\end{tikzcd}$$

In case of Mn^{3+}, $N = 3$.

$NE^\circ = 1 \times (+1.51) + 2(-1.18) = -0.85V$

oxidation number of Mn in Mn^{2+} is 2

$NE^\circ = 2 \times (-1.18) = -2.36V$ $N = 2$

In case of MnO_2, oxidation no of $Mn = +4$

$NE^\circ = (1 \times 0.95) - 0.85$

$= 0.10 V$ $N = 4$

In case of $MnO_4^{=}$, oxidation no. of $Mn = +6$

$NE^\circ = 2 \times 2.26 + 0.1$

$= 4.62 V$ $N = 6$

In case of MnO_4^-, oxidation no. of $Mn = +7$

$NE^\circ = 0.56 + 4.62$

$= 5.18V$ $N = 7$