

Oxidation-reduction reactions and redoxi titrimetry

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Oxidation-reduction reactions

OXIDATION-REDUCTION REACTIONS

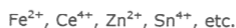
The tentative definition and rules of calculation of oxidation numbers (ON): "Imagine all bonding electrons partitioned in a chemical species in the way as they would belong to the more electronegative element. The virtual partial charge on the elements now is their oxidation number (or state)"

1. Elements have zero ON.
2. The total ON in an ion is equal to its charge and zero in a neutral compound.
3. Hydrogen always has +1 ON (except in alkaline hydrides, where -1)
4. Oxygen always has -2 ON (except in peroxides, where it's -1)

Examples: I_2 ; H_2O ; HNO_3 ; $NaOH$; MnO_4^- ; NH_3 ; Na_2SO_3 ; ClO_3^- ; Fe^{3+}

Oxidation-reduction reactions

In aqueous solution, inorganic compounds exist as ions:



It is clear that in these instances a change in the ON also changes the charge and also that it can only be done if electrons are involved.



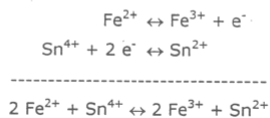
It is well known that if the ON of a compound increases (it releases electrons) it is called **oxidation**. Or, if the ON decreases (the compound takes up electrons) then it is a **reduction**. So oxidation/reduction (redox) reactions are electron transferring reactions. It also follows that they always come in pairs: if something gets oxidized, some other compounds must get reduced as well. This is also reflected in the names: the above examples are **half-reactions**.

Oxidation-reduction reactions

Hydrogen ions also frequently appear in half-reactions, like in:

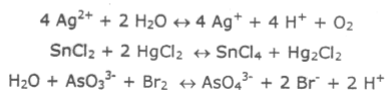


When a half-reaction pair is summarized in one stoichiometrically balanced equation that is called the sum (brutto) redox reaction:



Here the reducing agent is Fe^{2+} (it gets oxidized) and the oxidizing one is Sn^{4+} .

Examples: (what are the reducing/oxidizing agents here?)



Oxidation-reduction reactions

EXPERIMENTAL ILLUSTRATION OF REDOX REACTIONS

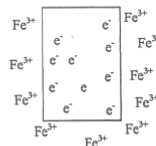
One should remember that metals conduct electricity and that they do it by conducting (transporting) electrons. On the contrary, electrolytes (acids/bases/salts) also conduct but they do it by transporting ions. The reason for the latter is that free electrons can not exist in aqueous solutions:



This implies that redox reactions should occur on the surface of a piece of metal when it is dipped into an electrolyte solution. Such an electrochemical system is called an **electrode** and its surface is an **interface**.

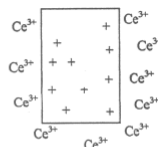
Oxidation-reduction reactions

Now consider a beaker with a Fe^{2+} solution and a piece of Pt metal dipped into it (we use Pt as this does not corrode. Pt = redox electrode):



which means that the metal gains a negative charge = negative potential !

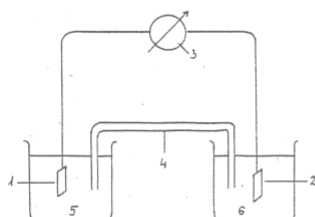
In another beaker containing Ce^{4+} and a piece of Pt metal:



so this piece of metal will have a positive charge = positive potential !

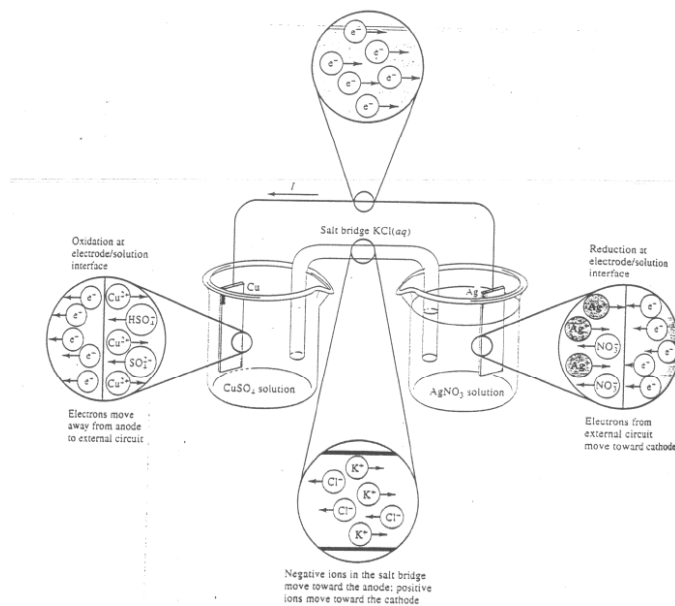
Oxidation-reduction reactions

Now if we connect the two electrodes to each other with a wire and the beakers with a salt bridge (the latter is needed because of reasons not discussed here) then electrons will transfer through the wire so current will flow → chemical energy is converted to electrical energy. The current will flow as long as there is still unreacted Fe^{2+} (in the first beaker) and Ce^{4+} (in the other) present. The voltage measurable between the two electrodes is called the **electromotive force (EMF)**. The whole is an **electrochemical cell**.



1. Sheet of platinum
2. " " " "
3. Galvanometer
4. Salt bridge
5. Solution of Fe^{2+}
6. Solution of Ce^{4+}

Oxidation-reduction reactions



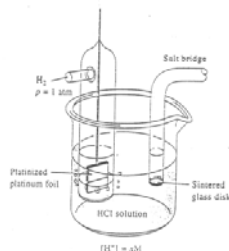
Oxidation-reduction reactions

We can not measure the potential of electrodes, only voltages between them → so a reference electrode is needed. In electrochemistry, the conventional potential reference is provided by a **standard hydrogen electrode**. This, by definition, has a potential of zero volt. Therefore, if the potential of a certain half-reaction (eg. Ce^{4+} reduction) is positive with respect to the std. hydrogen electrode then it means that the species involved (Ce^{4+}) is better oxidizing agent than H^+ ; and the opposite.

The electrode in contact with the half-system being reduced is the **cathode**, whereas the other is the **anode**. The electromotive force, in knowledge of the electrode potential values, can be calculated as:

$$\text{EMF} = E_{\text{cathode}} - E_{\text{anode}}$$

Examples for cell EMFs



Oxidation-reduction reactions

NERNST EQUATION

The Nernst theory gives the potential of a redox electrode. If the half-reaction is (unbalanced for charges!):



then in dilute solutions the electrode potential according to Nernst is:

$$E = E_0 + \frac{R \cdot T}{n \cdot F} \ln \left[\frac{A_{\text{ox}}}{A_{\text{red}}} \right]$$

where E_0 is the **normal potential** (concs are 1), R is the universal gas constant, T is temperature, n is the number of electrons being transferred, F is the Faraday constant. If E is to be calculated at 25°C then E_0 is called the **standard potential** and the formula can be rewritten to give:

$$E = E_0 + \frac{0.0591}{n} \lg \left[\frac{A_{\text{ox}}}{A_{\text{red}}} \right]$$

Oxidation-reduction reactions

If the half-reaction includes hydrogen ions, too then it should also appear in the Nernst equation. When doing this, one should consider that the $[A_{ox}]/[A_{red}]$ part of the formula actually refers to the $1/K$ value of the half-reaction. Example:



$$E = E_{0, \text{MnO}_4^-} + \frac{0.0591}{5} \lg \frac{[\text{MnO}_4^-] \cdot [\text{H}^+]^8}{[\text{Mn}^{2+}]}$$

Note: If either A_{ox} or A_{red} can be considered to be constant (like the conc. of a piece of metal) than we omit it from the formula. Example:



$$E = E_{0, \text{Ag}^+} + \frac{0.0591}{1} \lg [\text{Ag}^+]$$

Oxidation-reduction reactions

Example: (see potential table)

at 1 M concentrations and 25°C, H_3AsO_4 will oxidize I^- (0.559 V > 0.534 V)
but at 20:1 $[\text{I}_2]/[\text{I}^-]$ ratio, this system is the more positive one! (E= 0.572 V)

Tables of standard potentials (for all half-reactions assumed to run towards reduction) are assembled which can be well used judge which redox half-system is stronger oxidizer than the other. For instance, if the theoretical electromotive force would be negative for a certain complete system then this reaction will not be spontaneous.

Selected values of
STANDARD ELECTRODE POTENTIALS

Half reaction	E_{25}^0 , V
$\text{F}_2 + 2 \text{H}^+ + 2 \text{e}^- = 2 \text{HF}$	3.06
$\text{S}_2\text{O}_8^{2-} + 2 \text{e}^- = 2 \text{SO}_4^{2-}$	2.01
$\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- = 2 \text{H}_2\text{O}$	1.77
$\text{MnO}_4^- + 4 \text{H}^+ + 3 \text{e}^- = \text{MnO}_2 + 2 \text{H}_2\text{O}$	1.695
$\text{Ce}^{4+} + \text{e}^- = \text{Ce}^{3+}$	1.61
$\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- = \text{Mn}^{2+} + 4 \text{H}_2\text{O}$	1.51

Redox titrations

REDOX TITRATION CURVES

Let's consider the case of titrating Fe^{2+} with Ce^{4+} .

- at the very beginning there is only a very small amount of Fe^{3+} , so the potential is small: $E = E_{0,\text{Fe}} + 0.0591 \lg [\text{Fe(III)}]/[\text{Fe(II)}]$
- when a portion of Ce^{4+} is added, it reacts with a part of Fe^{2+} , so the potential will raise as $[\text{Fe(III)}]/[\text{Fe(II)}]$ ratio in the formula increases
- at 100% titration, the potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ system will be equal. Starting out from this condition it can be shown that

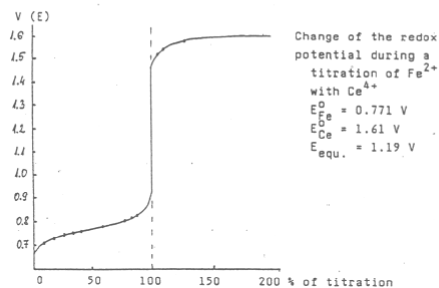
$$E_{\text{eq}} = \frac{E_{0,\text{Fe}} + E_{0,\text{Ce}}}{2}$$

or in general:

$$E_{\text{eq}} = \frac{n_A E_{0,A} + n_B E_{0,B}}{n_A + n_B}$$

Redox titrations

- if further Ce^{4+} is added (overtitration) then, as almost no Fe^{2+} is present any more, the potential will be determined by the $\text{Ce}^{4+}/\text{Ce}^{3+}$ system: $E = E_{0,\text{Ce}} + 0.0591 \lg [\text{Ce(IV)}]/[\text{Ce(III)}]$



Redox titrations

END-POINT INDICATION METHODS FOR REDOX TITRATIONS

At least four convenient methods can be used for end-point indication:

- potentiometric (instrumental method)
- redox (reversible) indicators
- irreversible indicators
- specific action indicators

Irreversible indicators: Certain pH indicator dyes can also be used as redox indicators. The background behind their operation is that redox reactions usually need an acidic pH and the electrode potential of the system being titrated increases as the titration proceeds. This allows the use of a coloured pH indicator which will be (irreversibly) destroyed right after the end-point due to the first excess of the oxidizing titrant. The drawback of the use of this type of indicators is that the local excess of titrant at the place of its dropping in also destroys a part of the dye so its concentration will gradually decrease. As a consequence of this, near the end-point extra drops of the indicator will be needed to see the colour change clearly → larger indicator error.

Redox titrations

Potentiometric end-point detection: a platinum (= redox electrode) can be used to monitor the electrode potential of the chemical system being titrated as the titration proceeds. As always, we need a reference electrode for such a measurement. The standard hydrogen electrode could be used, but it is very bulky. Therefore a saturated calomel electrode is commonly used. This has a potential of +0.246 V, so the potential of the indicator Pt electrode can be calculated from the equation:

$$EMF = U_{\text{measured}} = E_{\text{cathode}} - E_{\text{anode}}$$

and assuming that the indicator electrode is the cathode ($E_{\text{indicator}} > E_{\text{reference}}$) then:

$$E_{\text{indicator}} = U_{\text{measured}} + E_{\text{reference}} = U_{\text{measured}} + 0.246 \text{ V}$$

Redox titrations

Redox indicators: These coloured compounds have different colours in their oxidized and reduced state. Mostly this redox reaction of theirs is reversible therefore they represent a half-reaction on their own, for which:

$$E_{\text{indicator}} = E_{0,\text{indicator}} + \frac{0.0591}{n} \lg \frac{[\text{Ind}_{\text{ox}}]}{[\text{Ind}_{\text{red}}]}$$

If the solution potential reaches $E_{0,\text{indicator}}$ then the indicator will show its transient colour.

As with pH indicators, here again we can say that one or the other colour of the indicator can only be seen if

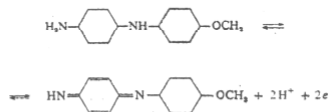
$$\frac{10}{1} < \frac{[\text{Ind}_{\text{ox}}]}{[\text{Ind}_{\text{red}}]} \quad \text{or} \quad \frac{1}{10} > \frac{[\text{Ind}_{\text{ox}}]}{[\text{Ind}_{\text{red}}]}$$

which is equivalent with saying that

$$E_{\text{indicator}} = E_{0,\text{indicator}} \pm \frac{0.0591}{n}$$

Redox titrations

Note that the larger is n the sharper the colour change can be. Also, the above potential may be influenced by the pH depending on the half-reaction. This reaction is illustrated below for variamin blue:



Indicator	$E_{0,\text{V}}$ pH = 0	Colour	
		red.	ox.
Nitroferroin	+ 1.3	red	blue
Ferroin	+ 1.2	red	blue
Diphenylamine-sulfonic acid	+ 0.084	colourless	violet red
Diphenylamine	+ 0.76	- " -	violet
Variamine blue	+ 0.71	- " -	blue
Methylene blue	+ 0.53	- " -	blue
Phenosaphranin	+ 0.28	- " -	blue
Saphranin T	+ 0.23	- " -	blue

Redoxi titrations

Specific action indicators: There are a few compounds which can act as a sensitive and selective redox indicator under certain conditions. Examples include thiocyanate for ferric ion and starch for iodine. In some cases the titrant is so strongly coloured that its excess can be easily noticed. This makes the use of any other indicator unnecessary. Example: KMnO_4 .

Redoxi titrations

REDOX TITRATION METHODS

Direct titration: if everything is fine about the reaction, that is it is stoichiometric, rapid and quantitative.

Back titration: if the reaction is too slow we add a known amount (in excess) of an adequate aiding (auxiliary) solution and the excess is back titrated using a titrant.

Indirect titration: first we make the sample to form a certain better titrable compound with the sample and we titrate this.

Reverse titration: we put the sample into the buret and use it to titrate the standard solution.

Redoxi titrations

Representative types of redox titration methods

> Oxidation methods

- Permanganometry
- Bromatometry
- Cerimetry
- Chromatometry
- Iodometry

> Reduction methods

- Titanometry
- Chromometry
- Ascorbinometry

Redoxi titrations - Permanganometry

Permanganometry

KMnO₄ solution is a widely used oxidimetric titrant due to its high redox potential and intense purple colour that helps end-point indication.

In an acidic medium, Mn(II) is very stable so:



In neutral or weakly basic medium, Mn(IV) is the most stable form, so:



A KMnO₄ standard solution is a powerful oxidizing agent and therefore is prone to contaminations. The solution should be kept in a dark container and not allowing it to get in contact with anything oxidizable (eg. rubber, cork). Traces of Mn(II) or Mn(IV) autocatalyse the decomposition.

Redoxi titrations - Permanganometry

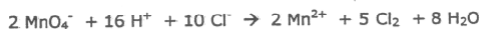
Primary standards used to standardize potassium-permanganate solutions include:

$(\text{COOH})_2 \cdot 2 \text{H}_2\text{O}$ that is crystalline oxalic acid

$\text{Fe}(\text{NH}_4)_2 (\text{SO}_4)_2 \cdot 2 \text{H}_2\text{O}$ that is Mohr salt

As_2O_3 that is arsenous trioxide

It is mainly used in acidic media. pH is usually set in by using sulphuric acid which is a non-oxidizable acid (as opposed to HCl):



Special indication methods are not needed as Mn(VII) has an intense purple colour itself which disappears if reduced to Mn(II).

Redoxi titrations - Permanganometry

Applications of permanganometry

Determination of Fe(II) and Fe(III)

Fe(II) can be directly titrated with KMnO_4 . If Fe(III) or the total iron ion content is to be determined then Fe(III) needs to be reduced to Fe(II) first. Sn(II) can be used for it in excess:



and then the excess of it is precipitated with mercury:



Now (or from the beginning) there is the problem of the presence of chloride. This can be overcome by using the Zimmermann-Reinhard reagent solution. This contains MnSO_4 , H_2SO_4 and phosphoric acid.

Mn(II) to suppress the oxidation of Cl^-

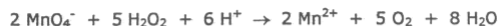
sulfuric acid to set the acidic pH

phosphoric acid to complex Fe(III) so to take away its yellow colour

Redoxi titrations - Permanganometry

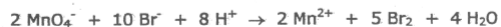
Determination of hydrogen peroxide

It is indeed a direct titration in which hydrogen-peroxide is oxidized to O₂.



Determination of bromide

Here bromide is oxidized to bromine, which needs to be removed by boiling.



Redoxi titrations - Bromatometry

Bromatometry

KBrO₃ is a strong oxidizing agent in acidic solution. In most of the cases, potassium-bromate is used as a titrant in the presence of bromide. In this case:



so the oxidizing power is determined by the Br₂/Br⁻ system (E₀= +1.08 V). Recrystallized potassium-bromate can be used to prepare a standard solution of precisely known concentration and it is stable on air. HCl is often used to set the pH to acidic.

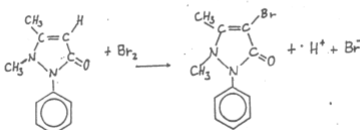
Indicators need to be used in bromatometry. For example methyl-orange is an appropriate irreversible indicator dye (red to colourless), and p-ethoxy chrisoidine (red to orange) is a reversible/redox indicator.

Redoxi titrations - Bromatometry

Applications of bromatometry

Determination of azophenium

Bromatometry is often used to measure unsaturated organic compounds through addition or substitution reactions of bromine. Indicator is p-ethoxy chrisoldine:



Determination of arsenic or antimony

These elements can also be directly titrated in HCl medium with KBrO₃.



Redoxi titrations - Bromatometry

Determination of iodide

In the presence of large amounts of bromide and HCl, bromate will form an interhalogene with iodide:



Aiding it with a small amount of organic solvent, the colour of bromine can be used as indicator.

Redoxi titrations - Cerimetry

Cerimetry

Ce(IV) ion is a strong oxidizing agent:



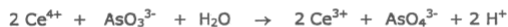
Standard solutions are mainly made using ceric sulphate in a sulphuric acid solution. For standardization, As_2O_3 or a stable Fe(II)-salt can be used. Osmium tetroxide is often needed, as a catalyst, to speed up the redox reactions done with Ce(IV). For indication, ferroin (red to pale blue) or diphenylamine (colourless to violet blue) reversible dyes can be used.

Redoxi titrations - Cerimetry

Applications of cerimetry

Determination of As(III)

In the presence of 3 drops of OsO_4 in sulphuric acid medium direct determination by the following reaction is possible (indicator is ferroin):



Determination of hydrogen peroxide

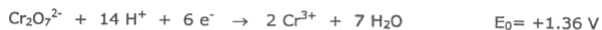
Hydrogen-peroxide also directly reacts with Ce(IV) ions (indicator is ferroin):



Redoxi titrations - Chromatometry

Chromatometry

Potassium dichromate ($K_2Cr_2O_7$) is also a strong oxidizing agent in highly acidic media:



It has some important advantages compared to $KMnO_4$ which include: *i*) stable and precise standard solution can be made from the pure salt; *ii*) it is not sensitive to light or chloride ions. However one disadvantage is that in the equivalence point the orange colour changes to green which might interfere with the colour of other substances present. Therefore an indicator is needed, such as diphenylamine (colourless to dark blue).

Redoxi titrations - Chromatometry

Applications of chromatometry

Determination of Fe(II)

In the presence of sulphuric acid, Fe(II) gets easily oxidized to Fe(III):



End-point indication by diphenylamine is a bit complicated by the fact that $E_{0, Fe} = +0.76 V$ and $E_{0, ind} = +0.77 V$ therefore not only the Cr(VI)/Cr(III) but also the Fe(III)/Fe(II) system can cause a colour change during the titration. To avoid this, phosphoric acid is added to the sample which complexes Fe(III) thus reducing the potential of the iron system.

Redoxi titrations - Iodometry

Iodometry

The standard redox potential of the I_2/I^- system is a middle value:



This means that iodine can be used as an oxidizing titrant for the titration of reducing samples and also that iodide can be converted to iodine by oxidizing samples and this iodine can be titrated using a special (auxiliary) titrant used in iodometry: $Na_2S_2O_3$. The latter is the more frequent application. The crucial basis reaction of iodometry therefore is:



Redoxi titrations - Iodometry

This reaction is very sensitive to the pH of the medium in which the titration is being conducted. The reason is that on one hand, iodine is unstable at alkaline pHs:



but in the presence of strong acids both thiosulfate and tetrathionate will decompose:



A standard solution of known concentration of iodine is not easy to prepare due to its volatility and low solubility in water. It is known however that iodide facilitates its dissolution by forming tri-iodide ions:



If prepared, As_2O_3 can be used to standardize the solution. It is more common, however, to use the $Na_2S_2O_3$ method (for oxidizing samples).

Redoxi titrations - Iodometry

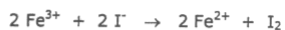
In this method we use an excess of iodide solution which will react with the oxidizing sample liberating a stoichiometric amount of iodine. This in turn is titrated using a standard $\text{Na}_2\text{S}_2\text{O}_3$ solution.

The standard thiosulfate solution is stabilized by adding amyl alcohol (to suppress the growth of thiobacterii) and sodium carbonate (to prevent acidification). Standardization is done using KBrO_3 , KIO_3 or $\text{K}_2\text{Cr}_2\text{O}_7$ primary standards. The indication method of iodometry is starch (intense blue).

Redoxi titrations - Iodometry

Applications of iodometry (oxidizing samples)

Determination of Fe(III)



Determination of Cu(II)



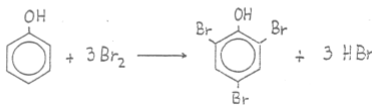
Determination of H_2O_2



Redoxi titrations - Iodometry

Determination of phenol according to Koppeschaar (indirect method)

Phenol can be brominated using bromine (generated by the reaction of BrO_3^- standard solution and an adequate amount of Br^-):



After this, the excess of bromine is titrated using iodometry. That is, after the addition of iodide, the resulting iodine is titrated using thiosulfate.

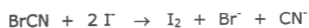
Redoxi titrations - Iodometry

Determination of thiocyanate according to Schulek (indirect method)

The reaction of thiocyanate with bromine is quantitative and gives BrCN :



The needed amount of bromine is added as bromine water and its excess is removed by the addition of enough phenol (see above). The bromine cyanide is measured by iodometry:



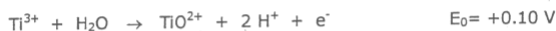
Reductometric methods

Reductometric methods are not widely used because of the inconveniences involved with the storage of their standard solution (they need to be kept under inert gas atmosphere to keep away oxygen that would oxidize them) but they are used in some special cases.

Redoxi titrations - Titanometry

Titanometry

Ti(III) is a strong reducing agent. Standard solution is usually prepared from $Ti_2(SO_4)_3$. The half-reaction is as follows:



Standardization of the titanometric solution is done using $K_2Cr_2O_7$.

As indicator, $Fe(SCN)_3$ is used in titanometry. Its intense purple-red colour disappears in the endpoint because of the reduction of Fe(III).

One useful application of titanometry is the determination of nitro and nitroso compounds by the following reaction:



Another application is the determination of Fe(III) using thiocyanate ion as indicator.

Redoxi titrations - Chromometry

Chromometry

Chromometry uses Cr(II) which is the most powerful reducing agent useful for analytical purposes:



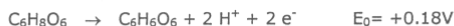
Due to its very reducing nature, Cr(II) standard solution must be prepared, standardized and stored under inert atmosphere. Preparation is done using Cr(III) reduced by metallic zinc. Standardization is done using $K_2Cr_2O_7$.

Indicators used include diphenyl amine and ferroin. Among applications we find the determination of dissolved oxygen and metallic ions.

Redoxi titrations - Ascorbinometry

Ascorbinometry

Upon reaction with oxidizing samples, ascorbic acid reduces to dehydroascorbic acid:



Many of the reactions in ascorbinometry tend to be slow, so elevated temperatures (50-60 °C) are often employed. Advantage is that it is not very sensitive to oxygen – so if we mask out the metallic ions causing its catalysed decomposition than it is not necessary to store under nitrogen. Standardization is done using the reaction with KIO_3/I^- liberating iodine which is then titrated with thiosulfate. Variamine blue is most frequently used endpoint indicator.

Applications of ascorbinometry include the determination of Fe(III) and noble metal ions:



Summary of redoxi titrimetry

Representative methods: permanganometry, iodometry, cerimetry, bromatometry, chromatometry

Pros: wide range of applications (determination of organics, inorganics, ions, etc.)

Cons: limited selectivity, limited stability of titrants, only relatively high concentrations can be determined

Titrant: 0.01-0.1 M solution, typically needs to be standardized

Conditions: sample has to be buffered (usually to an acidic pH)

Indicators: reversible (e.g. ferroin, diphenilamine, variamin blue, etc.) and irreversible indicator dyes, special action indicators (e.g. starch for I_2 , permanganate colour, etc.)