Objectives

At the end of this unit , the student is expected to be able to :

1- Understand the concept of the oxidation reduction titration .
2- Calculate the potential of the titrated solution at any point during the titration .
3- Select the suitable indicator for a certain titration .
4- Understand the factors affecting the redox titration .
5- Comprehend the pretreatment of the sample process prior to its redox titration .
6- realize the wide applications of the redox reactions an titrations .

Introduction

Another type of titration is the oxidation-reduction titration which is also called Redox titration , and is used to determine the oxidizing agent (oxidant) or reducing agent (reductant) in a solution. When performing redox titrations, either the reducing or oxidizing agent will be used as the titrant against the other agent. The purpose of this titration is to determine the transfer of electrons from one substance to the other, similar to that of a redox reactions , in order to determine the reductant or oxidant. The end point of such titrations can be determined by either a color changing indicator as in this unit or a potentiometer .There are numerous applications for the redox titration in chemistry , pharmaceutical preparations , environmental analysis , agriculture and many more .

Redox Titration Curves

To evaluate a redox titration we need to know the shape of its titration curve. In an acid–base titration or a complexation titration, the titration curve shows how the concentration of H_3O^+ (as pH) or M^{n+} (as pM) changes as we add titrant . Because in acid-base titration the indicator is sensitive for pH changes while in complexation titration the indicator is sensitive for changes in pM . For a redox titration it is convenient to monitor the titration reaction's potential instead of the concentration of one species because the indicator is sensitive for changes in potential as we will see later.

Redox titration curves

You may recall from unit 10 that the Nernst equation relates a solution’s potential to the concentrations of reactants and products participating in the redox reaction. Consider, for example, a titration in which an analyte in a reduced state, A_{red}, reacts with a titrant in an oxidized state, B_{ox}.

$$n_A\ (B_{OX} + n_B \leftrightarrow B_{RED})\ , \quad E^0_B \quad \text{(titrant)}$$

$$n_B\ (A_{red} \leftrightarrow A_{ox} + n_A)\ , \quad E^0_A \quad \text{(analyte)}$$

$$n_B\, A_{red} + n_A\, B_{ox} \leftrightarrow n_B\, A_{OX} + n_A\, B_{red}$$

Redox titration curves

where A_{ox} is the analyte's oxidized form, and B_{red} is the titrant's reduced form. The reaction's potential, E_{cell}^0 , is the difference between the standard potentials for each half-reaction.

$$E_{cell}^0 = E_B^0 - E_A^0$$

After each addition of titrant the reaction between the analyte (titrand) and the titrant reaches a state of equilibrium. Because the potential at equilibrium is zero, the analyte's and the titrant's reduction potentials are identical :

Redox titration curves

At equilibrium and at any point during titration :

$$E_{cll} = E_A - E_B = 0.0$$

$$E_A = E_B$$

This is an important observation because we can use either half-reaction to monitor the changes of potential during titration.

Before the equivalence point the titration mixture consists of appreciable quantities of the analyte’s oxidized and reduced forms. The concentration of unreacted titrant, however, is very small. The potential, therefore, is easier to calculate if we apply the Nernst equation for the analyte’s half-reaction

Redox titration curves

$$E = E_A = E_A^{0} + \frac{0.059}{n_A}\log\frac{[A_{OX}]}{[A_{RED}]} \qquad (1)$$

Note that at the middle of the titration where half of $[A_{OX}]$ is converted to $[A_{RED}]$ which means $[A_{OX}] = [[A_{RED}]$ and if the half reaction of the analyte is symmetrical , the potential of the titration solution (conical flask solution) equal to the standard potential of the analyte

$$E = E_A^{0} + \frac{0.059}{n_A}\log\frac{[A_{OX}]}{[A_{RED}]} = E_A^{0} + \frac{0.059}{n_A}\log 1 = E_A^{0}$$

Redox titration curves

After the equivalence point it is easier to calculate the potential using the Nernst equation for the titrant's half-reaction.

$$E = E_B = E_B^{0} + \frac{0.059}{n_B}\,\frac{[B_{ox}]}{[B_{RED}]} \qquad (2)$$

If the titrant half reaction is symmetrical , the potential of the titration solution will be equal to the standard potential of the titrant after adding double its equivalent amount i.e $[B_{OX}] = [B_{RED}]$, then , $E = E_B^0$

At equivalent point : From the balanced redox reaction equation we can say that at the equivalent point , n_A moles of B_{ox} have been added to n_B moles of A_{red} (see unit 3) so we can write the following equation :

Redox titration curves

$$\left\{\frac{[A_{RED}]}{[B_{OX}]}\right\}_{eq} = \frac{n_B}{n_A} = \left\{\frac{[A_{OX}]}{[B_{RED}]}\right\}_{eq}$$

From the above equation we also write the following equations :

$$\left\{\frac{[A_{OX}]}{[A_{RED}]}\right\}_{eq} = \left\{\frac{[B_{RED}]}{[B_{OX}]}\right\}_{eq}$$

$$\left\{\frac{[B_{OX}]}{[B_{RED}]} X \frac{[A_{OX}]}{[A_{RED}]}\right\}_{eq} = 1 \qquad (3)$$

The potential at equivalent point E_{eq} can be calculated either by using equation (1) or equation (2) . Multiplying equation (1) by n_A and equation (2) by n_B and adding them together[taking in consideration equation (3)] we obtain :

Redox titration curves

$$(n_A+n_B)E_{eq} = n_B E_B^0 + n_A E_A^0 + 0.059\log\left\{\frac{[B_{OX}]}{[B_{RED}]}\, X\, \frac{[A_{OX}]}{[A_{RED}]}\right\}_{eq} \qquad (4)$$

$$(n_A+n_B)E_{eq} = n_B E_B^0 + n_A E_A^0 + 0.059\log 1 = n_B\, E_B^0 + n_A\, E_A^0$$

$$E_{eq} = \frac{n_B\, E_B^0 + n_A\, E_A^0}{(n_A + n_B\,)} \qquad (5)$$

Equation (5) can be used for the calculation of E_{eq} for any redox titration except in the following two cases we should use equation (4) :

Case one : If one of the participants of the redox reaction does not change its oxidation state during the reaction e.g. H^+ in the titration of Fe^{2+} with MnO_4^- .

Redox titration curves

In this case we should derive equation (4) thus :

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

$$E_{eq} = E_{Fe} = E_{Fe}^0 + \frac{0.059}{n_{Fe}} \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \qquad (6)$$

$$E_{eq} = E_{Mn} = E^0{}_{Mn} + \frac{0.059}{n_{Mn}} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]} \qquad (7)$$

Multiplying equation (6) by n_{Fe} and equation (7) by n_{Mn} and adding the two equations together we obtain :

$$(n_{Fe} + n_{Mn})E_{eq} = n_{Fe}E_{Fe}^0 + n_{Mn}E_{Mn}^0 + 0.059 \log \frac{[Fe^{2+}][MnO_4^-][H^+]^8}{[Mn^{2+}]} \qquad (8)$$

Redox titration curves

From the above balanced equation we can write :

$$[Fe^{3+}] = 5\,[Mn^{2+}]$$

$$[Fe^{2+}] = 5\,[MnO_4^-]$$

Substituting in equation (8) and canceling we obtain :

$$(n_{Fe} + n_{Mn})E_{eq} = n_{Fe}\,E_{Fe}^{0} + n_{Mn}\,E_{Mn}^{0} + 0.059\,\log \frac{5[Mn^{2+}][MnO_4^-][H^+]^8}{5[MnO_4^-][Mn^{2+}]}$$

$$E_{eq} = \frac{n_{Fe}\,E_{Fe}^{0} + n_{Mn}\,E_{Mn}^{0}}{n_{Fe} + n_{Mn}} + \frac{0.059}{n_{Fe} + n_{Mn}}\log\,[H^+]^8 \qquad (9)$$

Redox titration curves

Note that equation (9) turns to equation (5) if [H^+] = 1.0 M .

Case two : If one of the half reactions is unsymmetrical . When one mole produce one mole or two moles produce two moles … etc we call the half reaction symmetrical otherwise it is unsymmetrical . For example , in the titration of Fe^{2+} by $Cr_2O_7^{2-}$, we can see that the $Cr_2O_7^{2-}$ half reaction is unsymmetrical :

$$Cr_2O_7^{2-} + 6\,Fe^{2+} + 14\,H^+ \leftrightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$$

Note , one mole $Cr_2o_7^{2-}$ produce two moles Cr^{3+}

Redox titration curves

Multiplying and adding as before we obtain :

$$(n_{Fe} + n_{Cr})E_{eq} = n_{Fe}E_{Fe}^{0} + n_{Cr}E_{Cr}^{0} + 0.059\ \log\frac{[Fe^{3+}][Cr_2O_7^{2-}][H^+]^{14}}{[Fe^{2+}][Cr^{3+}]^2} \qquad (10)$$

At equivalent point and from the balanced equation we obtain :

$$[Fe^{3+}] = \frac{6}{2}\,[Cr^{3+}] = 3\,[Cr^{3+}]$$

$$[Fe^{2+}] = 6\,[Cr_2O_7^{\,2-}]$$

Substituting in equation (10) and canceling we obtain :

Redox titration curves

$$E_{eq} = \frac{n_{Fe} E_{Fe}^{0} + n_{Cr} E_{Cr}^{0}}{n_{Fe} + n_{Cr}} + \frac{0.059}{n_{Fe} + n_{Cr}} \log \frac{3[Cr^{3+}][Cr_2O_7^{2-}][H^+]^{14}}{6[Cr_2O_7^{2-}][Cr^{3+}]^2}$$

$$E_{eq} = \frac{n_{Fe} E_{Fe}^{0} + n_{Cr} E_{Cr}^{0}}{n_{Fe} + n_{Cr}} + \frac{0.059}{n_{Fe} + n_{Cr}} \log \frac{[H^+]^{14}}{2[Cr^{3+}]}$$

The last equation indicates that E_{eq} in this titration depends on the concentration of both H^+ and Cr^{3+} .

Example: In the titration of 10 mL of 0.1 M Sn^{2+} by 0.2 M Ce^{4+} , calculate the potential of the titration solution in the conical flask after the addition of the following volumes of the

Redox titration curves

titrant Ce^{4+} solution : (1) 5 mL , (2) 10 mL , (3) 15 mL ? And also calculate the concentration of all ions at the equivalent point ?

Solution :

$$2\,(Ce^{4+} + e \leftrightarrow Ce^{3+}) \qquad E_{Ce}^{0} = 1.44\ V$$
$$Sn^{2+} \leftrightarrow Sn^{4+} + 2e \qquad E_{Sn}^{0} = 0.15\ V$$

$$2\,Ce^{4+} + Sn^{2+} \leftrightarrow 2\,Ce^{3+} + Sn^{4+}$$

First we calculate the volume of titrant at equivalent point V_{eq} thus :

Redox titration curves

mmoles Ce^{4+} = mmoles Sn^{2+}X 2 = 10 X 0.1 X 2 = 2

$$M_{Ce} = 0.2 = \frac{no.\ mmoles}{V_{eq}(mL)} = \frac{2}{V_{eq}(mL)} \quad \therefore V_{eq}(mL) = 10\ mL$$

(1) : After addition of 5 mL of Ce^{4+} solution (before equivalent point) , we apply the Nernst equation to Sn half reaction thus :

$$E = E_{Sn} = 0.15 + \frac{0.059}{2} \log \frac{\dfrac{(5\ X\ 0.2)\ X\ \frac{1}{2}}{(10+5)}}{\dfrac{[(10\ X\ 0.1) - (5\ X\ 0.2)\frac{1}{2}]}{(10+5)}} = 0.15\ V$$

Redox titration curves

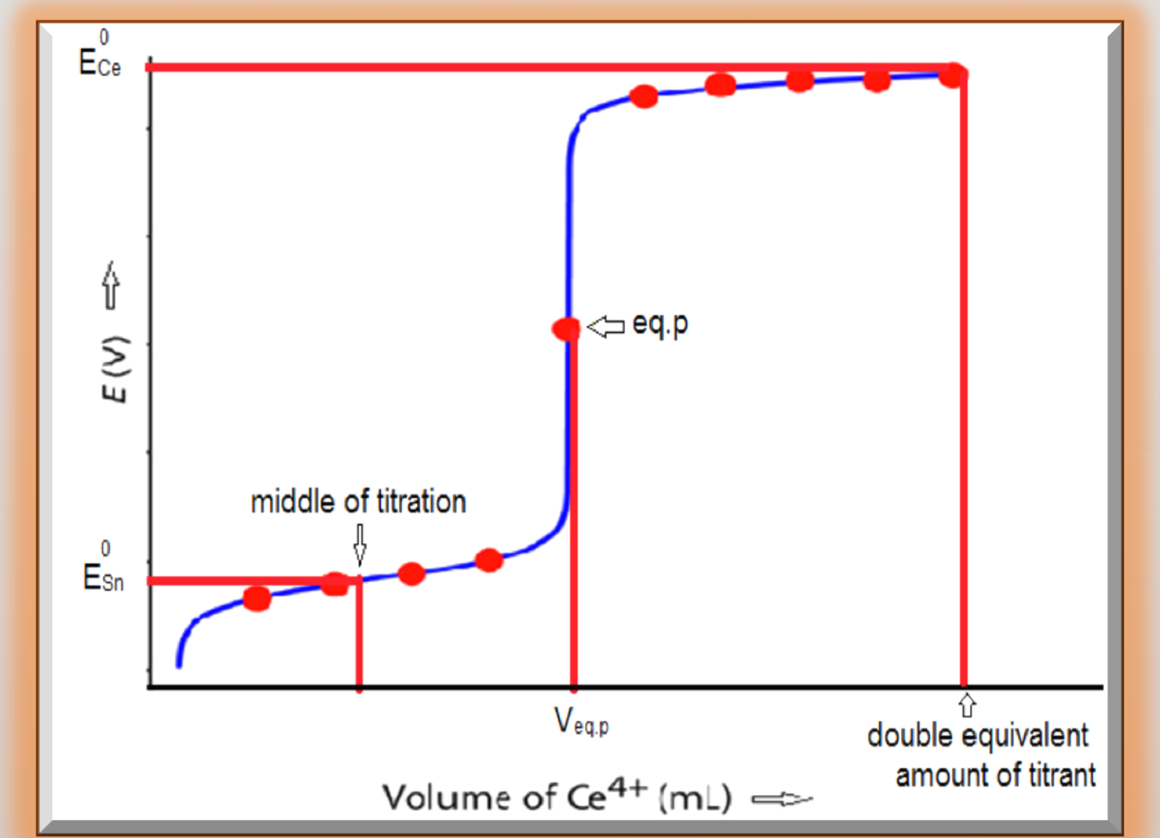
(2) : After adding 10 mL i.e. at equivalent point we apply equation (5) thus :

$$E_{eq.p.} = \frac{1\ X\ 1.44 + 2\ X\ 0.15}{(1+2)} = 0.58\ V$$

To calculate the concentration of the ions at equivalent point we apply Nernst equation to Sn half reaction thus :

$$E_{eq.p.} = 0.58 = E_{Sn} = 0.15 + \frac{0.059}{2} \log \frac{[Sn^{4+}]}{[Sn^{2+}]}$$

From this equation we can calculate the following :



Titration curve for the titration of Fe^{2+} with Ce^{4+}. eq.p is at middle of the curve .

Redox titration curves

$$\frac{[Sn^{4+}]}{[Sn^{2+}]} = 3.8\ X\ 10^{14}$$

$$[Sn^{4+}] = \frac{10\ X\ 0.1}{10+10} = 0.05\,M = \frac{[Ce^{3+}]}{2}$$

$$[Ce^{3+}] = 0.1\ M$$

$$\frac{[Sn^{4+}]}{[Sn^{2+}]} = \frac{0.05}{[Sn^{2+}]} = 3.8\ X\ 10^{14}$$

$$[Sn^{2+}]\ \approx 1.3\ X\ 10^{-16}\ M\ = \frac{[Ce^{4+}]}{2}$$

$$[Ce^{4+}] = 2.6\,X\ 10^{-16}\ M$$

(3) : After adding 15 mL i.e. after equivalent point we apply Nernst equation to titrant half reaction thus :

Redox titration curves

$$E = E_{Ce} = 1.44 + \frac{0.059}{1}\log\frac{\dfrac{[\,(15\,X\,0.2)-(10\;X\;0.1)\frac{2}{1}]}{(10+15)}}{\dfrac{(10\;X\;0.1)\;x\frac{2}{1}}{(10+15)}} = 1.42\;\;V$$

Example : In the titration of 10 mL 0.2 M of Fe^{2+} by 0.01 M of MnO_4^- , Calculate the potential of the conical flask solution after adding the following volumes of MnO_4^- titrant solution : (1) 10 mL , (2) $V_{eq.p}$, (3) 50 mL ?

Redox titration curves

Solution :

$$\begin{array}{l}
MnO_4^- + 8H^+ + 5\,e \leftrightarrow Mn^{2+} + 4H_2O \quad , \quad E_{Mn}^0 \; +1.51 \text{ V} \\
5 \; Fe^{2+} \quad \leftrightarrow \quad 5 \; Fe^{3+} + 5 \; e \quad , \quad E_{Fe}^0 \; = 0.77 \text{ V} \\
\hline
MnO_4^- + 8\,H^+ + 5\,Fe^{2+} \leftrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O
\end{array}$$

mmoles MnO_4^- =mmoles Fe^{2+}X 1/5=10 X 0.2 X 1/5 = 0. 4

$$M_{MnO_4^-} = 0.01 = \frac{no.\ mmoles}{V_{.eq.p}\,(ml)} = \frac{0.4}{V_{eq.p}\,(ml)}$$

$$\therefore\ V_{eq.p}\,(ml) = 40\ ml$$

Redox titration curves

(1) : After adding 10 mL of titrant solution i.e. before equivalent point we apply Nernst equation on analyte :

$$E = E_{Fe} = 0.77 + \frac{0.059}{1} \log \frac{\frac{(10 X 0.01)\frac{5}{1}}{(10+10)}}{\frac{[(10\ X\ 0.2)-(10 X 0.01)\frac{5}{1}]}{(10+10)}} \approx 0.74 V$$

(2) At equivalent point i.e after adding 40 mL of titrant solution we can apply equation (5) since $[H^{+}] = 1.0$ M

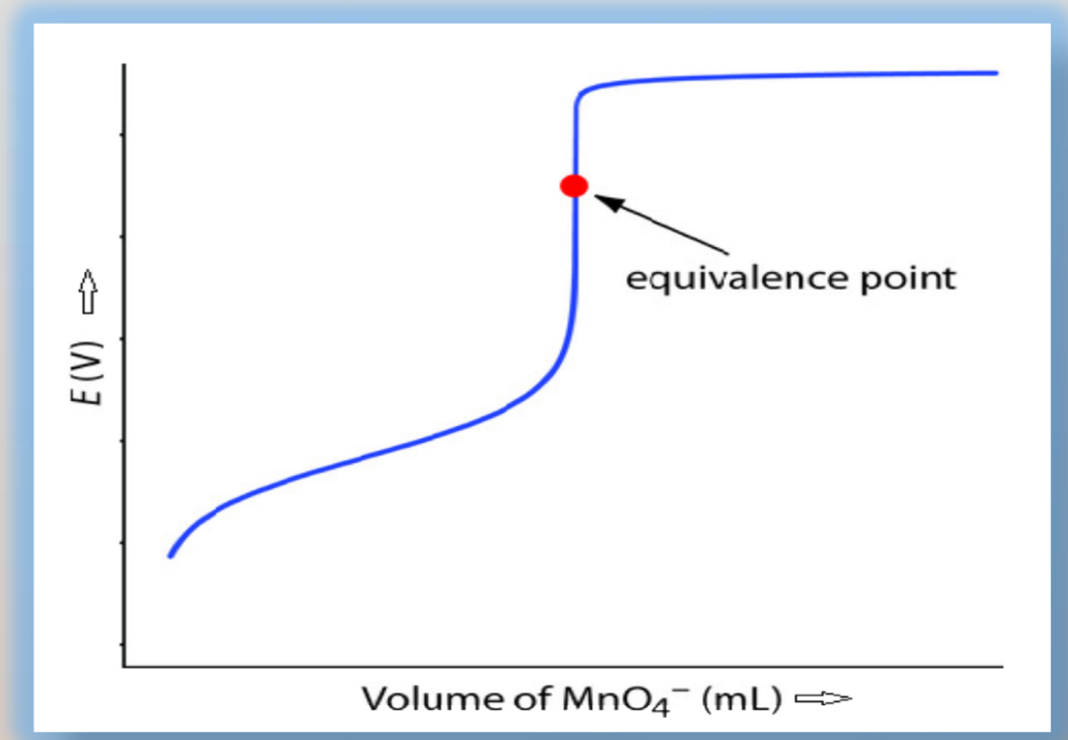
$$E_{eq} = \frac{5\ X\ 1.51 + 1\ X\ 0.77}{(5+1)} = 1.39\ V$$

Redox titration curves

(3) : After adding 50 mL i.e. after equivalent point we apply Nernst equation on the titrant , thus :

$$E = E_{Mn} = 1.51 + \frac{0.059}{5} \log \frac{\left\langle \frac{[(50 X 0.01) - (10 X 0.2)\frac{1}{5}]}{(10+50)} \right\rangle X (1)^8}{\frac{(10\ X\ 0.2)\frac{1}{5}}{(10+50)}} = 1.50 \quad V$$

You may have noticed that the potential in the titration conical flask solution increases during titration in both previous examples because we are titrating a reducing analyte by oxidizing titrant .When we reverse the



a typical titration curve for titration of Fe^{2+} with MnO_4^-. Note that the titration's equivalence point is asymmetrical so the eq.p. is not at the middle of the curve .

Factors affecting redox titration curve

titration , the potential will decrease .

1- Looking to the Nernst equation :

$$E = E^0 + \frac{0.059}{n} \log \frac{[OX]}{[RED]}$$

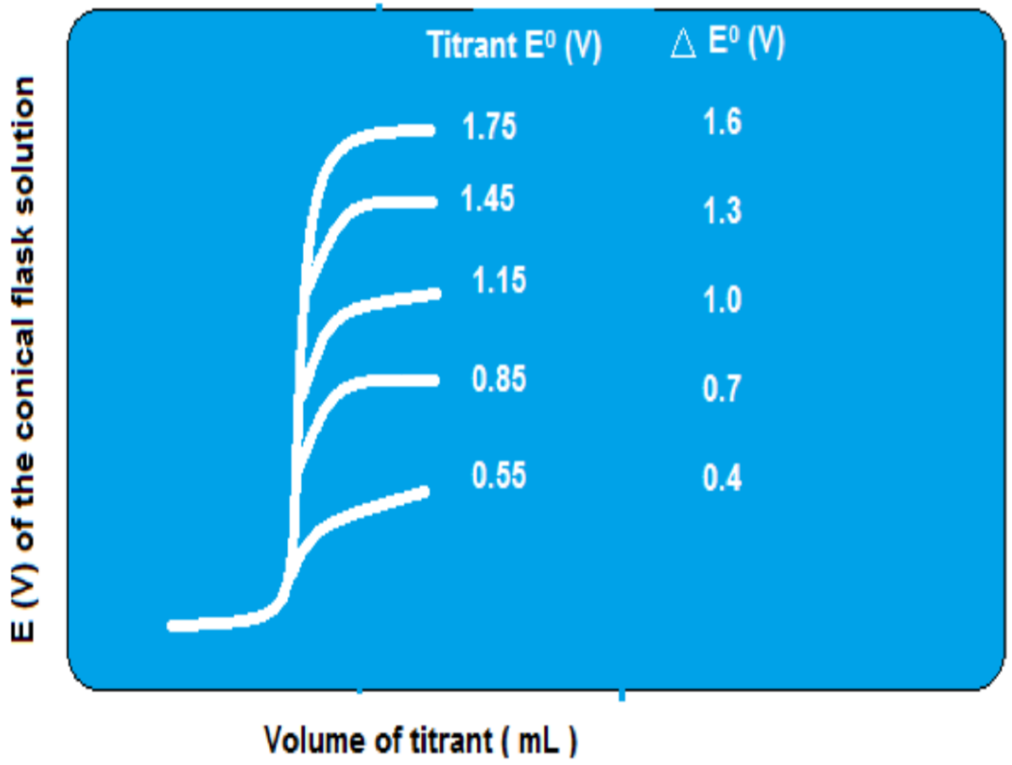
we can see that the ratio : [OX] / [RED] Is concentration independent because increasing of [OX] will lead to increasing of [RED] so that the ratio and then the potential will not be affected . Consequently , titration curves for redox reactions are usually independent of analyte and titrant concentrations . This behavior is in distinct contrast to that observed in other types of titration .

Factors affecting redox titration curve

2- Completeness of the reaction : The higher the value of K_{eq} the more complete will be the reaction . The value of K_{eq} depends on the difference between the standard potential of analyte and titrant (go back to unit 10) :

$$\log K_{eq} = \frac{N\Delta E^0}{0.059}$$

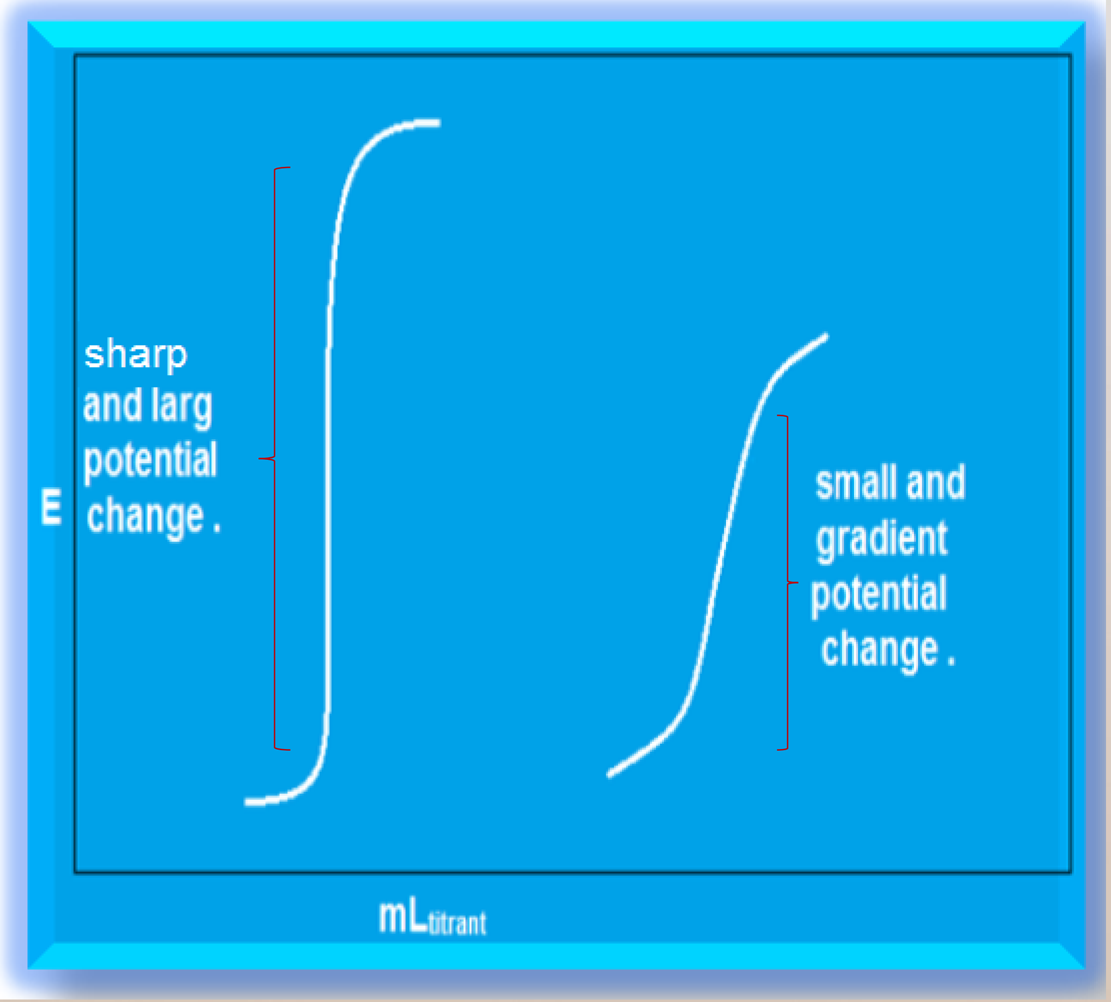
K_{eq} is also directly proportional to the number of electrons transferred during the redox reaction (N). The graph shows the effect of ΔE^0 on the shape of the titration curve . Note if in the graph (N = 1), the change in potential at equivalent point will be less .



Titration curve for the titration of Sn^{2+} ($E^0 = 0.15$ V) with various titrants (N for all reactions equal 2) .

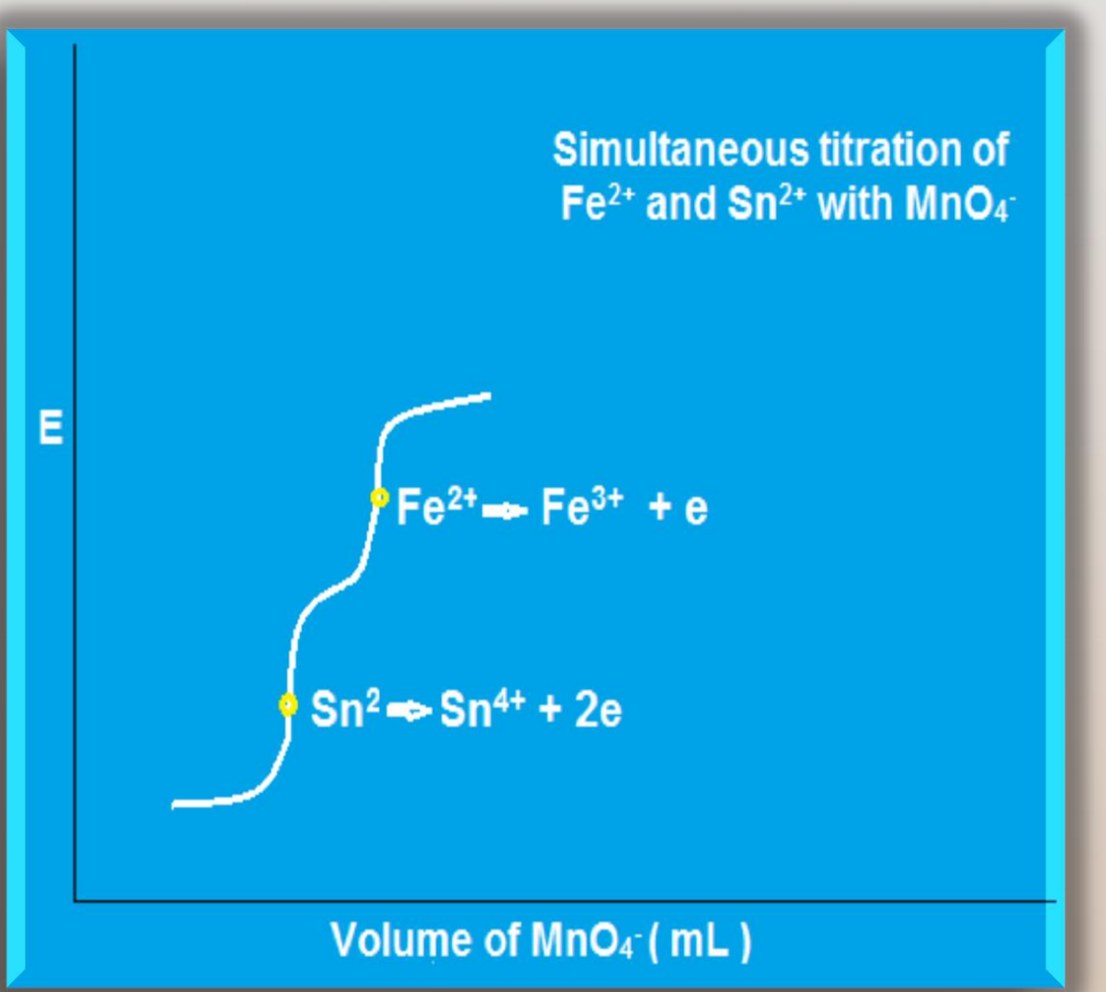
Factors affecting redox titration curve

3- If $n_{Ox} = n_{Red}$ the titration curve will be Symmetric and the equivalent point match the center point of the curve (see the previous titration curve for Fe^{2+} with Ce^{4+}) . But if $n_{Ox} \neq n_{Red}$, the curve is asymmetric and the two point do not match (see the previous curve for the titration of Fe^{2+} with MnO_4^-). The larger and the sharper the potential change at the equivalent point region the more successful the titration …why ? (see unit 8) .



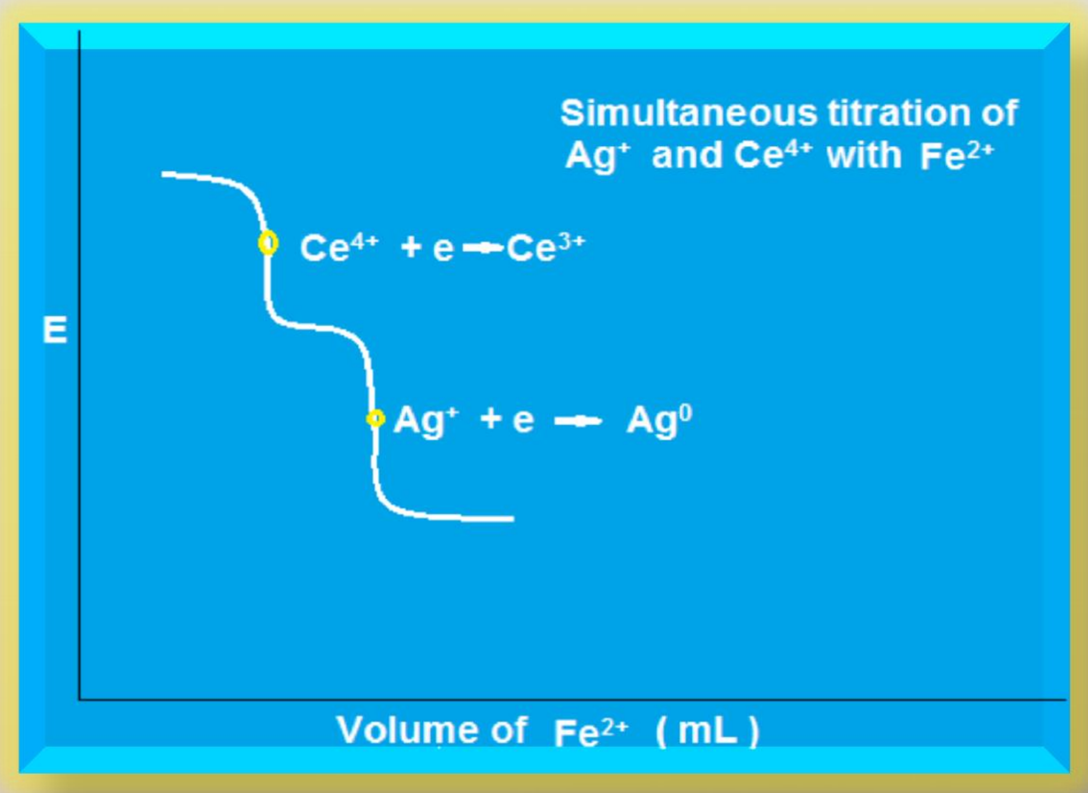
Titration of a mixture

It is possible to titrate simultaneously two reducing forms with standard solution of oxidizing form if there is a sufficient difference in their standard potentials . For example Fe^{2+} ($E^0 = 0.77$) and Sn^{2+} ($E^0 = 0.15$) can be titrated with MnO_4^- , where Sn^{2+} will react first because it is stronger as a reducing agent than Fe^{2+} .The result is two well separated equivalent points .



Titration of a mixture

Likewise , two oxidants e.g. Ag^+ (E^0=0.8) and Ce^{4+} (E^0 = 1.44) can be titrated with a standard solution of a reducing agent e.g. Sn^{2+} (E^0=0.15) . Note that if the difference between the standard potential of the mixture substances is not sufficient then the two equivalent point will overlap giving one equivalent point .



Equivalent point Detection

A redox titration’s equivalence point occurs when we react stoichiometrically equivalent amounts of analyte and titrant. As is the case with acid–base and complexation titrations . For an acid–base titration or a complexometric titration the equivalence point is almost identical to the inflection point on the steeping rising part of the titration curve i.e in the middle of this steep rise in the titration curve, which makes it relatively easy to find the equivalence point when you sketch these titration curves .

Equivalent point Detection

We call this a **symmetric equivalence point**. If the stoichiometry of a redox titration is symmetric (one mole of titrant reacts with each mole of analyte) then the equivalence point is symmetric. If the titration reaction’s stoichiometry is not 1:1, then the equivalence point is closer to the top or to bottom of the titration curve’s sharp rise. In this case we have an **asymmetric equivalence point**.

Equivalent point Detection

It is possible to derive the titration curve and from this curve you can find the titrant volume at the equivalent point , however , this method is time consuming and costly . The easiest way is to use an indicator . There are three types of indicators :

1- Self indicators : The oxidized and reduced forms of some titrants, such as MnO_4^-, have different colors. A solution of MnO_4^- is intensely purple. In an acidic solution, however, permanganate's reduced form, Mn^{2+}, is nearly colorless. When using MnO_4^- as a titrant, the analyte's solution remains colorless until the equivalence point. The first drop of excess MnO_4^- produces a permanent tinge of purple, signaling the end point.

Equivalent point Detection

2-Specific indicators : Some indicators form a colored compound with a specific oxidized or reduced form of the titrant or the analyte . Starch, for example, forms a dark blue complex with iodine I_3^-. We can use this distinct color to signal the presence of excess I_3^- as a titrant (a change in color from colorless to blue) or the completion of a reaction consuming I_3^- as the analyte (a change in color from blue to colorless). Another example of a specific indicator is thiocyanate, SCN^-, which forms a soluble red-colored complex of $Fe(SCN)^{2+}$ with Fe^{3+}.

Equivalent point Detection

3- True redox indicators : The most important class of indicators are substances that do not participate in the redox titration, but whose oxidized and reduced forms differ in color. When we add a **redox indicator** to the analyte, the indicator imparts a color that depends on the solution's potential. As the solution's potential changes with the addition of titrant, the indicator changes oxidation state and changes color, signaling the end point.

Equivalent point Detection

To understand the relationship between potential and an indicator's color, consider its reduction half-reaction

$$\mathrm{In_{ox}} + ne \leftrightarrow \mathrm{In_{red}}$$

where $\mathrm{In_{ox}}$ and $\mathrm{In_{red}}$ are, respectively, the indicator's oxidized and reduced forms.

For simplicity, $\mathrm{In_{ox}}$ and $\mathrm{In_{red}}$ are shown without specific charges. Because there is a change in oxidation state, $\mathrm{In_{ox}}$ and $\mathrm{In_{red}}$ cannot both be neutral.

Equivalent point Detection

The Nernst equation for this half-reaction is

$$E = E_{In}^{\,o} + \frac{0.059}{n_{In}} \log \frac{[In_{ox}]}{[In_{Red}]}$$

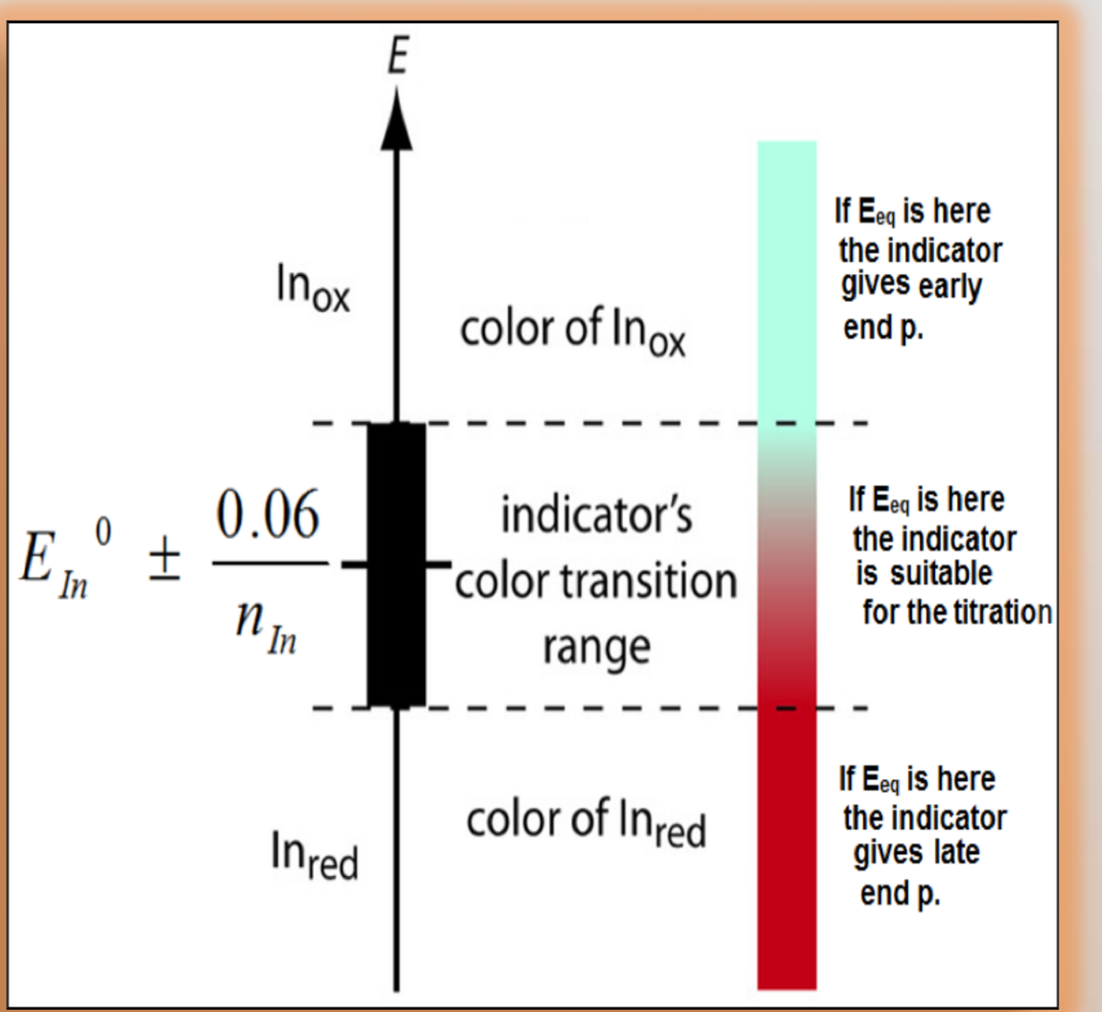
As discussed in unit 8 , if we assume that the indicator’s color changes from that of In_{ox} to that of In_{red} when the ratio $[In_{red}]/[In_{ox}]$ changes from 1 to 10, then the end point occurs when the solution’s potential is within the range :

Equivalent point Detection

$$\Delta E_{In} = E_{In}{}^{0} \pm \frac{0.059}{n_{In}} \approx E_{In}{}^{0} \pm \frac{0.06}{n_{In}}$$

This is the same approach we took in considering acid–base indicators and complexation indicators The diagram showing the relationship between *E* and an indicator's color. The ladder diagram defines potentials where $\mathrm{In_{red}}$ and $\mathrm{In_{ox}}$ are the predominate species. The indicator changes color when *E* is within the range :

$$E_{In}{}^{0} \pm \frac{0.06}{n_{In}}$$



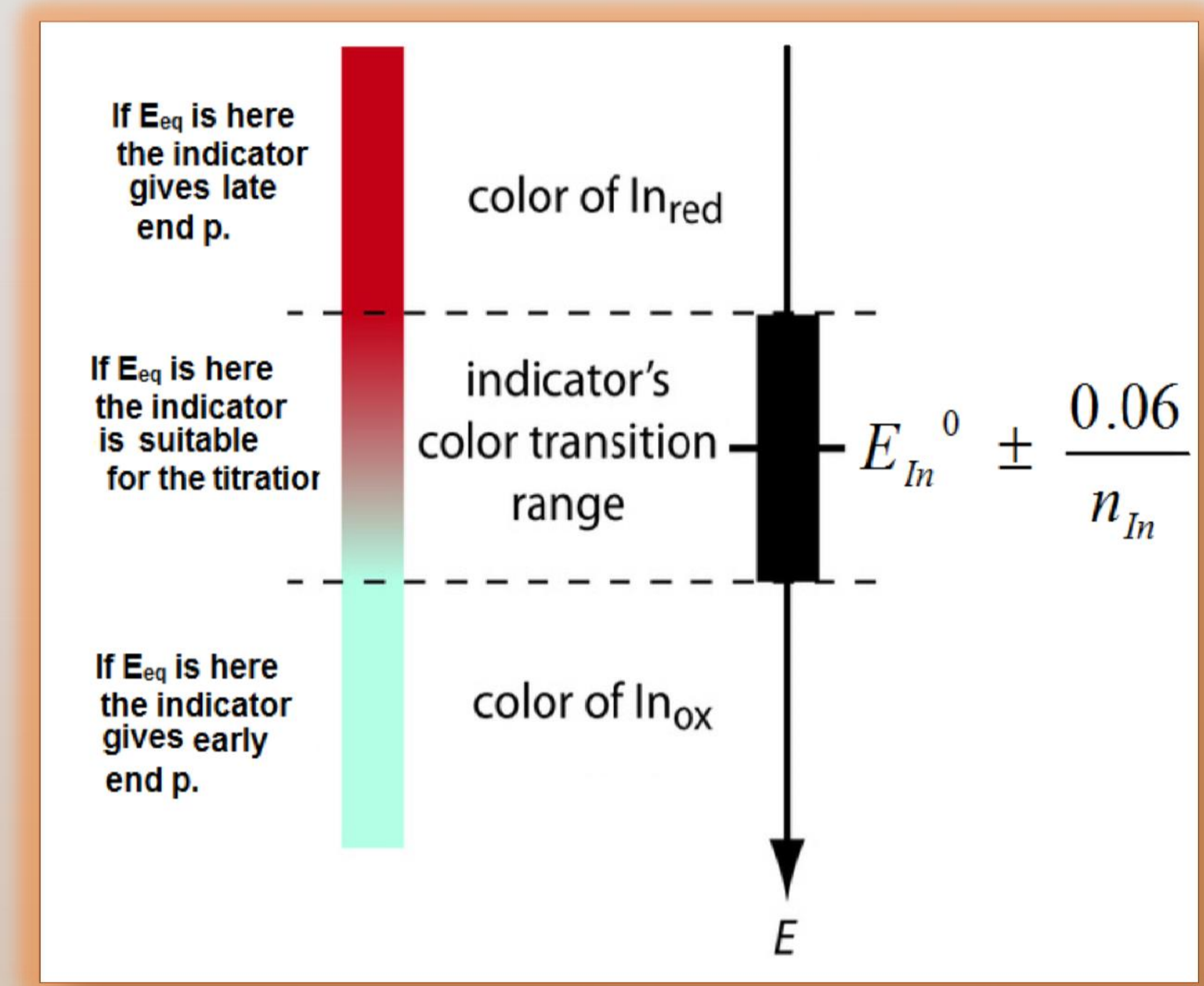
Equivalent point Detection

Note that if the equivalent point potential (E_{eq}) of the titration comes before the indicator's color transition range then , this indicator will give late end point and if it comes after , the indicator will give early end point but if E_{eq} is within the indicator's color transition range , then the indicator is suitable for the titration .

The discussion above is limited to the titration of reducing agent with oxidizing agent .

Equivalent point Detection

For the titration of oxidizing agent with reducing agent , the potential decreases during titration as shown in the diagram and all the previous information will be changed accordingly .



Equivalent point Detection

Example : In the titration of Sn^{2+} with Ce^{4+} , how the following indicators will behave with this titration :

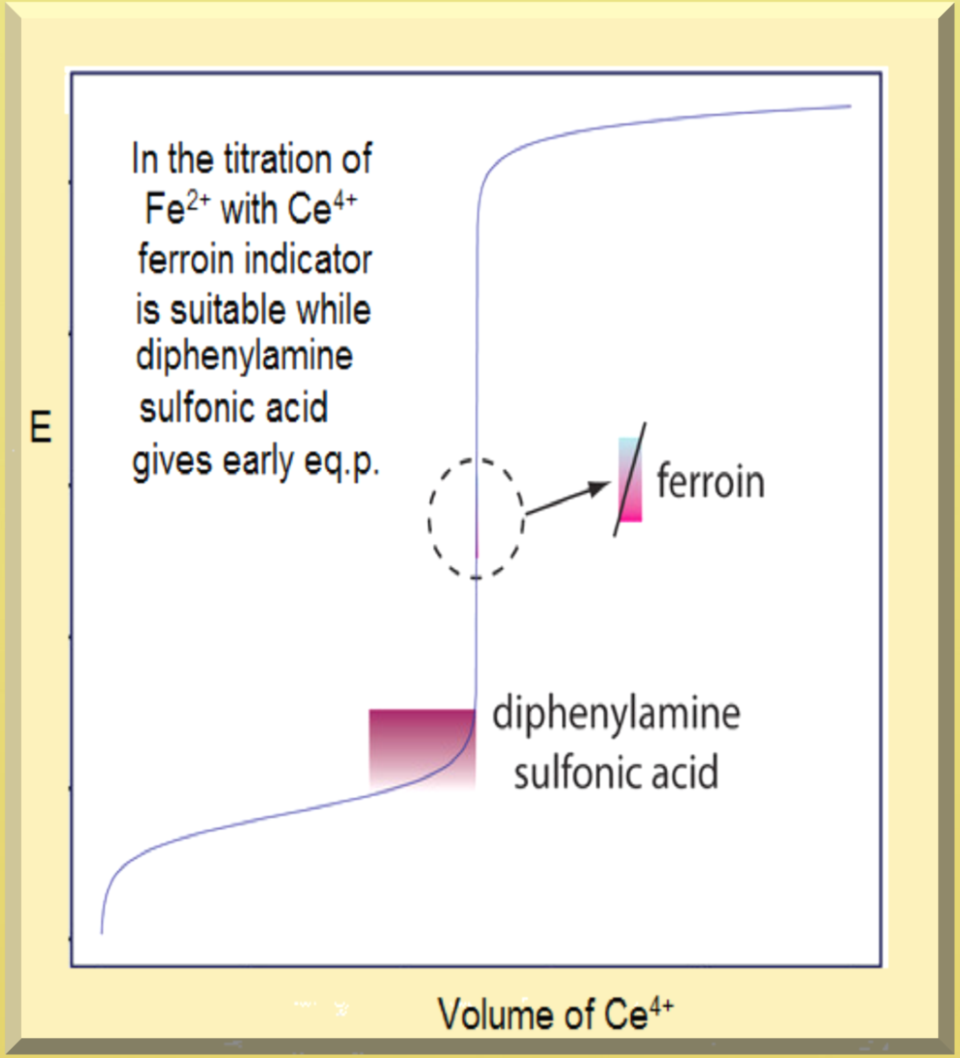
$$Ce^{4+} + e \leftrightarrow Ce^{3+} \qquad E_{Ce}^{0} = 1.44\ V$$

$$Sn^{4+} + 2e \leftrightarrow Sn^{2+} \qquad E_{Sn}^{0} = 0.15\ V$$

(1) The indicator which has $E_{In}^{0} = 0.65\ V$ and $n_{In} = 2$
(2) The indicator which has $E_{In}^{0} = 0.50\ V$ and $n_{In} = 2$
(3) The indicator which has $E_{In}^{0} = 0.53\ V$ and $n_{In} = 1$

Solution : First we calculate the potential at equivalent point E_{eq} thus :

$$E_{eq.p} = \frac{1X1.44 + 2X0.15}{1+2} = 0.58\ V$$



In the titration of Fe^{2+} with Ce^{4+} ferroin indicator is suitable while diphenylamine sulfonic acid gives early eq.p.

Equivalent point Detection

Then we calculate $E_{In}^{0} \pm (0.06/n_{In})$ for each indicator thus :

$$(1)\ \Delta E_{In} = 0.65 \pm \frac{0.06}{2} = 0.65 \pm 0.03\ (\textit{from}\ 0.62\ \textit{to}\ 0.68)$$

$$(2)\ \Delta E_{In} = 0.50 \pm \frac{0.06}{2} = 0.50 \pm 0.03\ (\textit{from}\ 0.47\ \textit{to}\ 0.53)$$

$$(3)\ \Delta E_{In} = 0.53 \pm \frac{0.06}{1} = 0.53 \pm 0.06\ (\textit{from}\ 0.47\ \textit{to}\ 0.59)$$

We are titrating a reducing agent with an oxidizing agent , therefore the potential is increasing during titration . Consequently , indicator (2) will change color before 0.58 (early eq.p.), indicator (3 is suitable and (2) will change color after passing 0.58 (late eq.p.)

Equivalent point Detection

Example : How the previous indicators will behave with a titration of an oxidizing agent with a reducing agent if its $E_{eq} = 0.65$ V ?

Solution : Since we are titrating an oxidizing agent with a reducing agent , the potential will decrease during titration , therefore , indicator (1) is suitable because 0.65 is within the indicator range (0.62 – 0.68) ,indicators (2) and (3) both change color after passing 0.65 , therefore , both give late eq.p.

Adjusting the Analyte’s Oxidation State

Sample Pretreatment :

If a redox titration is to be used in a quantitative analysis, the analyte must initially be present in a single oxidation state. For example, when a sample containing iron is dissolved, the resulting solution usually contains a mixture of iron(II) and iron(III) ions . Before titrating, we must either prereduce any Fe^{3+} to Fe^{2+} in order to titrate all iron as Fe^{2+} with oxidizing titrant or preoxidize any Fe^{2+} to Fe^{3+} in order to titrate all iron as Fe^{3+} with reducing titrant . This type of pretreatment can be accomplished using an auxiliary reducing agent (prereductant) or oxidizing agent (preoxidant) .

Adjusting the Analyte's Oxidation State

To be a preoxidant or a prereductant , a reagent must react quantitatively with the analyte and the reagent excess must be easily removable . A metal that is easy to oxidize—such as Zn, Al, and Ag can serve as an **auxiliary prereductant** . The metal, as a coiled wire or powder, is added to the sample where it prereduces the analye. Because any unreacted auxiliary prereducing agent will react with the oxidant titrant, it must be removed before beginning the titration. This can be accomplished by simply removing the coiled wire, or by filtering.

Adjusting the Analyte’s Oxidation State

An alternative method for using an auxiliary prereducing agent is to immobilize it in a column. To prepare a reduction column an aqueous slurry of the finally divided metal is packed in a glass tube equipped with a porous plug at the bottom. The sample is placed at the top of the column and moves through the column under the influence of gravity or vacuum suction.

Several reagents are commonly used as **auxiliary preoxidizing agents**, including ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, , hydrogen peroxide, H_2O_2 and sodium bismuthate $NaBiO_3$. Peroxydisulfate is a powerful oxidizing agent

$$S_2O_2^{-8}(aq) + 2e \longrightarrow 2SO_2^{-4}(aq)$$

capable of preoxidizing Mn^{2+} to MnO_4^-, Cr^{3+} to $Cr_2O_7^{2-}$, and Ce^{3+} to Ce^{4+}. Excess peroxydisulfate is easily destroyed by briefly boiling the solution.

Adjusting the Analyte's Oxidation State

The reduction of hydrogen peroxide in acidic solution provides another method

$$H_2O_2(aq)+2H^+(aq)+2e^- \rightarrow 2H_2O\ (l)$$

For preoxidizing an analyte. excess H_2O_2 is destroyed by briefly boiling the solution . Sodium bismuthate is another powerful preoxidizing agent , the excess reagent is then removed by filtration .

Redox Titrants

If it is to be used quantitatively, the titrant's concentration must remain stable during the analysis. Because a titrant in a reduced state is susceptible to air oxidation, most redox titrations use an oxidizing agent as the titrant. There are several common oxidizing titrants, including MnO_4^-, Ce^{4+}, $Cr_2O_7^{2-}$, and I_3^-. Which titrant is used often depends on how easy it is to oxidize the analyte. An analyte that is a weak reducing agent needs a strong oxidizing titrant if the titration reaction is to have a suitable end point

Redox Titrants

The two strongest oxidizing titrants are MnO_4^- and Ce^{4+}, for which the reduction half-reactions are

$$MnO_4^-(aq) + 8H^+(aq) + 5e \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$

$$Ce^{4+}(aq) + e \rightleftharpoons Ce^{3+}(aq)$$

Solutions of Ce^{4+} can be prepared from the primary standard cerium ammonium nitrate, $Ce(NO_3)_4 \bullet 2NH_4NO_3$ (expensive) , in 1 M H_2SO_4 . It is cheaper to use less expensive reagent grade material, such as Ce(OH)4, then, the solution is standardized against a primary standard reducing agent such as $Na_2C_2O_4$ or Fe^{2+}.

Redox Titrants

Despite its availability as a primary standard and its ease of preparation, Ce^{4+} is not as frequently used as MnO_4^- because it is more expensive. The standardization reactions are :

$$Ce^{4+}(aq) + Fe^{2+}(aq) \longrightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$$

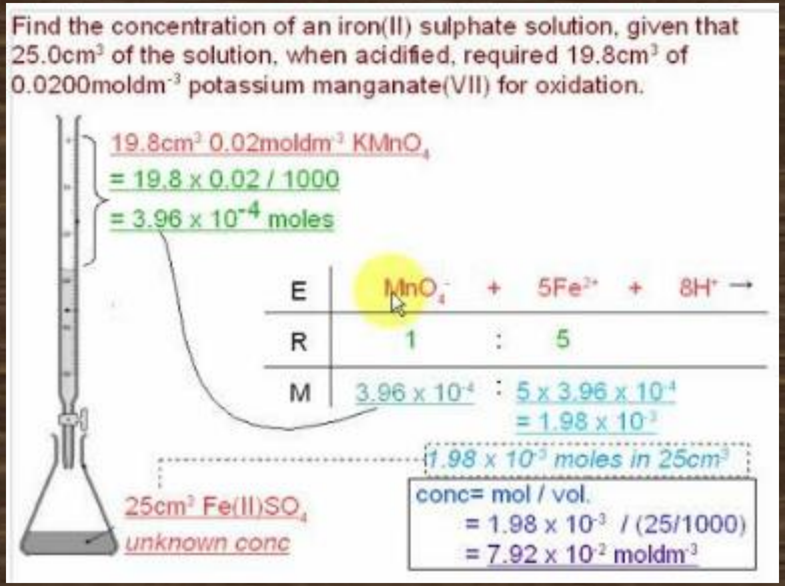
$$2Ce^{4+}(aq) + H_2C_2O_4(aq) \longrightarrow 2Ce^{3+}(aq) + 2CO_2(g) + 2H^+(aq)$$

Solutions of MnO_4^- are prepared from $KMnO_4$, which is not a primary standard. Aqueous solutions of permanganate are thermodynamically unstable due to its ability to oxidize water

$$4MnO_4^-(aq) + 2H_2O(l) \leftrightarrow 4MnO_2(s) + 3O_2(g) + 4OH^-(aq)$$

Redox Titrants

This reaction is catalyzed by the presence of MnO_2, Mn^{2+}, heat, light, and the presence of acids and bases. A moderately stable solution of permanganate can be prepared by boiling it for an hour and filtering through a sintered glass filter to remove any solid MnO_2 that precipitates. Standardization is accomplished against a primary standard reducing agent such as $Na_2C_2O_4$ or Fe^{2+} (prepared using iron wire), with the pink color of excess MnO_4^- signaling the end point.



Find the concentration of an iron(II) sulphate solution, given that $25.0cm^3$ of the solution, when acidified, required $19.8cm^3$ of $0.0200moldm^{-3}$ potassium manganate(VII) for oxidation.

$19.8cm^3$ $0.02moldm^{-3}$ $KMnO_4$
$= 19.8 \times 0.02 / 1000$
$= 3.96 \times 10^{-4}$ moles

E	MnO_4^-	+	$5Fe^{2+}$	+	$8H^+ \rightarrow$
R	1	:	5		
M	3.96×10^{-4}	:	$5 \times 3.96 \times 10^{-4}$ $= 1.98 \times 10^{-3}$		

1.98×10^{-3} moles in $25cm^3$

$25cm^3$ $Fe(II)SO_4$
unknown conc

conc= mol / vol.
$= 1.98 \times 10^{-3} / (25/1000)$
$= 7.92 \times 10^{-2}$ $moldm^{-3}$

VIDEO
You Tube

VIDEO
My Channel

Redox Titrants

A solution of MnO_4^- prepared in this fashion is stable for 1–2 weeks, although the standardization should be rechecked periodically. The standardization reactions are :

$$MnO_4^- (aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

$$2MnO_4^- (aq) + 5H_2C_2O_4(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Redox Titrants

Potassium dichromate is a relatively strong oxidizing agent whose principal advantages are its availability as a primary standard and the long term stability of its solutions. It is not, however, as strong an oxidizing agent as MnO_4^- or Ce^{4+}, which makes it less useful when the analyte is a weak reducing agent. Its reduction half-reaction is

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \leftrightarrow 2Cr3^+(aq)+7H_2O(l)$$

Although a solution of $Cr_2O_7^{2-}$ is orange and a solution of Cr^{3+} is green, neither color is intense enough to serve as a useful indicator. Diphenylamine sulfonic acid, whose oxidized form is red-violet and reduced form is colorless, gives a very distinct end point signal with $Cr_2O_7^{2-}$.

Redox Titrants

Iodometric titration : Iodine I_2 is another important oxidizing titrant. Because it is a weaker oxidizing agent than MnO_4^-, Ce^{4+}, and $Cr_2O_7^{2-}$, it is useful only when the analyte is a stronger reducing agent. This apparent limitation, however, makes I_2 a more selective titrant for the analysis of a strong reducing agent in the presence of a weaker reducing agent. The reduction half-reaction for I_2 is

$$I_2(aq) + 2e \leftrightarrow 2I^-(aq)$$

Because iodine is not very soluble in water, solutions are prepared by adding an excess of I^-. The complexation reaction

$$I_2(aq) + I^-(aq) \leftrightarrow I^{-3}(aq)$$

increases the solubility of I_2 by forming the more soluble triiodide ion, I_3^-. Even though

Redox Titrants

iodine is present as I_3^- instead of I_2, the number of electrons in the reduction half-reaction is unaffected .

$$I_3^- (aq) + 2e \leftrightarrow 3I^- (aq)$$

Solutions of I_2 are normally standardized against $Na_2S_2O_3$ using starch as a specific indicator for I_2 The standardization reaction is

$$I_2(aq) + 2S_2O_3^{2-} (aq) \rightarrow 2I^- (aq) + S_4O_6^{2-} (aq)$$

An oxidizing titrant such as MnO_4^-, Ce^{4+}, $Cr_2O_7^{2-}$, and I_2 is used when the analyte is in a reduced state. If the analyte is in an oxidized state, we can first reduce it with an auxiliary prereducing agent and then complete the titration using an oxidizing titrant .

Redox Titrants

Alternatively, we can titrate it using a reducing titrant.

Iodimetric titration : Iodide I^- is a relatively strong reducing agent that could serve as a reducing titrant except that a solution of I^- is susceptible to the air-oxidation of I^- to I_2 :

$$3I^-(aq) \leftrightarrow I_3^-(aq) + 2e$$

A freshly prepared solution of KI is clear, but after a few days it may show a faint yellow coloring due to the presence of I_3^-.
Instead, adding an excess of KI reduces the analyte, releasing a stoichiometric amount of I_2 .
The amount of I_2 produced is then determined by a back titration using thiosulfate, $S_2O_3^{2-}$, as a reducing titrant.

$$2S_2O_3^{2-}(aq) \leftrightarrow 2S_4O_6^{2-}(aq) + 2e$$

Redox Titrants

Solutions of $S_2O_3^{2-}$ are prepared using $Na_2S_2O_3{\bullet}5H_2O$, and must be standardized before use. Standardization is accomplished by dissolving a carefully weighed portion of the primary standard KIO_3 in an acidic solution containing an excess of KI. The reaction between IO_3^- and I^-

$$IO_3^- (aq) + 5I^- (aq) + 6H^+(aq) \rightarrow 3I_2 (aq) + 3H_2O(l)$$

liberates a stoichiometric amount of I_2 . By titrating this I_2 with thiosulfate, using starch as a visual indicator, we can determine the concentration of $S_2O_3^{2-}$ .The standardization titration is

$$I_2 (aq) + 2S_2O_3^{2-} (aq) \rightarrow 2I^- (aq) + S_4O_6^{2-} (aq)$$

Redox Titrants

Although thiosulfate is one of the few reducing titrants that is not readily oxidized by contact with air, it is subject to a slow decomposition to bisulfite and elemental sulfur. If used over a period of several weeks, a solution of thiosulfate should be restandardized periodically. Several forms of bacteria are able to metabolize thiosulfate, which also can lead to a change in its concentration. This problem can be minimized by adding a preservative such as HgI_2 to the solution.

Redox Titrants

Another useful reducing titrant is ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, in which iron is present in the +2 oxidation state. A solution of Fe^{2+} is susceptible to air-oxidation, but when prepared in 0.5 M H_2SO_4 it remains stable for as long as a month. Periodic restandardization with $K_2Cr_2O_7$ is advisable .

The titrant Fe^{2+} can be used to directly titrate the analyte . Alternatively, ferrous ammonium sulfate is added to the analyte in excess and the excess of Fe^{2+} is back titrating with a standard solution of Ce^{4+} or $Cr_2O_7^{2-}$.

Redox Titration Applications

The titrant Fe^{2+} can be used to directly titrate the analyte . Alternatively, ferrous ammonium sulfate is added to the analyte in excess and the excess of Fe^{2+} is back titrating with a standard solution of Ce^{4+} or $Cr_2O_7^{2-}$.

One of the most important applications of redox titrimetry is evaluating the chlorination of public water supplies by determining the total chlorine residual using the oxidizing power of chlorine to oxidize I^- to I_3^-. The amount of I_3^- is determined by back titrating with $S_2O_3^{2-}$.

Redox Titration Applications

Another important example of redox titrimetry, which finds applications in both public health and environmental analyses is the determination of dissolved oxygen. In natural waters, The sample is first treated with a solution of $MnSO_4$, the dissolved oxygen oxidizes Mn^{2+} to MnO_2 which oxidizes I^- to I_3^- .The amount of I_3^- formed is determined by titrating with $S_2O_3^{2-}$ using starch as an indicator.

One important example of redox titration is the determination of the chemical oxygen demand (COD) of natural waters and wastewaters by adding excess $K_2Cr_2O_7$ and titrating the excess by back titrating using ferrous ammonium sulfate as the titrant and ferroin as the indicator . Iodine has been used as an oxidizing titrant for a number of compounds of pharmaceutical interest .

Summary

In this unit , the calculations of the potential of the titration solution at any point of the titration have been investigated . The behavior of the true redox indicators and how we choose the suitable indicator for any redox titration have been discussed . The pretreatment of the sample solution prior to its redox titration has been studied . The application of the oxidation reduction titration is examined . All of the fundamentals of these subjects have been clarified using solved examples , tutorials , pictures , graphs ,videos and laboratory experiments .

OXIDATION REDUCTION TITRATION

Tutorial

Exercise 1 : In the titration of 10 mL 0.1 M of Sn^{2+} solution with 0.2 M Fe^{3+} solution :

$$Sn^{4+} + 2e \leftrightarrow Sn^{2+} \qquad E^0 = 0.15\ V$$

$$Fe^{3+} + e \leftrightarrow Fe^{2+} \qquad E^0 = 0.77\ V$$

Calculate the potential of the conical flask solution after adding 5 mL of titrant solution

Your answer :

Our answer next slide

OXIDATION REDUCTION TITRATION

Tutorial

Answer 1 : First we write the balanced reaction equation as we learned in unit 10 :

$$2\,Fe^{3+} + Sn^{2+} \leftrightarrow 2\,Fe^{2+} + Sn^{4}$$

Second we calculate the volume of titrant at the equivalent point as we previously knew :

mmoles Fe^{3+} = mmoles Sn^{2+} X 2/1 = 10 x 0.1 X 2/1 = 2 mmoles

2 mmoles Fe^{3+} = 0.2 X V_{ml}

V_{ml} at equivalent point = 2 / 0.2 = 10 ml

After adding 5 mL i.e before the equivalent point we apply Nernst equation to analyte thus :

$$E = 0.15 + \frac{0.059}{2} \log \frac{\dfrac{(5 X 0.2)\, X \frac{1}{2}}{(10+5)}}{\dfrac{(10 X 0.1) - (5 X 0.2)\, X \frac{1}{2}}{(10+5)}} = 0.15\ V$$

OXIDATION REDUCTION TITRATION

Tutorial

Exercise 2 : In the titration of 10 mL 0.1 M of Sn^{2+} solution with 0.2 M Fe^{3+} solution :

$$Sn^{4+} + 2e \leftrightarrow Sn^{2+} \qquad E^0 = 0.15\ V$$

$$Fe^{3+} + e \leftrightarrow Fe^{2+} \qquad E^0 = 0.77\ V$$

Calculate the potential of the conical flask solution after adding 15 mL of titrant solution?

Your answer :

Our answer next slide

OXIDATION REDUCTION TITRATION

Tutorial

Answer 2 :

First we write the balanced reaction equation as we learned in unit 10 :

$$2\,Fe^{3+} + Sn^{2+} \leftrightarrow 2\,Fe^{2+} + Sn^{4}$$

Second we calculate the volume of titrant at the equivalent point as we previously knew :

mmoles Fe^{3+} = mmoles Sn^{2+} X 2/1 = 10 x 0.1 X 2/1 = 2 mmoles

2 mmoles Fe^{3+} = 0.2 X V_{ml}

V_{ml} at equivalent point = 2 / 0.2 = 10 ml

After adding 15 mL i.e after the equivalent point we apply Nernst equation to titrant thus :

$$E = 0.77 + \frac{0.059}{1}\log\frac{\dfrac{(15\,X\,0.2) - (10\,X\,0.1)\,x\,\dfrac{2}{1}}{(10+15)}}{\dfrac{(10\,X\,0.1)\,X\,\dfrac{2}{1}}{(10+15)}} = 0.75\,V$$

OXIDATION REDUCTION TITRATION

Tutorial

Exercise 3 : In the titration of 10 mL 0.1 M of Sn^{2+} solution with 0.2 M Fe^{3+} solution :

$$Sn^{4+} + 2e \leftrightarrow Sn^{2+} \qquad E^0 = 0.15\ V$$

$$Fe^{3+} + e \leftrightarrow Fe^{2+} \qquad E^0 = 0.77\ V$$

Calculate the potential of the conical flask solution at the equivalent point ?

Your answer :

Our answer next slide

Tutorial

Answer 3 :

$$E_{eq.p.} = \frac{1X0.77 + 2X0.15}{(1+2)} = 0.357\ V$$

OXIDATION REDUCTION TITRATION

Tutorial

Exercise 4 : In the titration of an oxidant analyte with a reductant titrant which has an equivalent point potential of 0.32 V , does the following redox indicator suitable , give an early or give late equivalent point :

$$In_{OX} + 2e \leftrightarrow In_{RED} \qquad E_{In}^{0} = 0.4\ V$$

Your answer :

Our answer next slide

OXIDATION REDUCTION TITRATION

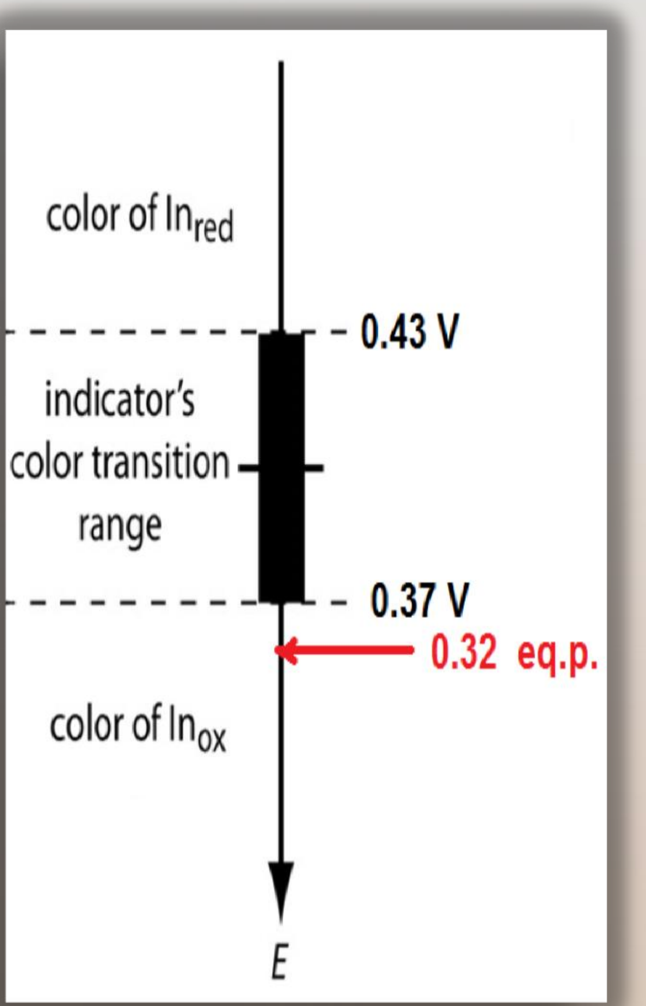
Tutorial

Answer 4 : We are titrating an oxidant analyte with a reductant titrant , therefore the potential of the conical flask solution is decreasing .

$$\Delta E_{In} = E_{In}^{\;0} \pm \frac{0.059}{n_{In}} = 0.4 \pm \frac{0.059}{2}$$

$$= 0.4 \pm 0.03 \quad (0.43 \ to \ 0.37\,V \ )$$

That means the indicator starts changing its color at 0.43 V and the change will be completed at 0.37 V before reaching the equivalent point at 0.32 V. Accordingly this indicator will give an early equivalent point .



Tutorial

Exercise 5 : Sketch the titration curve for the titration of two analytes A ($E^0_A = 0.2$ V) and B ($E^0_B = 0.5$ V) with titrant D ($E^0_D = 1.5$ V) ?

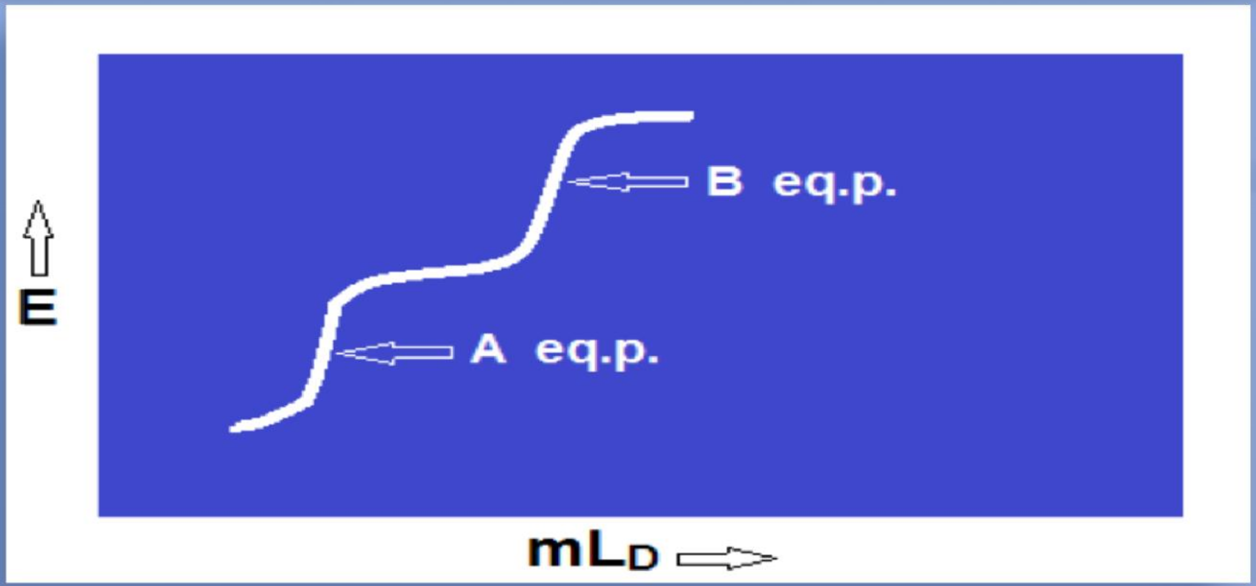
Your answer :

Our answer next slide

OXIDATION REDUCTION TITRATION

Tutorial

Answer 5 : It is clear from the values of the standard potentials that we are titrating two reducing agents with an oxidizing agent (i.e the potential is increasing during titration) and A will react first with D because A is stronger as a reducing agent than B ($E^0_B < E^0_A$) .



OXIDATION REDUCTION TITRATION

Tutorial

Exercise 6 : For the determination of calcium in blood , an excess of $Na_2C_2O_4$ has been added to 5 mL of blood sample . The formed CaC_2O_4 precipitate is separated by filtration and dissolved in an acid solution . The content of Ca in the final solution is titrated with 0.001 M MnO_4^- solution according to the following equation :

$$5\,C_2O_4^{2-} + 2\,MnO_4^- + 16\,H^+ \rightarrow 10\,CO_2 + 2Mn^{2+} + 8\,H_2O$$

Calculate the concentration of Ca (aw = 40) in blood sample in ppm unit ?

Your answer :

Our answer next slide

OXIDATION REDUCTION TITRATION

Tutorial

Answer 6 :

mmoles MnO_4^- = 5X0.001 = 0.005

mmoles $C_2O_4^{2-}$ = mmoles MnO_4^- X 5/2

= 0.005 X 5/2 = 0.0125 = mmoles Ca

Wt. Ca = 0.0125 X 40 = 0.5 mg

$$ppm\ Ca = \frac{0.5(mg)}{5(mL)X10^{-3}\ (L)} = 100\ mg/L$$

OXIDATION REDUCTION TITRATION

Tutorial

Exercise 7 : Calculate potential for the titration of 50.0 mL of 0.0500 M Sn^{2+} with 0.100 M Tl^{3+} after adding 10 mL of titrant . The titration reaction is

$$Sn^{2+} + Tl^{3+} \rightarrow Sn^{4+} + Tl^{+}$$

$$E^0_{Sn} = 0.15\ V \ , \quad E^0_{Tl} = 0.77\ V$$

Your answer :

Our answer next slide

OXIDATION REDUCTION TITRATION

Tutorial

Answer 7 : The volume of Tl^{3+} needed to reach the equivalence point is

$V_{eq.\ P.} = V_{Tl} = M_{Sn}\ V_{Sn}\ /\ M_{Tl} = (0.050M)(50.0mL) / 0.100M = 25.0mL$

Before the equivalence point, the concentration of unreacted Sn^{2+} and the concentration of Sn^{4+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Sn^{4+}/Sn^{2+} half-reaction. The concentrations of Sn^{2+} and Sn^{4+} after adding 10.0 mL of titrant are

$[Sn^{2+}] = [(0.050M)(50.0mL)-(0.100M)(10.0mL)] / [50.0mL+10.0mL] = 0.0250M$

$[Sn^{4+}] = [(0.100M)(10.0mL)] / (50.0mL+10.0mL) = 0.0167M$

and the potential is

$E = +0.139V + 0.059 / 2\ \log 0.0167M / 0.0250M = +0.13\ V$

Tutorial

Exercise 8 : Calculate potential for the titration of 50.0 mL of 0.0500 M Sn^{2+} with 0.100 M Tl^{3+} after adding 40 mL of titrant . The titration reaction is

$$Sn^{2+} + Tl^{3+} \rightarrow Sn^{4+} + Tl^{+}$$

$$E^0_{Sn} = 0.15\ V \quad , \quad E^0_{Tl} = 0.77\ V$$

Your answer :

Our answer next slide

Tutorial

Answer 8 : After the equivalence point, the concentration of Tl^+ and the concentration of excess Tl^{3+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Tl^{3+}/Tl^+ half-reaction. After adding 40.0 mL of titrant, the concentrations of Tl^+ and Tl^{3+} are :

$[Tl^+] = [(0.0500M)(50.0mL)] \; / \; (50.0mL+40.0mL) = 0.0278M$

$[Tl^{3+}] = \big[[(0.100M)(40.0mL)] - [(0.0500M)(50.0mL)]\big] / (50.0mL+40.0mL) = 0.0167M$

and the potential is

$E = +0.77V + 0.059 / 2 \log 0.0167M 0.0278M = +0.76 V$

OXIDATION REDUCTION TITRATION

Tutorial

Exercise 9 : Calculate potential for the titration of 50.0 mL of 0.0500 M Sn^{2+} with 0.100 M Tl^{3+} at the equivalent point . The titration reaction is

$$Sn^{2+} + Tl^{3+} \rightarrow Sn^{4+} + Tl^{+}$$

$$E^0_{Sn} = 0.15\ V \ , \quad E^0_{Tl} = 0.77\ V$$

Your answer :

Our answer next slide

Tutorial

Ansswer 9 : At the titration's equivalence point, the potential $E_{eq.p}$ is

$$E_{eq.p} = (0.139V+0.77V) / 2 = 0.45 \text{ V}$$

على الراغبين الاستماع الى محاضرات الاستاذ الدكتور/ ابراهيم زامل الزامل باللغة العربية عن هذا الموضوع الرجوع الى الروابط التالية :

معايرات الاكسدة و الاختزال

معايرات الاكسدة و الاختزال ٢