

جامعة الانبار

كلية : الصيدلة

قسم : الكيمياء الصيدلانية

اسم المادة باللغة العربية: الكيمياء التحليلية

اسم المادة باللغة الإنكليزية: **Analytical Chemistry**

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عنوان المحاضرة باللغة العربية: تسحيحات الاكسدة والاختزال

عنوان المحاضرة باللغة الإنكليزية : **Oxidation-Reduction Titration**

9.1 Equilibria in Oxidation-Reduction system

Oxidation-reduction, or redox, processes involve the transfer of electrons from one reactant to another. Volumetric methods based upon electron transfer are more numerous and more varied than those for any other reaction type.

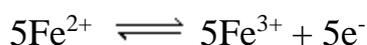
Oxidation involves the loss of electrons by a substance and reduction the gain of electrons. In any oxidation-reduction reaction, the molar ratio between the substance oxidized and the substance reduced is such that the number of electrons lost by one species is equal to the number gained by the other. This fact must always be taken into account when balancing equations for oxidation-reduction reactions.

Oxidizing agents or oxidants possess a strong affinity for electrons and cause other substances to be oxidized by abstracting electrons from them. In the process, the oxidizing agent accepts electrons and is thereby reduced. Reducing agents or reductants have little affinity for electrons and, in fact, readily give up electrons thereby causing some other species to be reduced. A consequence of this electrons transfer is the oxidation of the reducing agent.

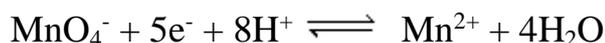
Separation of an oxidation-reduction reaction into its component parts (that is, into half-reactions) is a convenient way of indicating clearly the species that gains electrons and the one that losses them. Thus, the overall reaction:



is obtained by combining the half-reaction for the oxidation of iron(II):



with that for the reduction of permanganate:



Note that it was necessary to multiply the first half-reaction through by 5 to eliminate the electrons from the overall equation.

9.2 Balancing of Redox Equations

The redox equations can be balanced by two methods:

* *The change in oxidation numbers method*

By this method we follow the rules:

- 1- Determine the oxidation numbers for all the elements involved in the reaction.
- 2- From the oxidation numbers determine the oxidizing and reducing agents.
- 3- Count the difference in the oxidation numbers from the oxidizing and reducing agents, and according to it chose the numbers for alternate multiplication, in order to equalize the number of lost and gained electrons.
- 4- Balance the other ions that did not change.

Example 1

Balance the following equation:

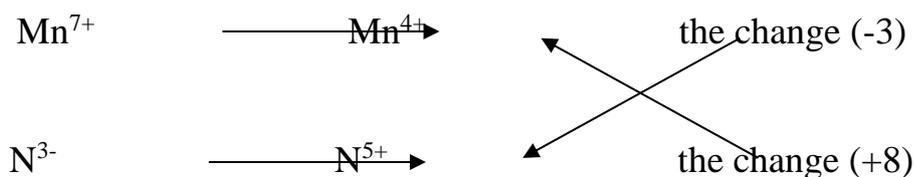


We determine the oxidation numbers:



-2

Note the change in the manganese and nitrogen oxidation numbers.



To maintain the total number of oxidation numbers, we need 8 manganese atoms for each 3 nitrogen atoms.



The oxidation number of potassium did not change, so we balance it and also we balance the oxygen and hydrogen atoms.



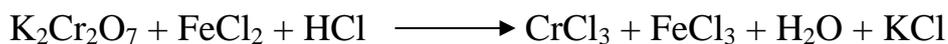
*** *The ion-electron method***

To use this method we follow the rules:

- 1- Divide the reaction to oxidation reaction and reduction reaction, and write it in ionic form.
- 2- Balance the number of atoms for each half-reaction.
- 3- Balance each half-reaction electrically by the addition of a suitable number of electrons to the more electropositive side.
- 4 - The number of electrons in each half-reaction must be equal, if not use the alternate multiplication.
- 5- Add the two balanced half reactions to each other.
- 6- The molecular equation can be obtained from the ionic equation by addition of ions with the reactants and distribute it over the products.
- 7- We may need to add water molecules or its ions (H^+ , OH^-) to balance the equation.

Example 2

Balance the following equation:



The equation in the ionic form is:



The reduction half-reaction is:



To balance the number of atoms we multiply Cr^{3+} by 2, water by 7, and hydrogen by 14, the equation becomes:



Now we balance the electrons on each side of the reaction. The number of positive charges in the reactants is 12 and in the products is 6 only, and to reduce 12 positive charges to 6 we need to add 6 electrons to the reaction:



The number of atoms and charges in this half reaction is balanced.

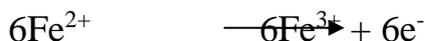
The oxidation half-reaction is:



The number of atoms is equal, but the number of charges is not, and to balance it we add 1 electron to the more electropositive side.



and to make the number of electrons equal we multiply the last equation by 6, then add the two equations:



addition



To obtain the molecular equation, we add the other ions and distribute it over the products:



9.3 Auxiliary Oxidizing and Reducing Reagents

The analyte in an oxidation-reduction titration must be in a single oxidation state at the outset. Often, the steps that precede the titration, such as dissolving the sample and separating interferences, convert the analyte to a mixture of oxidation states. For example, when a sample containing iron is dissolved, the resulting solution usually contains a mixture of iron(II) and iron(III) ions. If we choose to use a standard oxidant to determine iron, we must first treat the sample solution with an auxiliary reducing agent to convert all of the iron to iron(II). If we plan to titrate with a standard reductant, however, pretreatment with an auxiliary oxidizing reagent is needed.

To be useful as a preoxidant or a prereductant, a reagent must react quantitatively with the analyte. In addition, any reagent excess must be easily removable because the excess reagent usually interferes with the titration by reacting with the standard solution.

9.4 Auxiliary Reducing Reagents

A number of metals are good reducing agents and have been used for the pre-reduction of analytes. Included among these are zinc,

aluminum, cadmium, lead, nickel, copper, and silver (in the presence of chloride ion). Sticks or coil of the metal can be immersed directly in the analyte solution. After reduction is judged complete, the solid is removed manually and rinsed with water. The analyte solution must be filtered to remove granular or powdered forms of the metal. An alternative to filtration is the use of a redactor, such as Jones redactor, which has a diameter of about 2 cm and holds a 40 to 50 cm column of amalgamated zinc.

Zinc can be amalgamated by allowing its granules to stand briefly in a solution of mercury(II) chloride, where the following reaction occurs:

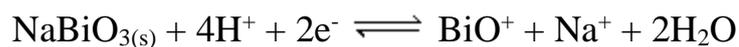


Zinc amalgam is nearly as effective for reduction as the pure metal and has the important virtue of inhibiting the reduction of hydrogen ions by zinc. This side reaction needlessly uses up the reducing agent and also contaminates the sample solution with a large amount of zinc(II) ions. Solutions that are quite acidic can be passed through a redactor without significant hydrogen formation.

9.5 Auxiliary Oxidizing Reagents

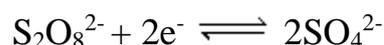
**** Sodium Bismuthate***

Sodium bismuthate is a powerful oxidizing agent capable, for example, of converting manganese(II) quantitatively to permanganate ion. This bismuth salt is a sparingly soluble solid with a formula that is usually written as NaBiO_3 , although its exact composition is somewhat uncertain. Oxidations are performed by suspending the bismuthate in the analyte solution and boiling for brief period. The unused reagent is then removed by filtration. The half-reaction for the reduction of sodium bismuthate can be written as:

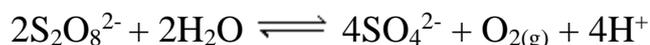


*** Ammonium Peroxydisulfate**

Ammonium peroxydisulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, is also a powerful oxidizing agent. In acidic solution, it convert chromium(III) to dichromate, cerium(III) to cerium(IV), and manganese(II) to permanganate. The half-reaction is:

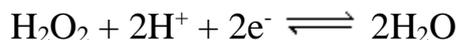


The oxidations are catalyzed by trace of silver ion. The excess reagent is easily decomposed by a brief period of boiling:



*** Sodium Peroxide and Hydrogen Peroxide**

Peroxide is a convenient oxidizing agent either as the sodium salt or as a dilute solution of the acid. The half-reaction for hydrogen peroxide in acidic solution is:



After oxidation is complete, the solution is freed of excess reagent by boiling:



9.6 Applying Standard Reducing Agents

Standard solutions of most reductants tend to react with atmospheric oxygen. For this reason, reductants are seldom used for direct titration of oxidizing analytes; indirect methods are used instead. The two most common reductants are iron(II) and thiosulfate ions.

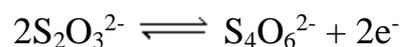
*** Iron(II) solutions**

Solutions of iron(II) are easily prepared from iron(II) ammonium sulfate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Mohr's salt), or from the closely related iron(II) ethylenediamine sulfate $\text{FeC}_2\text{H}_4(\text{NH}_3)_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Oesper's salt). Air oxidation of iron(II) takes place rapidly in neutral solutions but is inhibited in the presence of acids, with most stable preparations being about 0.5 M in H_2SO_4 . Such solutions are stable for no more than one day. Numerous oxidizing agents are conveniently determined by treatment of the analyte solution with a measured excess of standard iron(II) followed by immediate titration of the excess with a standard solution of potassium dichromate or cerium(IV). Just before or just after the analyte is titrated, the volumetric ratio between the standard oxidant and the iron(II) solution is established by titrating two or three aliquots of the latter with former.

This procedure has been applied to the determination of organic peroxides; hydroxylamine; chromium(VI); cerium(IV); molybdenum(VI); nitrate, chlorate, and perchlorate ions; and numerous other oxidants.

* *Sodium Thiosulfate*

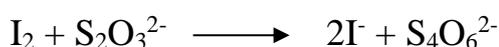
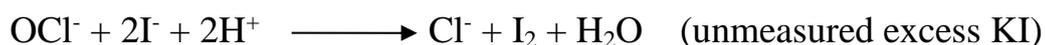
Thiosulfate ion ($\text{S}_2\text{O}_3^{2-}$) is a moderately strong reducing agent that has been widely used to determine oxidizing agents by an indirect procedure that involves iodine as an intermediate. With iodine, thiosulfate ion is oxidized quantitatively to tetrathionate ion ($\text{S}_4\text{O}_6^{2-}$) according to half-reaction:



The quantitative reaction with iodine is unique. Other oxidants can oxidize the tetrathionate ion to sulfate ion.

The scheme used to determine oxidizing agents involves adding an unmeasured excess of potassium iodide to a slightly acidic solution of

the analyte. Reduction of the analyte produces a stoichiometrically equivalent amount of iodine. The liberated iodine is then titrated with a standard solution of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, one of the few reducing agents that is stable toward air oxidation. An example of this procedure is the determination of sodium hypochlorite in bleaches. The reactions are:



The quantitative conversion of thiosulfate ion to tetrathionate ion requires a pH smaller than 7. If strongly acidic solution must be titrated, air oxidation of the excess iodide must be prevented by blanking the solution with an inert gas, such as carbon dioxide or nitrogen.

****Detecting end points in iodine-thiosulfate titration***

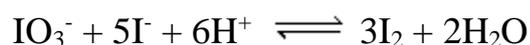
A solution that is about 5×10^{-6} M in I_2 has a discernible color, which corresponds to less than one drop of a 0.05 M iodine solution in 100 mL. Thus, provided that the analyte solution is colorless, the disappearance of the iodine color can serve as the indicator in titrations with sodium thiosulfate.

More commonly, titrations involving iodine are performed with a suspension of starch as an indicator. The deep blue color that develops in the presence of iodine is believed to rise from the absorption of iodine into the helical chain of β -amylose, a macromolecular component of most starches. The closely related α -amylose forms a red adduct with iodine. This reaction is not easily reversible and is thus undesirable. In commercially available soluble starch, the alpha fraction has been removed to leave principally β -amylose; indicator solutions are easily prepared from this product.

Aqueous starch suspensions decompose within a few days, primarily because of bacterial action. The decomposition products tend to interfere with the indicator properties of the preparation and may also be oxidized by iodine. The rate of decomposition can be inhibited by preparing and storing the indicator under sterile conditions and by adding mercury(II) iodide or chloroform as a bacteriostat.

****Standardizing thiosulfate solution***

Potassium iodate is an excellent primary standard for thiosulfate solutions. In this application, weighed amounts of primary-standard grade reagent are dissolved in water containing an excess of potassium iodide. When this mixture is acidified with a strong acid, the following reaction occurs instantaneously:



The liberated iodine is then titrated with the thiosulfate solution. The stoichiometry of the reaction is:



Other primary standards for sodium thiosulfate are potassium dichromate, potassium bromate, potassium hydrogen iodate, potassium hexacyanoferrate(III), and metallic copper. All these compounds liberate stoichiometric amounts of iodine when treated with excess potassium iodide.

9.7 Applying Standard Oxidizing Agents

The choice among oxidizing agents depends on the strength of the analyte as a reducing agent, the rate of reaction between oxidant and analyte, the stability of the standard oxidant solutions, the cost, and the availability of a satisfactory indicator.

**** The strong oxidants—potassium permanganate and cerium(IV)***

Solutions of permanganate ion and cerium(IV) ion are strong oxidizing reagents whose applications closely parallel one another. Half-reactions for the two are:



The formal potential shown for the reaction of cerium(IV) is for solutions that are 1 M in sulfuric acid. In 1 M perchloric acid and 1 M nitric acid, the potentials are 1.70 V and 1.61 V, respectively. Solutions of cerium(IV) in the latter two acids are not very stable and thus find limited application.

The half-reaction shown for permanganate ion occurs only in solutions that are 0.1 M or greater in strong acid. In less acidic media, the product may be Mn(III), Mn(IV), or Mn(VI), depending on conditions.

Despite some advantages of cerium solutions, like stability, over permanganate solutions, the latter are more widely used. One reason is the color of permanganate solutions, which is intense enough to serve as an indicator in titrations. A second reason for the popularity of permanganate solutions is their modest cost.

****Detecting the end points***

A useful property of a potassium permanganate solution is its intense purple color, which is sufficient to serve as an indicator for most titrations. If you add as little as 0.01 to 0.02 mL of a 0.02 M solution of permanganate to 100 mL of water, you can perceive the purple color of the resulting solution. If the solution is very dilute, diphenylamine sulfonic acid or the 1,10-phenanthroline complex of iron(II) provides a sharper end point.

The permanganate end point is not permanent because excess permanganate ions react slowly with the relatively larger concentration of manganese(II) ions present at the end point, according to the reaction:

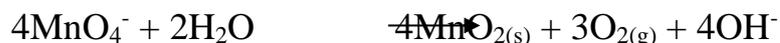


The equilibrium constant for this reaction is about 10^{47} , which indicates that the equilibrium concentration of permanganate ion is incredibly small even in highly acidic media. Fortunately, the rate at which this equilibrium is approached is so slow that the end point fades only gradually over a period of perhaps 30 seconds.

Solutions of cerium(IV) are yellow-orange, but the color is not intense enough to act as an indicator in titrations. Several oxidation-reduction indicators are available for titrations with standard solutions of cerium(IV). The most widely used of these is the iron(II) complex of 1,10-phenanthroline or one of its substituted derivatives.

****The preparation and stability of standard solutions***

Aqueous solutions of permanganate are not entirely stable because of water oxidation:



Although the equilibrium constant for this reaction indicates that the products are favored, permanganate solutions, when properly prepared, are reasonably stable because the decomposition reaction is slow. It is catalyzed by light, heat, acids, bases, manganese(II), and manganese dioxide.

Moderately stable solutions of permanganate ion can be prepared if the effects of these catalyst, particularly manganese dioxide, are minimized. Manganese dioxide is a contaminant in even the best grade

of solid potassium permanganate. Removal of manganese dioxide by filtration before standardization markedly improves the stability of standard permanganate solutions. Before filtration, the reagent solution is allowed to stand for about 24 hours or is heated for a brief period to hasten oxidation of the organic species generally present in small amounts in distilled and deionized water. Paper cannot be used for filtration because permanganate ion reacts with it to form additional manganese dioxide.

Standardized permanganate solutions should be stored in the dark. Filtration and restandardization are required if any solid is detected in the solution or on the walls of the storage bottle. In any event, restandardization every 1 or 2 weeks is a good precautionary measure.

The most widely used compounds for the preparation of solution of cerium(IV) are cerium(IV) ammonium nitrate $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$, cerium(IV) ammonium sulfate $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, cerium(IV) hydroxide $\text{Ce}(\text{OH})_4$, Ce(IV) hydrogen sulfate $\text{Ce}(\text{HSO}_4)_4$. Primary-standard cerium ammonium nitrate is available commercially and can be used to prepare standard solutions of the cation directly by weigh. More commonly, less expensive reagent-grade cerium(IV) ammonium nitrate or ceric hydroxide is used to prepare solutions that are subsequently standardized. In either case, the reagent is dissolved in a solution that is at least 0.1 M in sulfuric acid to prevent the precipitation of basic salts.

Sulfuric acid solutions of cerium(IV) are remarkably stable and can be stored for months or heated at 100°C for prolonged periods without a change in concentration.

****Standardizing permanganate and cerium(IV) solutions***

Sodium oxalate is a widely used primary standard. In acidic solutions, the oxalate ion is converted to the undissociated acid. Thus, its reaction with permanganate can be described by:



The reaction between permanganate ion and oxalic acid is complex and proceeds slowly even at elevated temperature unless manganese(II) is present as a catalyst. Thus, when the first few milliliters of standard permanganate are added to a hot solution of oxalic acid, several seconds are required before the color of the permanganate ion disappears. As the concentration of manganese(II) builds up, however, the reaction proceeds more and more rapidly as a result of autocatalysis.

Sodium oxalate is also widely used to standardize Ce(IV) solutions. The reaction between Ce^{4+} and $\text{H}_2\text{C}_2\text{O}_4$ is:



Cerium(IV) standardization against sodium oxalate are usually performed at 50°C in a hydrochloric acid solution containing iodine monochloride as a catalyst.

*** *Potassium dichromate***

In its analytical applications, dichromate ion is reduced to green chromium(III) ion:



Dichromate titrations are generally carried out in solutions that are about 1 M in hydrochloric or sulfuric acid. In these media, the formal potential for the half-reaction is 1.0 to 1.1 V.

Potassium dichromate solutions are indefinitely stable, can be boiled without decomposition, and do not react with hydrochloric acid.

Moreover, primary standard reagent is available commercially and at modest cost.

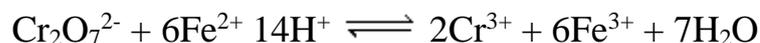
****Preparing dichromate Solution***

For most purposes, reagent-grade potassium dichromate is sufficiently pure to permit the direct preparation of standard solutions; the solid is simply dried at 150°C to 200°C before being weighed.

The orange color of a dichromate solution is not intense enough for use in end point detection. Diphenylamine sulfonic acid is an excellent indicator for titrations with this reagent, however. The oxidized form of the indicator is violet, and its reduced form is essentially colorless; thus, the color change observed in a direct titration is from the green of chromium(III) to violet.

****Applying potassium dichromate solutions***

The principal use of dichromate is the volumetric titration of iron(II) based on the reaction:



Often, this titration is performed in the presence of moderate concentration of hydrochloric acid.

The reaction of dichromate with iron(II) has been widely used for the indirect determination of a variety of oxidizing agents. In these applications, a measured excess of an iron(II) solution is added to an acidic solution of the analyte. The excess iron(II) is then back-titrated with standard potassium dichromate. Standardization of the iron(II) solution by titration with the dichromate is performed concurrently with the determination because solution of iron(II) tend to be air oxidized. This method has been applied to the determination of nitrate, chlorite,

permanganate, and dichromate ions as well as organic peroxides and several other oxidizing agents.

*** Iodine**

Iodine is a weak oxidizing agent used primarily for the determination of strong reductants. The most accurate description of the half-reaction for iodine in these applications is:



where I_3^- is the triiodide ion.

Standard iodine solutions have relatively limited application compared with the other oxidants we have described because of their significantly smaller electrode potential. Occasionally, however, this low potential is advantageous because it imparts a degree of selectivity that makes the determination of strong reducing agents in the presence of weak ones. Iodine solution lack stability, however, and must be restandardized regularly.

****Standardizing and applying iodine solution***

Iodine solutions can be standardized against anhydrous sodium thiosulfate or barium thiosulfate monohydrate, both of which are available commercially. Often, solutions of iodine are standardized against solutions of sodium thiosulfate that have in turn been standardized against potassium iodate or potassium dichromate.